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TREATABILITY STUDY REPORT FOR OPERABLE UNIT 1 VOLUME 1 FINAL NOVEMBER 30, 1993 REF: 5284

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TREATABILITY STUDY REPORT
OPERABLE UNIT 1

FERNALD ENVIRONMENTAL MANAGEMENT PROJECT
FERNALD, OHIO

REMEDIAL INVESTIGATION and FEASIBILITY STUDY

VOLUME 1

NOVEMBER 30, 1993

U.S. DEPARTMENT OF ENERGY
FERNALD SITE OFFICE

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EXECUTIVE SUMMARY

The Treatability Study Report for Operable Unit 1 (OU1) of the Fernald Environmental Management Project (FEMP) describes and evaluates waste treatment technologies for remediation of the OU1 waste pits. The information presented supports the preparation of the OU1 Feasibility Study (FS) Report and the Proposed Plan.

The FEMP is a U.S. Department of Energy (DOE) facility near Fernald, Ohio, which operated from 1952 to 1989 providing high purity uranium metal products to support United States defense programs. Operable Unit 1 is located on the western portion of the site. The FEMP is a 425 hectare (1050 acre) facility northwest of downtown Cincinnati near Fernald, Ohio, a small farming community. The primary mission of the FEMP during its 37 years of operation was the processing of "feed" materials to produce high purity uranium metal. These high purity uranium metals were then shipped to other DOE or U.S. Department of Defense (DOD) facilities for use in the nation's weapons program.

In 1986 the U.S. Environmental Protection Agency (EPA) and DOE entered into a Federal Facility Compliance Agreement (FFCA) covering environmental impacts associated with the FEMP. In response to the FFCA, a site-wide RI/FS was initiated pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by the Superfund Amendment and Reauthorization Act (SARA). Production operations at the facility were suspended in 1989 and focus was shifted to environmental restoration and waste management activities.

The purpose of the OU1 Treatability Study is to evaluate potential remediation technologies for feasibility, effectiveness, and reliability. The Treatability Report is prepared to support specific informational needs of FS alternative evaluation. Consistent with the Amended Consent Agreement and following consideration of comments received from the public and other interested parties, selection of the preferred cleanup alternative will be documented in a Record of Decision (ROD).

DESCRIPTION OF OPERABLE UNIT 1

FEMP storage facilities were used for storing low-level radioactive wastes generated by the various chemical and metallurgical processes used at the facility since uranium production operations began in the early 1950s. The waste pit area (Operable Unit 1) consists of Waste Pits 1, 2, 3, 4, 5, and 6; the Burn Pit (also used for the disposal and burning of waste); the Clearwell (primarily a settling basin for surface water runoff); miscellaneous structures and facilities such as berms, liners, concrete pads, underground piping, utilities, railroad tracks, fencing; and environmental media. Operable Unit 1 is located west of the former production area and covers approximately 9.4 hectares (37.7 acres). Paddy's Run, an intermittent tributary of the Great Miami River, runs along the west side of the FEMP property between Operable Unit 1 and the site boundary. Two types of disposal methods were generally used: a "wet" system for slurries where the wastes were pumped to the pit, and "dry" backfill type operations.

The majority of the hazardous constituents identified during the characterization of Operable Unit 1 were introduced to the plant in feed materials for the refining process. These materials were the raw feedstock from which uranium metal and thorium products were separated in plant operations. Feed materials included uranium-bearing ores and ore concentrates (which had been processed prior to receipt to remove certain radionuclides other than uranium), thorium-bearing ores, residues from other DOE facilities (which were found to have high uranium content), uranium from the nation's gaseous diffusion plants, and irradiated uranium-bearing materials from DOE facilities involved in the production of plutonium for weapons.

The production of uranium or thorium products was a multi-stage process involving chemical extraction or leaching, treatment, and manufacturing. Uranium-bearing feedstock was first dissolved in nitric acid to form a liquid from which the uranium content could be extracted from other impurities in the feedstock. These impurities include other radioactive members of the uranium decay series and potentially hazardous metals such as arsenic, chromium, nickel, and lead. This initial step produced a large portion of the waste which was disposed of in the Operable Unit 1 waste units, either as slurries or solids, referred to as raffinates. After this initial step, the separated uranium was further treated to improve its purity or prepare it for the manufacturing processes. These later

treatment steps produced additional wastes from filtering and settling operations (chemical precipitation wastes, filter cake and sump cake), drying operations (cold metal oxides or raffinates), chemical conversion (trailer cake, magnesium fluoride, and depleted slag), heat treatment (contaminated liquids), expended equipment (graphite and ceramics, pumps, piping, etc.), vessels, and containers contaminated with uranium and other hazardous constituents. Other wastes generated in the refinement process and site support activities include pollution control products (bag house residues), flyash from the heating plant, residues from the process water treatment plant (lime slurry), and construction debris.

Waste inventory records indicate that Waste Pit 1 contains 1075 metric tons (MT) of uranium; Waste Pit 2 contains 175 MT of uranium; Waste Pit 3 contains 846 MT of uranium and 97 MT of thorium; Waste Pit 4 contains 2203 MT of uranium and 74 MT of thorium; Waste Pit 5 contains 527 MT of uranium and 72 MT of thorium; and Waste Pit 6 contains 1432 MT of uranium. Waste inventory records do not contain information about the content of uranium and thorium in the Burn Pit and Clearwell.

Waste Pit 1 is considered a dry pit, since the waste slurries were filtered or calcined to remove water before they were placed in the pit. This waste pit received primarily neutralized waste filter cakes, vacuum-filtered sludges from production activities, magnesium fluoride slag, scrap graphite, and contaminated brick. It was, however, used as a settling basin for liquids removed from Waste Pit 2 in 1958 and 1959. Waste Pit 1 was closed and covered with clean fill in 1959. This waste pit is currently classified as a RCRA Solid Waste Management Unit.

Waste Pit 2 is also considered a dry pit and received primarily waste filter cakes, vacuum-filtered production sludge, magnesium fluoride slag, scrap graphite, contaminated brick, and concentrated raffinate residues. However, Waste Pit 2 was also used as a settling basin for neutralized, concentrated raffinate during 1958 and 1959, prior to completion of Waste Pit 3, because the drying equipment available at that time could not process all of the raffinate being produced by plant operations. Waste Pit 2 was closed and covered with clean fill in 1964. This waste pit is currently classified as a RCRA Solid Waste Management Unit.

Waste Pit 3 was the first waste pit built specifically for settling solids from liquid waste streams. Primarily, lime-neutralized raffinate slurries, as well as contaminated storm water, were pumped to Waste Pit 3. After Waste Pit 2 was filled, Waste Pit 3 received vacuum-filtered production sludge, neutralized liquid from process systems, neutralized refinery sludges, and cooling water from heat treatment operations. Starting in December 1958, lime sludge from the Water Treatment Plant was added to supplement the lime used for raffinate neutralization. Also, large quantities of neutralized residues from acid leaching of uranium-bearing magnesium fluoride slag were pumped to Waste Pit 3 during the late 1960s, prior to completion of Waste Pit 5. In 1973, fill material including filter cake, slag leach residue, lime sludge, and flyash was placed in Waste Pit 3 and construction activities were initiated to cover this waste pit with soil. Waste Pit 3 covering activities were complete in 1977. This waste pit is currently classified as a RCRA Solid Waste Management Unit.

Waste Pit 4 received solid wastes that included process residues, scrap uranium metal, off-specification intermediate uranium products and residues, thorium metal and residues, and contaminated ceramics. The process residues included filter sludges, raffinates, graphite, magnesium fluoride slag, and pyrophoric uranium-bearing materials. Thorium metal and residues were hauled to the waste pits in drums and were placed in Waste Pit 4 when additional metal recovery was not economically feasible. At least 100 drums were deposited on the west side of this waste pit. Waste Pit 4 also received noncombustible trash including cans, concrete, asbestos, and construction rubble. Lime was occasionally added to standing water within Waste Pit 4 for uranium precipitation prior to the transfer of liquids to Waste Pit 5 for settling and discharge. Barium chloride was also disposed of in Waste Pit 4 from 1980 to 1983. Disposal activities in Waste Pit 4 were terminated in 1985. The waste pit was closed in 1986 and cover activities started. Waste Pit 4 is currently classified as a RCRA Hazardous Waste Management Unit and has undergone interim closure. Final closure of Waste Pit 4 will be completed in conjunction with remedial actions under CERCLA.

Waste Pit 5 served as a settling basin for slurries including neutralized raffinates, slurries from the acid leaching of uranium-bearing slags, and sump slurries which were generally filtered to remove solids. Lime sludge was added to this waste pit to supplement the lime used to neutralize the raffinate and heat treatment quench water were discharged directly to Waste Pit 5. Both the supernatant and

sludges produced by the co-precipitation of thorium wastes with barium carbonate and aluminum sulfate, and the precipitation of uranium with calcium oxide were deposited in Waste Pit 5. The discharge of slurried waste materials into Waste Pit 5 was stopped in 1983 and use of this waste pit as a settling basin was discontinued in 1987. Waste Pit 5 is currently classified as a RCRA Hazardous Waste Management Unit.

Waste Pit 6 received only noncoarse, nonpyrophoric materials (this excludes uranium and thorium in metallic form), including magnesium fluoride slag, process residues, and filter cakes from vacuum filtering operations to protect the membrane liner. Extrusion residue and heat treatment quench water were also deposited in Waste Pit 6. Use of Waste Pit 6 ceased in 1985. Waste Pit 6, which is currently covered by water, is classified as a RCRA Solid Waste Management Unit.

The Burn Pit was used primarily as an isolated spot to burn contaminated combustibles such as laboratory chemicals; pyrophoric metals (e.g. uranium metal cuttings) and reactive chemicals; oils, contaminated combustible material; and cafeteria debris, cans, napkins, and skids. The Burn Pit was filled in 1968 during the construction of Waste Pit 5. The actual inventory of materials disposed of in the Burn Pit is not currently available. Investigations of that issue are ongoing and results will be provided in preliminary stages of the FS.

The Clearwell received surface water runoff from the waste pits and surface liquid from Waste Pits 3 and 5. It acted as a final settling basin prior to periodic pumping to the Great Miami River. The Clearwell is currently classified as a RCRA Solid Waste Management Unit.

TREATABILITY STUDY APPROACH

The EPA's Guide for Conducting Treatability Studies Under CERCLA (EPA 1989a) outlines a three-tiered approach to conducting treatability studies for a Superfund site. The remedy evaluation phase

of the RI/FS, in accordance with proposed revised EPA guidance, may require a maximum of three tiers of treatability testing:

- Remedy screening
- Remedy selection
- Remedy design

Treatment methods considered for remediation may require full, limited, or no treatability testing based on the amount of previous information available which is directly applicable to the waste. The three levels of treatability testing are divided into pre-Record of Decision (ROD) and post-ROD studies. Remedy screening and remedy selection testing are pre-ROD studies, and the remedy design studies are post-ROD.

Pre-ROD treatability studies provide critical performance and cost data needed to (1) evaluate all potentially applicable treatment alternatives and (2) select an alternative for remedial action based on the nine RI/FS evaluation criteria. The detailed analysis of alternatives phase of the RI/FS follows the development and screening of alternatives and precedes the actual selection of a remedy in the ROD.

During the detailed analysis, all remedial alternatives are evaluated based on nine RI/FS evaluation criteria. These criteria are as follows:

- Overall protection of human health and the environment
- Compliance with ARARs
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility, or volume through treatment
- Short-term effectiveness
- Implementability
- Cost
- State acceptance
- Community acceptance

Remedy screening is the first step in the tiered approach. Its purpose is to determine the feasibility of a treatment alternative for the contaminants/matrix of interest. These tests are typically conducted

under conditions favorable to the technology. These small-scale studies are designed to provide a qualitative evaluation of the technology and are conducted with minimal levels of Quality Assurance/Quality Control (QA/QC). Tests conducted under this tier are generic in nature (not vendor specific). If the feasibility of the treatment cannot be demonstrated, the alternative should generally be screened out at this time.

The remedy selection tier of the treatability study program is designed to determine whether a treatment alternative can meet the operable unit's cleanup criteria and at what cost. The purpose of this tier is to generate the performance and cost data necessary for remedy evaluation in the detailed analysis of alternatives phase of the Feasibility Study (FS). The cost data developed in this tier should support costs estimates of +50 percent/-30 percent accuracy. The performance data will be used to determine if the technology will meet ARARs or cleanup goals. Remedy selection studies are typically small-scale, incorporating generic tests using bench- or pilot-scale equipment in either the laboratory or field. The study costs are higher than those encountered in the remedy screening tier and require longer durations to complete. The levels of QA/QC are moderate to high because the data from these studies will be used to support the ROD.

In the remedy design tier treatability study, detailed scale-up, design, performance, and cost data are generated to implement and optimize the selected remedy. Remedy design studies are performed, usually as part of the remedy implementation. These studies are performed with the purpose of generating detailed, scale-up design and cost data; they require moderate levels of QA and are vendor-specific.

All treatability work was performed based on work plans prepared in accordance with the EPA's Guide for Conducting Treatability Studies Under CERCLA Interim Final (EPA 1988) and Final (EPA 1992).

TECHNOLOGIES

The following represents the treatability technologies and studies covered by this OU1 Treatability Study Report:

Vitrification

- Vitrification Remedy Screening/Remedy Selection Studies;
  Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1

- Vitrification Remedy Design - Laboratory Scale;
  Work Plan - GTS Duratek/CUA, Nov. 1992, Remedy Design Laboratory Studies, Part I: Vitrification

- Vitrification Remedy Design - Bench Scale (MAWS);
  Work Plan - R.M. Parsons, Nov. 1992, OU1 Minimum Additive Waste Stabilization Remedial Design Bench-Scale Treatability Study Work Plan

Cement Solidification/Stabilization (CSS)

- CSS Remedy Screening/Remedy Selection Studies;
  Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1

- Long Term Durability of S/S Hazardous Waste Forms;
  Work Plan - University of Cincinnati, Jan. 1993, Long-Term Durability Testing (Waste form testing)

Thermal Treatment & Particle Agglomeration

- Work Plan - University of Cincinnati, Nov. 1993, CRU1 CRSP Work Plan

SUMMARY AND CONCLUSIONS

The following is a summary of the findings and conclusions of the Operable Unit 1 Treatability Study Report:

The potential robustness of a process is perhaps the most important consideration for evaluation of these treatment processes because the waste pit contents are extremely heterogeneic in nature. Full

characterization prior to excavation is not possible. The treatment process chosen must be robust enough to handle the wide variety of materials to be processed.

Vitrification

These treatability studies have evaluated the use of vitrification for treatment of the OU1 pit wastes. Waste from each of the waste pits has been characterized for glass forming constituents. Crucible melts have been performed for a broad range of potential vitrification formulas. More in-depth crucible studies have been performed to evaluate process parameters such as conductivity and viscosity. In addition several small continuous process melter runs have been made with material from Waste Pit 5. The vitrified products from these experiments have been analyzed and tested for leach resistance. The results from these experiments are summarized in Section 4.0 of this report. The conclusions reached regarding vitrification as a treatment alternative for the waste pit materials are as follows:

(1) Waste Pit material can be vitrified (i.e. a non-crystalline glass product can be formed) with the proper formulation and use of additives. Variations in chemical composition within the waste pit material significantly impact the required formulation and amount of additives required.

(2) Vitrification was very effective in reducing the mobility of the contaminants. Leach test results from the TCLP and the PCT demonstrated that the glass matrix effectively prevents uranium, thorium, and other contaminants from leaching.

(3) A significant reduction in volume of waste was also achieved by vitrification. The amount of volume reduction was greatly dependent on the waste pit material and the required amount of additives to achieve a vitrified product.

(4) Preliminary results show that fluoride can be captured in an off-gas system and recycled into the feed batch.

(5) Heavy metals and radionuclides appear to be retained in the glass melt minimizing off-gas problems

Recommendations

Sufficient data has been developed from the treatability work performed to date to evaluate vitrification as a treatment alternative as part of the RI/FS process. Should vitrification be selected as the treatment alternative for all or part of the waste pit material, additional and extensive pilot testing would be required to support design and operations planning. Although fairly extensive laboratory data has been developed for vitrification of the waste pit materials, no body of industrial data or experience is available to support the evaluation of this treatment option.

Cement Solidification

Cement solidification testing was performed on waste from each of the waste pits. A broad range of potential formulations were tested. Portland cement (Type I and II) and blast furnace slag (BFS) were tested as binders. Additives tested included Type F flyash, site flyash, absorbents and sodium silicate. Solidified samples were allowed to cure and were tested for Unconfined Compressive Strength (UCS), leach resistance (TCLP and 5 day static), permeability and durability. Results of the cement solidification testing are summarized in Section 4.0 of this report.

The conclusions reached regarding cement solidification as a treatment alternative for the waste pit material based on these treatability studies are as follows:

(1) Cement solidification was effective in controlling leachability as tested by the TCLP. All formulations pass the TC regulatory criteria in the TCLP leachate.

(2) The leachability of uranium was effectively controlled in the stabilization process with the exception of Waste Pit 4 due to the large quantity present in the raw waste.

(3) Formulations developed would appear to be capable of scale-up without significant problems. No significant increase in temperatures were observed during mixing amd no observable gases were released during mixing.

(4) Typically formulations with greater than 43 percent portland cement Type II were effective in meeting the UCS requirements of 500 psi set for an on-site retrievable waste form and controlling the leaching of uranium and gross alpha and beta.

(5) The typical bulking factor for the cement stabilization was relatively high. The increase in volume may significantly impact the cost of disposal both on or off-site.

(6) Waste Pit 4 showed significant uranium in the TCLP leachate. Due to the high uranium content in the Waste Pit 4 samples, Waste Pit 4 may require pretreatment or treatment with an alternative technology.

(7) No significant problems were encountered with "setting" of the waste mixtures in Waste Pits 1, 3, 4, 5, 6, and the Clearwell. The Burn Pit would not set with the addition of cement but did set with the addition of blast furnace slag to the mixture. Waste Pit 2 also experienced problems with setting in the preliminary stage most probably due to the presence of organics in the waste.

(8) Permeabilities of all of the solidified samples were low.

(9) Solidified samples passed the criteria set for durability testing (Wet/Dry and Freeze/Thaw). The addition of blast furnace slag to the solidification mixtures had a detrimental effect on their durability.

Recommendations

Sufficient data exists at this stage of the RI/FS process to evaluate cement stabilization as a treatment option. Cement stabilization is a widely utilized technology for treatment of predominately inorganic wastes. Cement stabilization has often been used for stabilization of low level radioactive wastes and is in common use today. Cost and implementability data are available from the literature.

If cement stabilization is selected in the FS/PP as a treatment option for any of the waste pit material, additional testing would be required to refine formulations and develop operational data for remedial design.

Due to the extreme heterogeneity of the waste pits, pretreatment alternatives to reduce the possibility of spikes or pockets of high concentrations of contaminants should be investigated. These may include blending and/or drying of the waste prior to solidification.

Thermal Treatment and Particle Agglomeration

Thermal Treatment

Thermal treatment studies were initiated in 1993 to develop data on waste drying. Drying may be used as a primary treatment for the waste pit material before shipment to an off-site disposal facility. Drying may also be used as a pretreatment for either vitrification or cement solidification treatment alternatives.

Baseline testing has only recently begun. Physical characterization and baseline crucible studies are underway to determine the effects of temperature on the waste material. Data from these studies will be included in an addendum to this report in Spring 1994.

Thermal treatment has been used to treat residues from the processing of uranium for many years at the FEMP. Based on this experience and the extensive information available from industry on thermal treatment of residues the following conclusions were reached:

(1) Waste from the waste pits can be effectively dried and packaged for shipment to an off-site disposal facility.

(2) Thermal treatment of the waste will significantly reduce the volume.

(3) High temperature drying (above the calcining temperature) will require more complex off-gas treatment due to the decomposition of organics and salts.

(4) The dried waste will pass TCLP leach criteria (based on evaluation of the raw waste characterization).

(5) A wide variation in the feed material will not significantly affect the thermal process at lower temperatures (below the calcining temperature).

Recommendations

To ensure full-scale implementability, the entire process would need to be tested in a pilot-scale test program. This program should include testing of dewatering during retrieval and feed preparation,

and to establish parameters for drying and off-gas treatment. The advantages and disadvantages of higher temperature drying (ie. creation of a clinkered material (to about 2600° F) should also be evaluated.

To fully assess the process parameters for a drying process, the test program must determine the drying behavior of the waste (i.e., a drying profile as a function of time and temperature). This program will determine what the actual operating temperature, residence time, and dryer size should be for the materials to be dried. It will also provide data for determining off-gas treatment parameters.

Particle Agglomeration

If drying is used as a primary treatment alternative the dried material may pose a dusting problem for handling and shipping. Several methods for agglomeration of the dried waste have been investigated. These include pelletizing and polymer encapsulation.

This option is a combination of the previously described drying process followed by an agglomeration step using water or other additives as binders. Agglomeration technology is a process of size enlargement or upgrading of otherwise finer particles. The forms of product, depending on the reason for agglomeration, can be spheres, pellets, irregular extrusions, or merely loosely bound aggregates or clusters.

To date only tests with a surrogate material have been performed. Based on these surrogate tests and information available from studies at other DOE sites the following conclusions were reached:

(1) This technology is implementable. There is a long industrial history of agglomeration. The agglomeration equipment is reliable and easy to construct, operate, and maintain. Prospective technologies are readily available as are equipment vendors and specialists.

(2) The agglomeration process may require the addition of water or other binders.

(3) Agglomeration can successfully reduce the dusting hazard for dried waste

(4) Waste does not need to be completely dry for successful encapsulation or agglomeration.

(5) High waste loadings in proportion to the binder can be achieved.

(6) Chemical variations in the feed material have little or no effect on the polymer encapsulation process since the waste particles are microencapsulated and no chemical interaction occurs.

Recommendations

To prove technology applicability and implementability, further test work would be necessary. The testing should identify the appropriate technology and develop basic process parameters, including:

(1) Feed size
(2) Moisture content
(3) Surface Requirements (ft^2/ton of feed)
(4) Additives

This technology could be used to decrease dusting when handling and shipping the end product. The energy required for drying and encapsulation is moderately high, and depending on the amount of polymer required for treatment, the operation and maintenance costs could impact cost.

Further testing should be performed to define the agglomeration process parameters and the agglomerated waste form requirements for transportation. Tests with actual pit waste would need to be performed at a bench scale. Additional pilot studies would also need to be performed.

Summary

All of the technologies tested are capable of treating the waste materials in OU1. The engineering and implementation risk and cost associated with the options may vary significantly. Cement stabilization is a well proven technology but is extremely waste specific and significant variations in the waste material may cause difficulty in implementation. Vitrification may provide increased protection against leachability and reduced volume but the process is unproven at scale.

Vitrification, cement solidification, and thermal treatment will be evaluated in the OU1 Feasibility Study. Further testing of a treatment process to support remedial design will be based on the alternative chosen in the OU1 FS and Proposed Plan.

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1.0 INTRODUCTION

This report describes and evaluates waste treatment technologies for remediation of U.S. Department of Energy's (DOE) Operable Unit 1 (OU1) at the Fernald Environmental Management Project (FEMP). Operable Unit 1 includes six waste pits, the Clearwell, Burn Pit, and associated berms, soils, and support facilities.

The goal of this report is to evaluate each waste treatment technology for feasibility, effectiveness, and reliability. The information presented in this report supports the analysis presented the Operable Unit 1 Feasibility Study (FS) Report and Proposed Plan, and will be used to support the remedial design for Operable Unit 1.

This report is designed to meet the requirements of the U.S. Environmental Protection Agency's (EPA) "Guide for Conducting Treatability Studies under CERCLA".

Volume 1 of this Treatability Study Report summarizes the information contained in the appendices (Volume 2) and consists of the following, in accordance with EPA guidance:

- Executive Summary, which provides a brief overview of the content and conclusions of the treatability study report.
- Section 1.0 provides descriptions of the site, waste streams, remediation technologies studied, and previous treatability studies conducted at the site.
- Section 2.0 presents and discusses conclusions and recommendations drawn from the data evaluations.
- Section 3.0 discusses the treatability approach for each technology studied.
- Section 4.0 discusses treatability data, results, and quality assurance. Data summaries and standard operating procedures are included or referenced as appendices.

1.1 DESCRIPTION AND HISTORY OF THE FEMP

1.1.1 Overview

The FEMP is a 425 hectares (1050 acres), government-owned, contractor-operated facility located in southwestern Ohio approximately 29 kilometers (km) (17 miles) northwest of downtown Cincinnati (Figure 1-1). The facility is located just north of Fernald, Ohio, a small farming community, and lies on the boundary between Hamilton and Butler counties (Figure 1-2). Of the total site area, 345 hectares (850 acres) are in Morgan and Crosby townships of Hamilton County, and 80 hectares (200 acres) are in Ross Township of Butler County.

Production operations at the FEMP occurred in the fenced 55-hectare (136-acre) tract of land known as the former production area, located near the center of the site (Figure 1-3). Liquid and solid wastes were generated by the various operations at the FEMP during its production life of 1952 to 1989. Prior to 1984, solid and slurried wastes from FEMP processes were deposited in the on-site waste storage area. This area, located west of the production facilities, includes six low-level radioactive waste storage pits; two earthen-bermed concrete silos containing K-65 residues; one concrete silo containing metal oxides; one unused concrete silo; two lime sludge ponds; a burn pit; a clearwell; a solid waste landfill; and a biosurge area to treat wastewater. The waste storage pits, burn pit, and clearwell portion of the waste storage area has been designated Operable Unit 1 (Figure 1-4). The remaining FEMP site consists of forest and pasture lands.

1.1.2 Integration of the FEMP with the DOE System

The primary mission of the FEMP during its 37 years of operation was the processing of "feed" materials to produce high purity uranium metal. These high purity uranium metals were then shipped to other DOE or U.S. Department of Defense (DOD) facilities for use in the nation's weapons program. A depiction of the FEMP's integration with other DOE facilities is presented in Figure 1-5.

Feed materials at the FEMP included pitchblende ores from mines in the former Belgian Congo and Australia; uranium concentrates (yellowcake) from uranium mills in Canada and other foreign

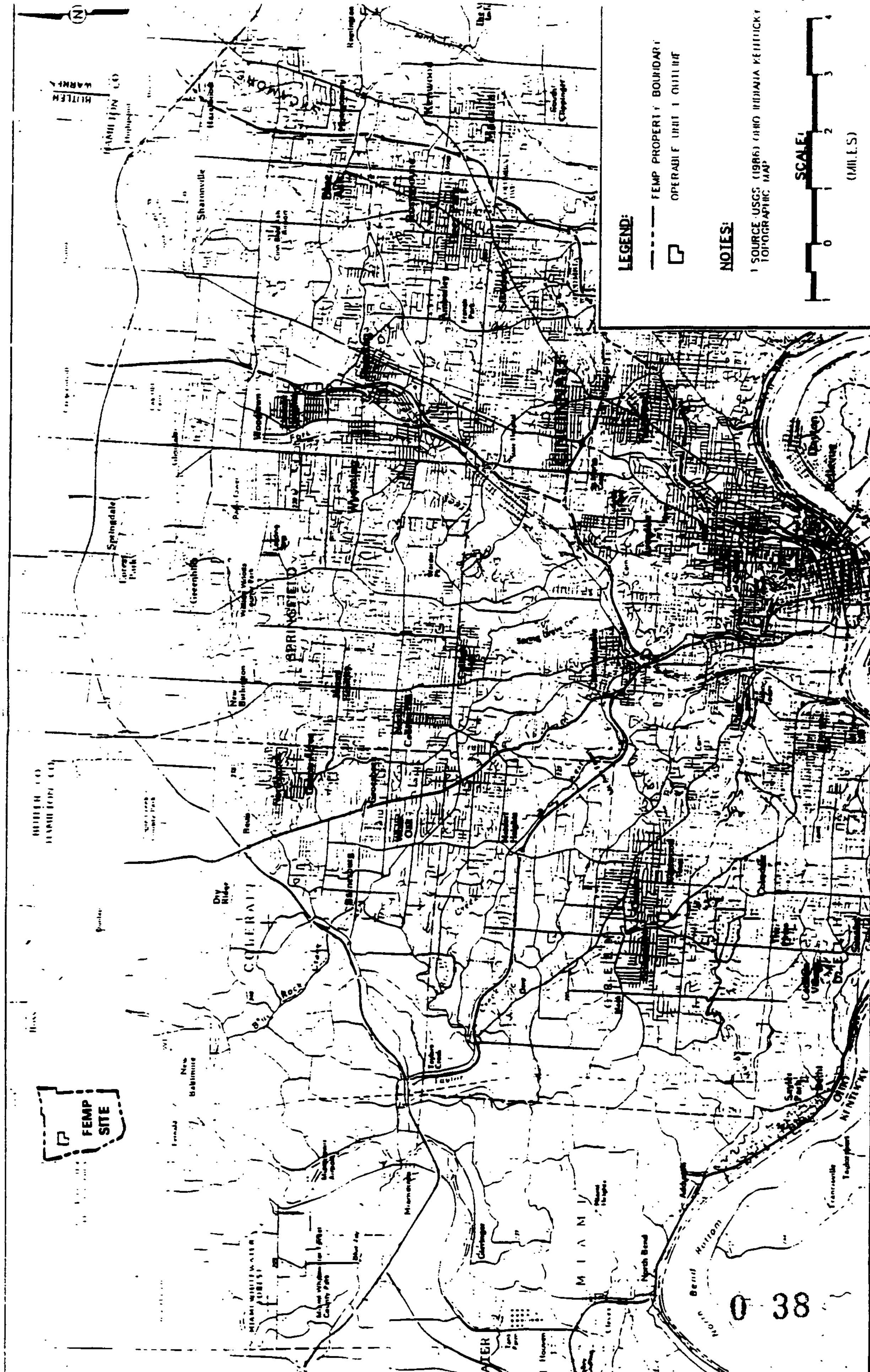
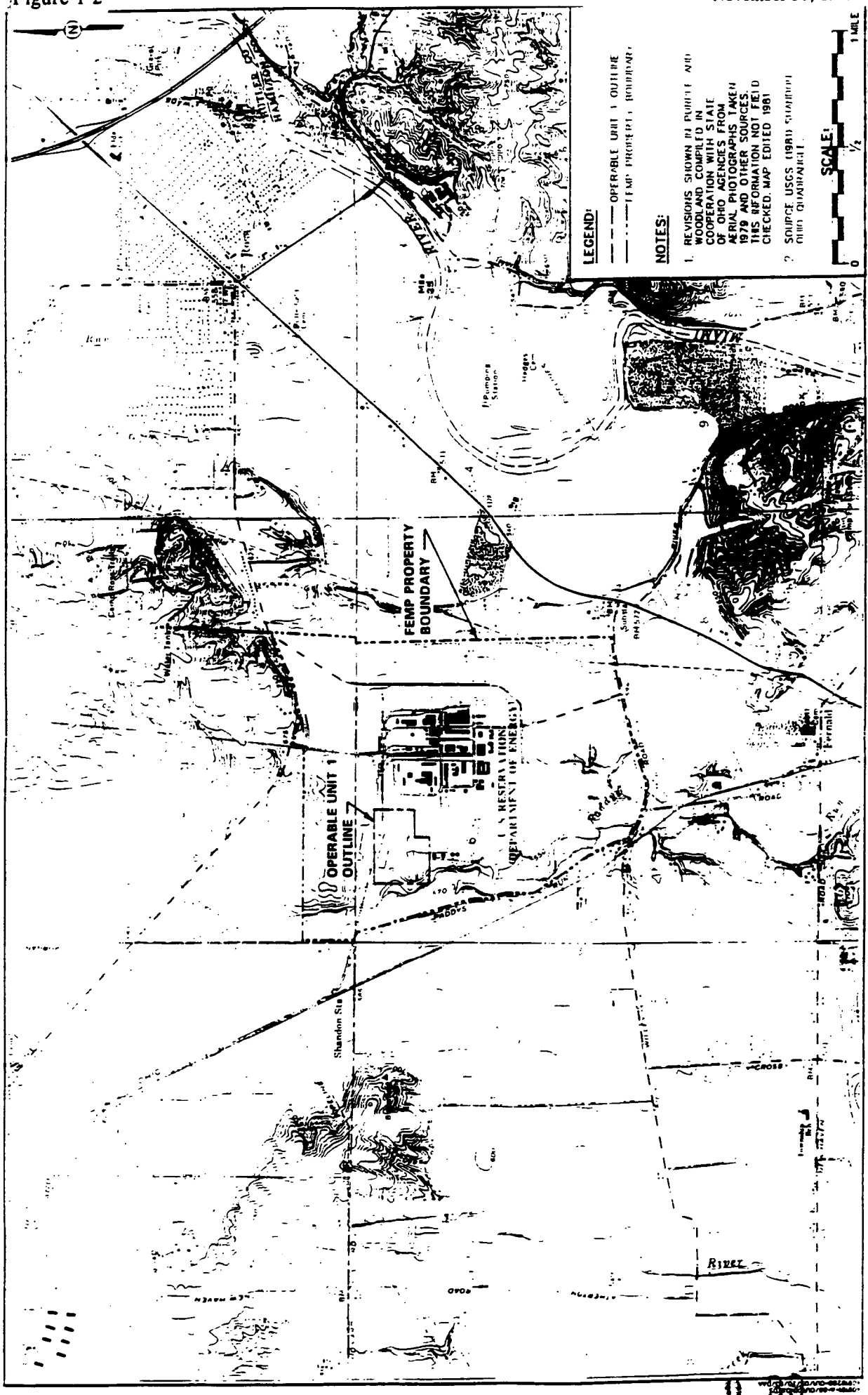
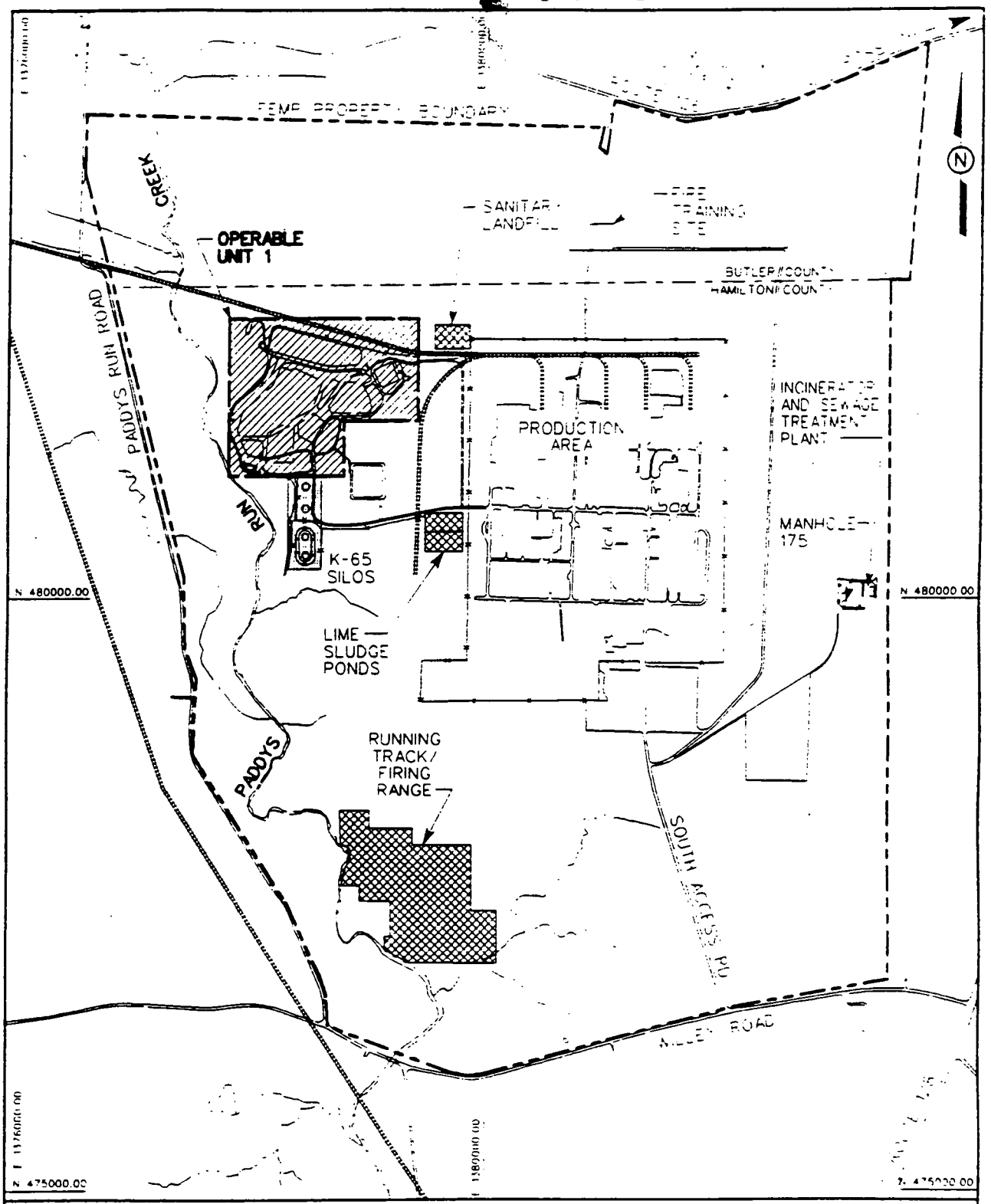


FIGURE 1-1. SOUTHWEST OHIO MAP

0 38


LEGEND:
OPERABLE UNIT 1 OUTLINE
FEMP PROPERTY BOUNDARY
NOTES:
1. REVISIONS SHOWN IN PURPLE AND WOODLAND COMPILED IN COOPERATION WITH STATE OF OHIO AGENCIES FROM AERIAL PHOTOGRAPHS TAKEN 1979 AND OTHER SOURCES. THIS INFORMATION NOT FIELD CHECKED. MAP EDITED 1981
2. SOURCE USGS (1980) SHANDON OHIO QUADRANGLE
SCALE:
0
1/2
1 MILE
FIGURE 1-2. FEMP SITE LOCATION MAP
FEMP PROPERTY BOUNDARY
OPERABLE UNIT 1 OUTLINE
U.S. RESERVATION
DEPARTMENT OF ENERGY
Shandon Sta
RIVER
IRVIN
Pumping Station
Hodges Cem
Wilson Tank
Cemetery
Fernald
Sunset
Rockdale
ROAD
CROSS
RIVER

5283



NOTE:

1. OPERABLE UNIT 3 INCLUDES ALL BUILDINGS, PIPELINES, AND ABOVEGROUND STRUCTURES IN THE PRODUCTION AREA. OPERABLE UNIT 5 INCLUDES GROUNDWATER, SURFACE WATER, SOILS, FLORA AND FAUNA, IN THE REGIONAL AREA AS WELL AS THE PRODUCTION AREA.

LEGEND:

- FENCE LINE
- DRAINAGE WAY
- CSX RAIL LINE
- OPERABLE UNIT 1 OUTLINE
- FEMP PROPERTY BOUNDARY
- OPERABLE UNIT 1
- OPERABLE UNIT 2
- OPERABLE UNIT 4

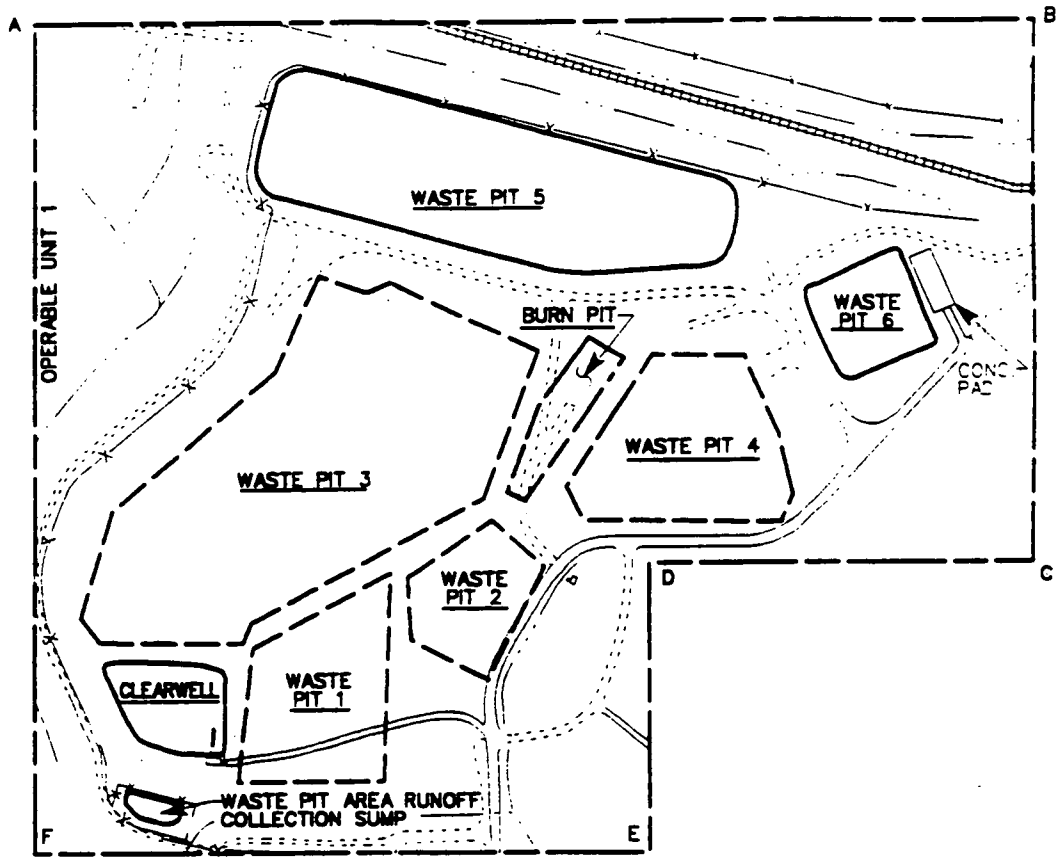
SCALE:

0 1200 FEET

0 40

FIGURE 1-3. LOCATION OF OPERABLE UNIT 1 WITHIN THE FEMP

- 5283



NOTES:

1. PITS 1, 2, 3 AND THE BURN PIT ARE COVERED WITH SOIL CAPS AND VEGETATED.
2. PIT 4 HAS AN INTERIM CAP.
3. PITS 5, 6 AND CLEARWELL ARE WATER COVERED
4. COORDINATES SHOWN ARE OHIO STATE PLANAR COORDINATES, ADJUSTED PER THE NORTH AMERICAN DATUM (NAD) OF 1983.
5. OPERABLE UNITS (OU) ARE IDENTIFIED. OU 5 INCLUDES GROUNDWATER, SURFACE WATER, SOILS, FLORA & FAUNA IN THE AREA OTHERWISE IDENTIFIED.

OU1 STATE PLANAR COORDINATES		
POINT	NORTHING	EASTING
A	482364	1377824
B	482364	1379432
C	481499	1379432
D	481499	1378812
E	481033	1378812
F	481033	7824

LEGEND:

- FENCE LINE
- DRAINAGE WAY
- CSX RAIL LINE
- PAVED ROADWAY
- GRAVEL ROADWAY
- OPERABLE UNIT 1 OUTLINE
- COVERED PIT OUTLINE
- OPEN PIT OUTLINE

SCALE:
0 300 FEET

FIGURE 1-4. OPERABLE UNIT 1 SITE MAP

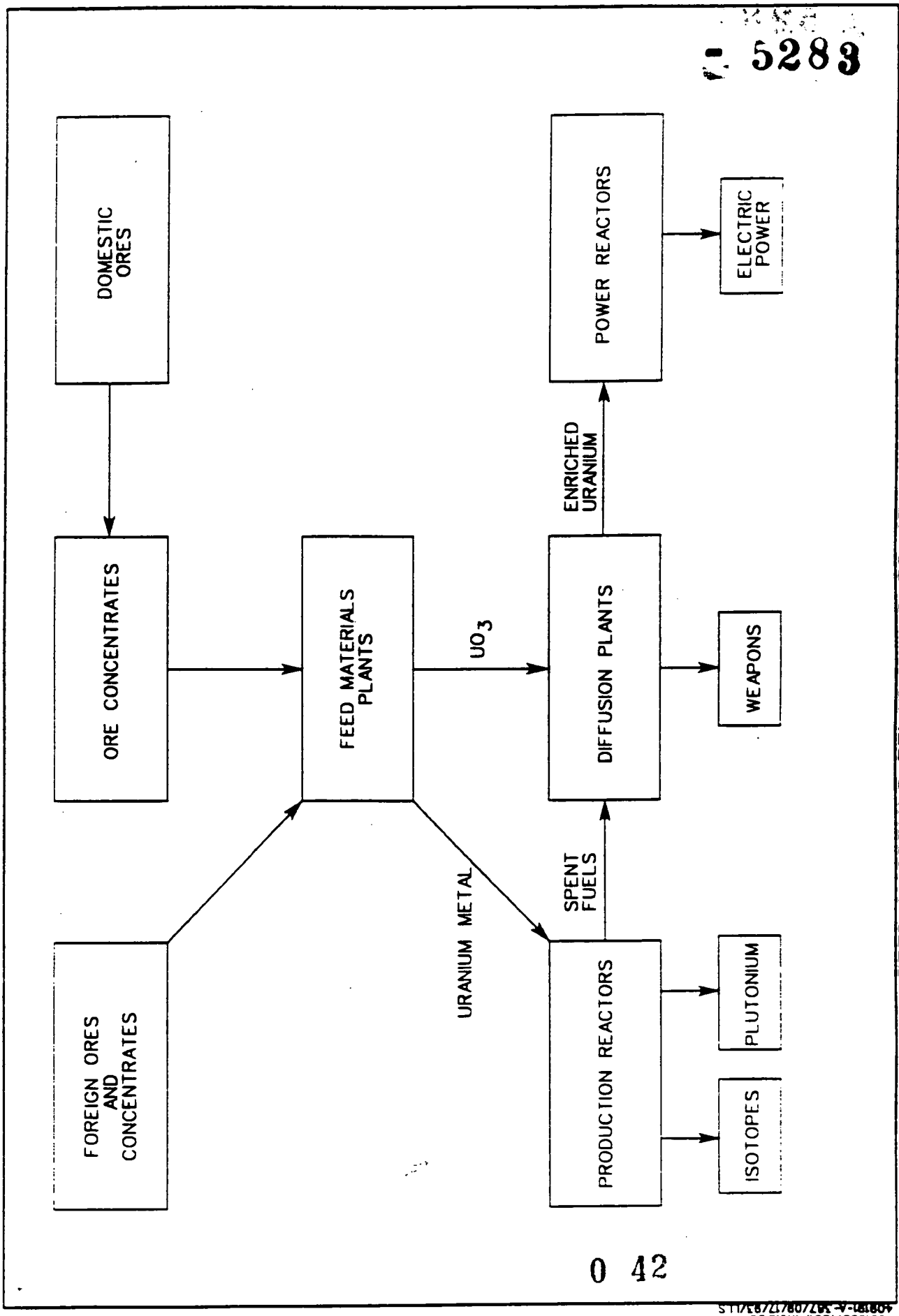


FIGURE 1-5. FEED MATERIALS RELATIONSHIP TO AEC PRODUCTION SYSTEMS

5283

0 42

4098387.OU1/XNOX/DS
4098B0-A-387/08/17/93/11S

countries as well as the United States; uranium trioxide (UO_3) from Port Hope, Canada; uranium tetrafluoride (green salts - UF_4) from excess inventory at the nation's gaseous diffusion plants; uranium hexafluoride (UF_6), also from the gaseous diffusion plants; slightly enriched recycled material from the Hanford Reactor Site and Savannah River plants; and recovered uranium-bearing residues from processing operations at the FEMP and elsewhere.

As described in Section 1.1.3, these feed materials were converted into high purity uranium metal, cast into various shapes, machined in some instances, and then transported to other DOE facilities. Depleted uranium metal derbies were transported to the Y-12 Plant in Oak Ridge, Tennessee. Some derbies and flat billets were shipped to the Rocky Flats Plant near Golden, Colorado. After 1962, uranium ingots were center drilled and then sent to Reactive Metals, Incorporated, (RMI) Titanium Company's Extrusion Plant, in Ashtabula, Ohio, for extrusion. The resulting extruded billets, which consisted of slightly enriched uranium metal, were then shipped to the Hanford Reactor Site near Richland, Washington. Extruded uranium tubes, consisting of depleted uranium metal, were returned to the FEMP for cutting and surface machining to produce target element cores. These depleted uranium metal target cores were shipped to the Savannah River Site near Augusta, Georgia. A description of the uranium metal products is provided in the next section.

1.1.3 Description of the FEMP Facility and Operations

Several chemical and metallurgical processes were used at the FEMP for the manufacture of uranium metal products (Figure 1-6). In general, these processes occurred in 7 of the FEMP's more than 50 production, storage, and support buildings. The physical layout of those buildings is shown in Figure 1-7. Much of the discussion of the refining process and handling of Operable Unit 1 wastes is excerpted from the following documents and will not be specifically referenced in all instances in the text:

- "Uranium Processing Technology" (Harrington and Ruehle 1959)
- "A Closer Look at Uranium Metal Production, A Technical Overview" (FMPC 1988)

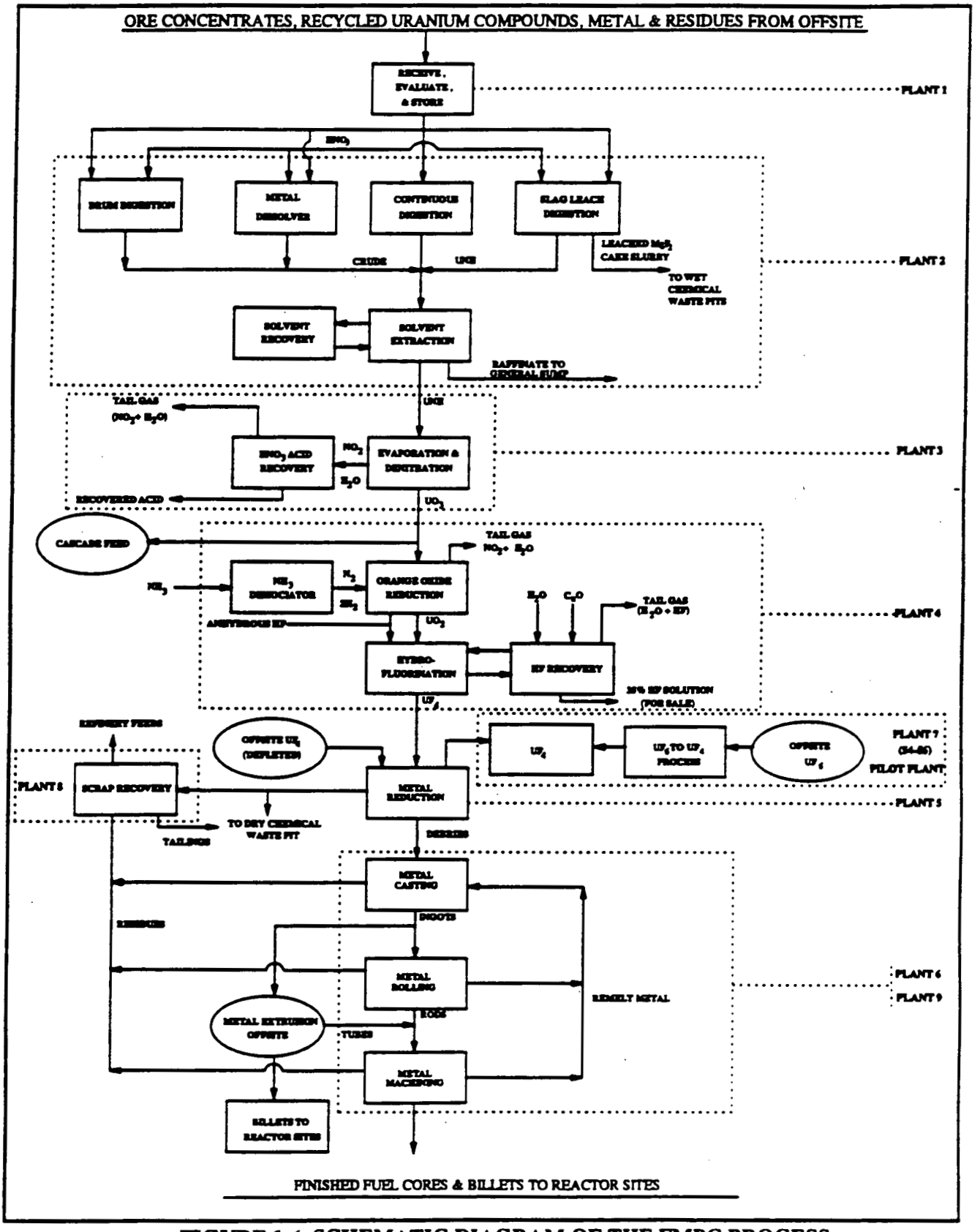
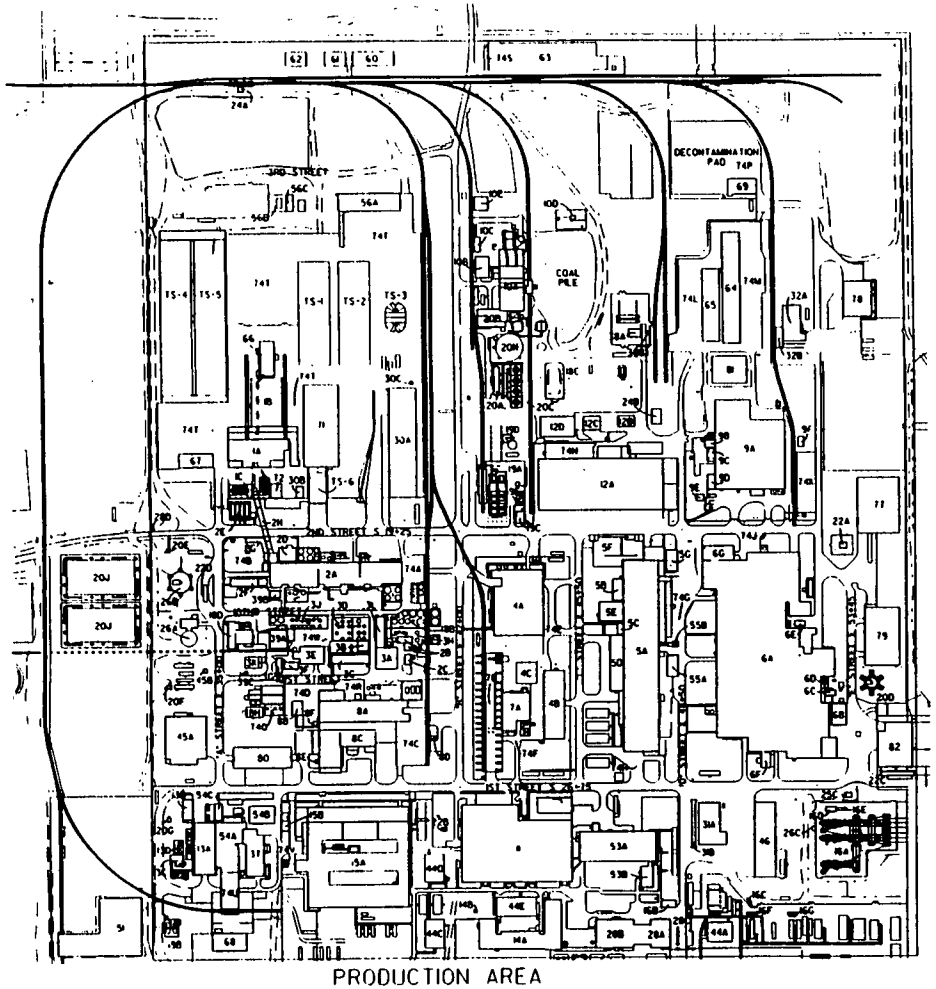


FIGURE 1-6 SCHEMATIC DIAGRAM OF THE FMPC PROCESS

0 44



FEMP SITE INDEX

TS-1	TENSION SUPPORT STRUCTURE #1
TS-2	TENSION SUPPORT STRUCTURE #2
TS-3	TENSION SUPPORT STRUCTURE #3
TS-4	TENSION SUPPORT STRUCTURE #4
TS-5	TENSION SUPPORT STRUCTURE #5
TS-6	TENSION SUPPORT STRUCTURE #6
1A	PREPARATION PLANT
1B	PLANT 1 STORAGE BLDG.
1C	PLANT 1 ORE SILOS
2A	ORE REFINERY PLANT
2B	GENERAL/REFINERY SUMP CONTROL BLDG.
2C	BULK LIME HANDLING BLDG.
2D	METAL DISSOLVER BLDG.
2E	NFS STORAGE & PUMP HOUSE
2F	COLD SIDE ORE CONVEYOR
2G	HOT SIDE ORE CONVEYOR
2H	CONVEYOR TUNNEL (FROM PLANT 1)
3A	MAINTENANCE BLDG.
3B	OZONE BLDG.
3C	MAIN CONTROL HOUSE
3D	MAIN TOWERS
3E	HOT RAFFINATE BLDG.
3F	MARSHALL SYSTEM
3G	RETRIGERATION BLDG.
3H	REFINERY SUMP
3J	COMBINED RAFFINATE TANKS
3K	OLD COOLING WATER TOWER
3L	ELECTRICAL POWER CENTER BLDG.
4A	GREEN SALT PLANT
4B	PLANT 4 WAREHOUSE
4C	PLANT 4 MAINTENANCE BLDG.
5A	METALS PRODUCTION PLANT
5B	PLANT 5 INGOT PICKLING
5C	PLANT 5 ELECTRICAL SUBSTATION
5D	WEST DERBY BREAKOUT/SLAG MILLING
5E	PLANT 5 FILTER BLDG.
5F	PLANT 5 COVERED STORAGE PAD
5G	PLANT 5 INGOT STORAGE SHELTER
6A	METALS FABRICATION PLANT
6B	PLANT 6 COVERED STORAGE AREA
6C	PLANT 6 ELECTROSTATIC PRECIPITATOR (SOUTH)
6D	PLANT 6 ELECTROSTATIC PRECIPITATOR (CENTRAL)
6E	PLANT 6 ELECTROSTATIC PRECIPITATOR (NORTH)
6F	PLANT 6 SALT OIL HEAT TREAT BLDG.
6G	PLANT 6 SUMP BLDG.
7A	PLANT 7
7B	PLANT 7 OVERHEAD CRANE
8A	RECOVERY PLANT
8B	PLANT 8 MAINTENANCE BLDG.
8C	ROTARY KILN/DRUM RECONDITIONING
8D	PLANT 8 RAILROAD FILTER BLDG.
8E	DRUM CONVEYOR SHELTER
8F	PLANT 8 OLD DRUM WASHER
9A	SPECIAL PRODUCTS PLANT
9B	PLANT 9 SUMP TREATMENT FACILITY
9C	PLANT 9 DUST COLLECTOR
9D	PLANT 9 SUBSTATION
9E	PLANT 9 CYLINDER SHED
9F	PLANT 9 ELECTROSTATIC PRECIPITATOR
10A	BOILER PLANT
10B	BOILER PLANT MAINTENANCE BLDG.
10C	WET SALT STORAGE BIN
10D	CONTAMINATED OIL/GRAPHITE BURN PAD
10E	UTILITIES (HEAVY EQUIP. BLDG. (PROPOSED)
11	SERVICE BLDG.
12A	MAIN MAINTENANCE BLDG.
12B	CYLINDER STORAGE BLDG.
12C	LUMBER STORAGE BLDG.
12D	MAINTENANCE BLDG. WAREHOUSE (PROPOSED)
13A	PILOT PLANT WET SIDE
13B	PILOT PLANT MAINTENANCE BLDG.
13C	SUMP PUMP HOUSE
13D	PILOT PLANT THORIUM TANK FARM
14A	ADMINISTRATION BLDG.
14B	BLDG. 14 EOC GENERATOR SET
15A	LABORATORY
15B	LABORATORY CHEMICAL STORAGE BLDG.
16A	MAIN ELECTRICAL STATION
16B	ELECTRICAL SUBSTATION
16C	ELECTRICAL PANELS & TRANSFORMER
16D	MAIN ELECTRICAL SWITCH HOUSE
16E	MAIN ELECTRICAL TRANSFORMERS
16F	TRAILER SUBSTATION #1
16G	TRAILER SUBSTATION #2
16H	IO PLEXS NORTH SUBSTATION
16J	IO PLEXS SOUTH SUBSTATION
16K	BOW SURGE LAGOON
16L	GENERAL SUMP
16M	COAL PILE RUNOFF BASIN
16N	BIOSENTRIFICATION TOWERS
16P	STORM WATER RETENTION BASINS
16Q	PIT #5 SLUICE GATE
16R	CLEARWELL PUMP HOUSE
16S	BOW EFFLUENT TREATMENT FACILITY
16T	METHANOL TANK
16U	LOW NITRATE TANK
16V	HIGH NITRATE TANK
16W	HIGH NITRATE STORAGE TANK
16X	WASTE PIT AREA STORM WATER RUNOFF CONTROL
16Y	DISSOLVED OXYGEN BLDG.
16Z	MAIN VALVE HOUSE
19A	MAIN TANK FARM
19B	PILOT PLANT AMMONIA TANK FARM
19C	TANK FARM CONTROL HOUSE
19D	OLD NORTH TANK FARM
19E	TANK FARM LIME SLITTER BLDG.
20A	PUMP STATION & POWER CENTER
20B	WATER PLANT
20C	COOLING TOWERS
20D	ELEVATED POTABLE STORAGE TANK
20E	WELL HOUSE #1
20F	WELL HOUSE #2
20G	WELL HOUSE #3
20H	PROCESS WATER STORAGE TANK
20J	LIME SLURRY PITS
22A	GAS METER BLDG.
22B	STORM SEWER LIFT STATION
22C	TRUCK SCALE
22D	SCALE HOUSE & WEIGH SCALE
22E	UTILITY TRENCH TO PIT AREA
23	METEOROLOGICAL TOWER
24A	RAILROAD SCALE HOUSE
24B	RAILROAD ENGINE HOUSE
25A	CHLORINATION BLDG.
25B	W.W. #175/EFF. LINE/SAMPLING BLDG.
25C	SEWAGE LIFT STATION BLDG.
25D	U.V. DISINFECTION BLDG.
25E	DIGESTER & CONTROL BLDG.
25F	SLUDGE DRYING BEDS
25G	PRIMARY SETTLING BASINS
25H	TRICKLING FILTERS
25J	IO PLEXS SEWAGE LIFT STATION
26A	PUMP HOUSE-HP FIRE PROTECTION
26B	ELEVATED WATER STORAGE TANK
26C	MAIN ELECTRICAL STRAINER HOUSE
28A	SECURITY BLDG.
28B	HUMAN RESOURCES BLDG.
28C	GUARD POST ON SOUTH END OF "D" STR.
28D	GUARD POST ON WEST END OF "2ND" STR.
30A	CHEMICAL WAREHOUSE
30B	DRUM STORAGE WAREHOUSE
30C	OLD TEN TON SCALE
30A	CRANE HOUSE/GARAGE
30B	OLD TRUCK SCALE
32A	MAGNESIUM STORAGE BLDG.
32B	BLDG. 32 COVERED LOADING DOCK
34A	R-65 STORAGE TANK (NORTH)
34B	R-65 STORAGE TANK (SOUTH)
34C	RTS BLDG.
35A	METAL OXIDE STORAGE TANK (NORTH)
35B	METAL OXIDE STORAGE TANK (SOUTH)
37	PILOT PLANT ANNEX
38A	PROPANE STORAGE
38B	CYLINDER FILLING STATION
39A	INCINERATOR BLDG.
39B	WASTE OIL DECANT SHELTER
39C	INCINERATOR SPRINKLER RISER HOUSE
39D	SEWAGE TREATMENT PLANT INCINERATOR
44A	TRAILER COMPLEX (6-PLEX)
44C	TRAILER COMPLEX (7-PLEX S)
44D	TRAILER COMPLEX (7-PLEX N)
44E	TRAILER COMPLEX (10 PLEX)
45A	RUST ENGINEERING BLDG.
45B	UTILITY SHED EAST OF RUST TRAILERS
46	HEAVY EQUIPMENT BLDG.
51	SIX TO FOUR REDUCTION FACILITY #2
53A	HEALTH & SAFETY BLDG.
53B	BI-VHO BLDG.
54A	SIX TO FOUR REDUCTION FACILITY #1
54B	PILOT PLANT SHELTER
54C	PILOT PLANT DISSOCIATOR SHELTER
55A	SLAG RECYCLING BLDG.
55B	SLAG RECYCLING PIT/ELEVATOR
56A	CP STORAGE WAREHOUSE
56B	STORAGE SHED (WEST)
56C	STORAGE SHED (EAST)
60	QUONSET HUT #1
61	QUONSET HUT #2
62	QUONSET HUT #3
63	EC-2 WAREHOUSE
64	THORIUM WAREHOUSE
65	KOLOI PLANT 5 WAREHOUSE
66	DRUM RECONDITIONING BLDG.
67	PLANT 1 THORIUM WAREHOUSE
68	PILOT PLANT WAREHOUSE
69	DECONTAMINATION BLDG.
71	GENERAL IN-PROCESS WAREHOUSE
72	DRUM STORAGE BUILDING
73A	FIRE BRIGADE TRAINING CENTER BLDG.
73B	FIRE TRAINING POND
73C	FIRE TRAINING TANK
73D	FIRE TRAINING BURN TROUGH
73E	CONFINED SPACE BURN TANK
74A	PLANT 2 EAST PAD
74B	PLANT 2 WEST PAD
74C	PLANT 8 EAST PAD
74D	PLANT 8 WEST PAD
74E	PLANT 4 PAD
74F	PLANT 1 PAD
74G	PLANT 5 EAST PAD
74H	PLANT 5 SOUTH PAD
74J	PLANT 6 PADS
74K	PLANT 9 PAD
74L	BUILDING 65 WEST PAD
74M	BUILDING 64 EAST PAD & R.R. DOCK
74N	BUILDING 12 NORTH PAD
74P	DECONTAMINATION PAD
74Q	PLANT 8 OLD METAL DISSOLVER PAD
74R	PLANT 8 NORTH PAD
74S	BUILDING 63 WEST PAD
74T	PLANT 1 STORAGE PAD
74U	PILOT PLANT PAD
74V	LABORATORY PAD
74W	INCINERATOR BLDG. PAD
77	FINISHED PRODUCTS WAREHOUSE (4A)
78	D & D BUILDING
79	PLANT 6 WAREHOUSE
80	PLANT 8 WAREHOUSE
81	PLANT 9 WAREHOUSE
82	RECEIVING/INCOMING MAT'LS. (WSP.
88	CLEARWELL LINE
89	PARKING LOTS
176	INTERIM OFFICE SPACE
177	INTERIM OFFICE SPACE
180	INTERIM OFFICE SPACE
181	INTERIM OFFICE SPACE

LEGEND:

- ROADWAY
- FENCE LINES
- BUILDING OUTLINES
- CSX RAIL LINES
- INDICATES PROPOSED LOCATIONS OF STRUCTURES.

SCALE: 100 0 100 200 300 FEET

NOTE:

1. SOURCE - FEMP CADD SITELIST.DGN MAR. 12, 1993.

FIGURE 1-7. EXISTING PRODUCTION AREA LAYOUT

1.1.3.1 Processing

Impure starting materials, or feed materials, were first introduced into the process through the sampling plant (Plant 1). Here the materials were sampled to determine the uranium concentration and the uranium enrichment status. Ore concentrates and impure feed materials from the recovery plant (Plant 8) were transferred to the refinery (Plant 2/3), where they were dissolved in nitric acid (HNO_3) and the uranium was purified through solvent extraction to yield a solution of uranyl nitrate (UNH). Evaporation and denitrification converted the uranyl nitrate solution to UO_3 powder.

Beginning in 1962, residues were received from two DOE facilities, Hanford and Savannah River plants, for reprocessing. Trace quantities of fission products and transuranics resided within these materials. These feed streams generally contained less than 3 parts per billion (ppb) of transuranics such as plutonium (Pu)-239 and less than 10 parts per million (ppm) of fission products such as technetium (Tc-99). Beginning in 1965, the uranium values from the residues generated from processing this material at the FEMP were prepared in Plant 8, and recovered in Plant 2/3 (refinery).

Uranium trioxide from Plant 2/3 was transported to the green salt plant (Plant 4), where it was reduced with hydrogen to form uranium dioxide (UO_2) and then converted to UF_4 by reacting with anhydrous hydrogen fluoride. The UF_4 was then transported to Plant 5 (a metals production plant) where it was blended with magnesium (Mg) metal granules and placed in a closed refractory-lined steel pot. At approximately 650°C (1200°F), the UF_4 and the magnesium would initiate an exothermic reaction. The resulting product was a 135- to 165-kilogram (kg) (300 to 375 pound [lb]) piece of pure uranium metal and a by-product, magnesium fluoride (MgF_2) slag. The resultant piece of uranium metal had the shape of a gentleman's top hat, or derby, as it was called. Approximately 50 percent of the magnesium fluoride slag was then used to line the furnace pots.

Some of the derbies were shipped directly to other government sites, such as the plant in Oak Ridge, Tennessee, and the Rocky Flats Plant near Golden, Colorado. However, most remained in Plant 5 where they were remelted along with uranium scrap-metal from earlier machining operations and poured into graphite molds to form cylindrical or flat ingots. Flat ingots consisted of depleted

uranium metal. These flat ingots were top-cropped, sampled, analyzed, and inspected in the metals fabrication plant (Plant 6), and then shipped to the Rocky Flats Plant.

The cylindrical ingots consisted of depleted, normal, or slightly enriched uranium. From plant startup until approximately 1962, the cylindrical ingots were top-cropped, sampled, and analyzed prior to being heat treated and rolled into rods. The rods were machined into fuel cores and shipped to nuclear reactors at various government sites, including Hanford and Savannah River. This process continued at a reduced level until 1970.

During the early 1960s, a process was added where these ingots were machined and cored in Plant 9, heat treated in Plant 6, and then sent to RMI in Ashtabula, Ohio. At RMI, depleted uranium ingots were extruded into tubes. The ingots, which consisted of slightly enriched uranium, were upset forged, machined, then shipped to the Hanford site. The extruded tubes consisting of depleted uranium were returned to Plant 6 at the FEMP. There, they were cut into sections, heat treated, machined to final dimensions, and inspected for final product quality. The completed target element cores were shipped to the DOE Savannah River site.

Small amounts of thorium were processed at the FEMP on several occasions from 1954 through 1975. Thorium operations were conducted in Plants 1, 4, 6, 8, 9, and the pilot plant. The FEMP served as the thorium repository for DOE and maintains storage facilities for a variety of thorium materials. Thorium materials are no longer being received at the FEMP for storage. Existing thorium inventories have now been declared waste and are being over-packed for shipment to DOE's Nevada Test Site (NTS) for disposal.

1.1.3.2 Major Wastes Types

In general, all of the wastes generated on site, as well as some wastes shipped from other DOE/DOD facilities, were disposed of onsite. Therefore, a wide variety of materials were disposed of in the waste pits. However, the overwhelming percentage, both in mass and volume, is accounted for in three major waste streams: general sump sludge, neutralized raffinate, and magnesium fluoride. The

following descriptions include these and other significant waste streams, their source, and the data used to determine their occurrence in the waste pits.

- General Sump Sludge: The general sump consisted of a series of batch tanks that received an average of 1.6 million gallons per month of filtrates from the various processing plants, as well as wastewater from the laboratory (0.3 to 0.9 million gallons per month) and general decontamination and cleanup water.

  Prior to discharging the filtrate to the general sump, the individual processing plants would neutralize the waste streams and filter them to remove the uranium values. The filtrates were then analyzed to ascertain that the uranium content was within allowable discard limits (generally <0.0004 pounds per gallon). If so, the filtrates were discharged to the general sump (Figure 1-8).

  Prior to discharge to the waste pits, the filtrate in the general sump was neutralized with calcium oxide (CaO), to obtain maximum precipitation of radioactive materials, and mixed. After 1984, the solids were settled and the supernatant pumped to the waste pits. The settled solids were transferred to Plant 8 for filtering and packaging for disposal. The filtrate from the Plant 8 filtering operation was returned to the general sump.

  As discussed in Appendix F.6.3 of the Remedial Investigation Report, a combination of actual records and estimates was used to establish the amount of liquid and its uranium content pumped from the general sump to the waste pits. Operating records that show the flow and the uranium content were available from fiscal year (FY) 67 through FY 84. For other years, where records were incomplete or nonexistent, a correlation based on production in Plant 5 was used.

  An average solids content in the liquid pumped from the general sump to the waste pits of 3 percent was used. This amount is based on a reported range of 2½ percent to 10 percent and measurements for a 3-month period in 1979 that indicate the solids content is at the lower end of the range.

  Many substances would have precipitated with the lime neutralization in the general sump. Because the wastewater had been filtered in the individual processing plants, it has been assumed that 50 percent of the nonuranium solids deposited in the waste pits from the general sump was lime.

  The majority of the flow from the general sump was discharged to Waste Pits 3 and 5. However, prior to the opening of Waste Pit 3 in December 1958, it is known that the general sump discharged to Waste Pit 2. It has been assumed that the general sump discharged to Waste Pit 1 prior to the opening of Waste Pit 2 in 1957.

Figure 1-8

- 5283

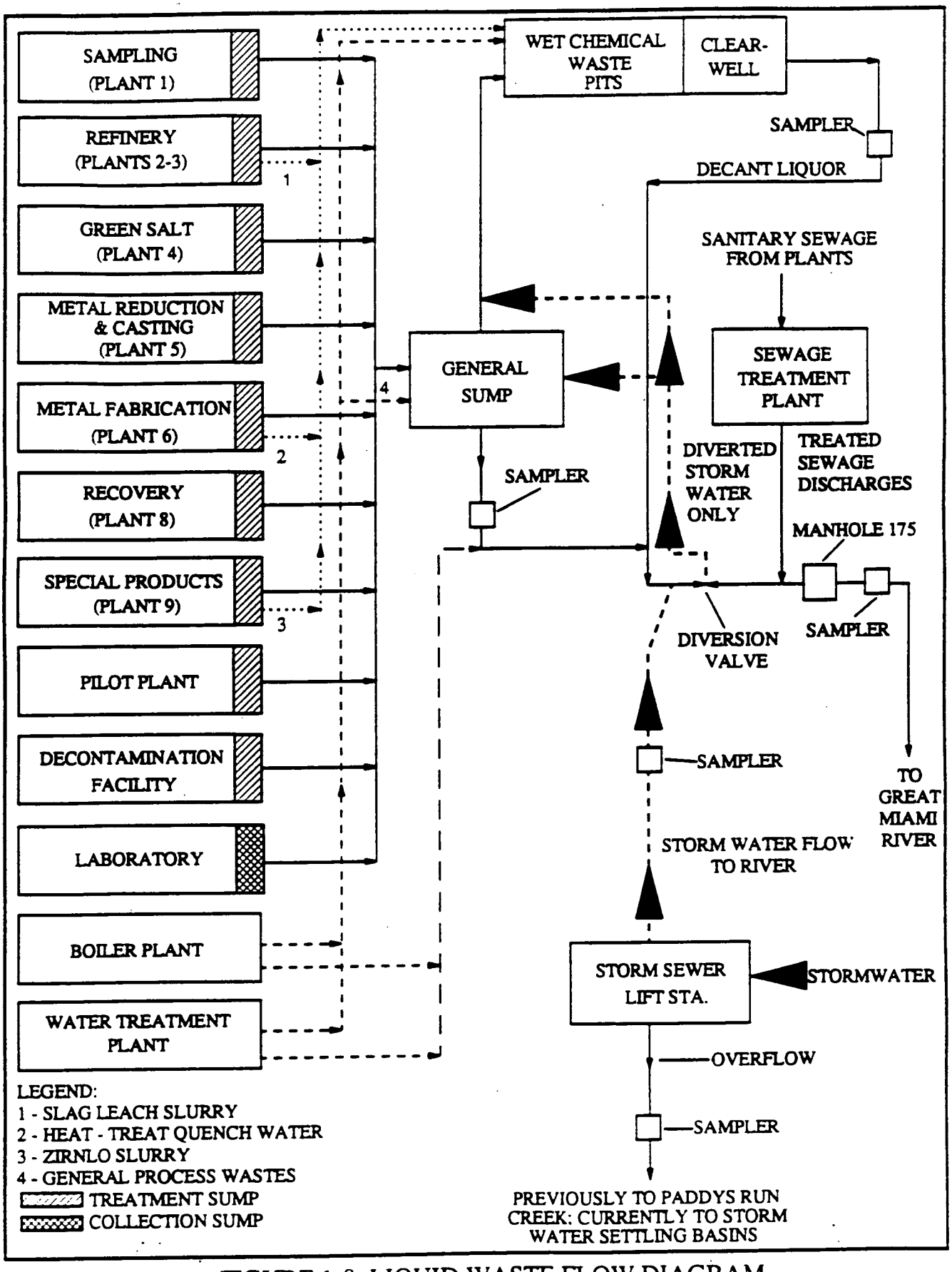


FIGURE 1-8 LIQUID WASTE FLOW DIAGRAM

0 49

Appendix F.6.3 of the RI Report details the estimates of the amount of sludge generated by the general sump and deposited in the waste pits.

- Neutralized Raffinate: In the refinery operation, uranium-bearing feed materials were digested in nitric acid to solubilize the uranium. The uranium was then extracted, leaving most of the nitric acid, impurities associated with the materials being processed, and small quantities of insoluble, nonextractable uranium in the resulting "raffinate" solution. Before 1960, these raffinates were calcined prior to disposal. If the raffinate resulted from the processing of ore concentrates with a high radium content (non-K-65 material - See Appendix F.6.4 of the RI Report for further discussion), it was called "hot raffinate," which was neutralized and pumped as a slurry to the silos. Otherwise, the raffinate was called "cold metal oxide", most of which was placed in Silo 3. As discussed further in Appendix F.6.4 of the RI Report, it is likely that some "hot raffinates" were mixed with "cold metal oxides" and deposited in Waste Pits 2 and 3. After 1960, the process gradually progressed to neutralization of the raffinate slurry, resulting in "neutralized raffinates."

The amount and characteristics of the raffinate waste were dependent on the characteristics of the refinery feed material. During the first two decades of operation, refinery feeds included uranium ore concentrates from numerous mines and processors around the world. The range of composition of these concentrates is shown in Appendix F.6.2 of the RI Report. An average composition of ore concentrates, based on more than 700 samples from 38 mines, was used to estimate the composition of raffinates generated from the processing of concentrates. With removal of the uranium from the ore concentrates, the impurities could be concentrated up to three times in the raffinate, depending on the original split between impurities and uranium. Therefore, significant concentrations of impurities such as arsenic (0.01 percent to 2.4 percent), chromium (0.1 percent to 0.12 percent), and thorium (0.003 percent to 3 percent) are expected in the waste pits associated with raffinates.

An estimated 2.74 metric tons (MT) of neutralized raffinate was generated for every MT of uranium produced from ore concentrates through the refinery. Approximately 70 percent of this amount was liquid, implying that 0.822 MT of solids was generated for every metric tons of uranium (MTU) of production from ore concentrates.

As discussed previously, the neutralized raffinates generated from the recovery of uranium from process residues were different than that generated from processing ore concentrates. The residues were generated from other process operations and had a uranium content above the Economical Discard Level (EDL). The residues were, therefore, reprocessed to recover the uranium. Because the residues had already been processed, the primary impurities were corrosion products from the process itself. An estimated 2.43 MT of neutralized raffinate was generated for every MT of uranium produced from residues

through the refinery. At 70 percent moisture, this equates to 0.728 MT of solids generated for every MTU of production from residues.

The neutralized raffinates primarily contained the impurities from the ore concentrates and residues, nitrates, lime, and 0.5 percent total uranium (wet basis - 1.67 percent dry basis). The raffinates were pasty in consistency and ranged in color from yellow to blue, including brown, orange, and red. The color depended on the primary impurities included. The neutralized raffinates were deposited in slurry form to Waste Pits 3 and 5, with a small amount deposited in Waste Pit 2.

Appendix F.6.4 of the RI Report details the estimates of the amount of neutralized raffinate generated from the production of UO_3 in the refinery and deposited in the waste pits. Also included is an estimate of the contribution of the associated impurities to the composition of the waste pits, which will be discussed in more detail in Section 1.2.1.

- Magnesium Fluoride (MgF_2): The reduction of UF_4 (green salt) using magnesium metal to produce uranium metal generates MgF_2 slag. Theoretically, the production of 1 MTU generates 0.54 MT of slag. Appendix F.6.5 of the RI Report details the amount of MgF_2 generated in Plant 5 and deposited in the waste pits. This material was deposited in the waste pits in primarily three forms:

  - *Depleted Slag*: The reduction of depleted UF_4 in Plant 5 generated depleted MgF_2 slag. A small amount of C-oxide was deposited in Waste Pits 1 and 2 from 1955 to 1963. C-oxide was generated when dolomite was used to line the reduction pots, prior to MgF_2 being used for that purpose. The C-oxide contained (dry basis) approximately 5 percent uranium, a trace of magnesium metal, and 47.5 percent MgF_2 and 47.5 percent dolomite.

    The remainder of the depleted slag was deposited in Waste Pits 4 and 6. On a dry basis, the composition of the depleted slag (dry basis) is approximately 94.6 percent MgF_2, 5.4 percent uranium in various oxidation states, and trace amounts of elemental magnesium. The waste material was white to black in color, granular, and 0.03 to 1 inch in size.

  - *Trailer Cake*: Prior to 1965, MgF_2 slag from the reduction of normal and enriched UF_4 was transferred to Plant 8 to recover the uranium values. In Plant 8, the uranium was recovered by dissolving it in hydrochloric acid (HCl), followed by a series of precipitation steps. The insoluble materials remaining after the acid digestion were filtered out and the resulting trailer cake transported to Waste Pits 1, 2, 3, and 4.

    In addition to the trailer cake generated by the reduction of UF_4 produced on site, the facility received depleted C-oxide and interim reprocessing plant residues (IRP

tailings) from Mallinckrodt Chemical Works (MCW) in Weldon Springs Missouri from 1959 to 1965. The names are not significant except that the IRP tailings had already been processed to recover some of the uranium. Both of these materials were reprocessed to recover as much uranium as possible. The resultant residue (14,955 MT) was transported to Waste Pit 3 as trailer cake.

Trailer cake (dry basis) is approximately 96.5 percent MgF_2, 3 percent filter aid (diatomaceous earth), and 0.5 percent uranium, with some amount of nitrates. The trailer cake was white to gray in color and granular, with 100 percent less than 0.03 inches and 90 percent smaller than 50 microns.

- *Slag Leach Slurry*: After 1965, milled MgF_2 slag from the reduction of normal and enriched UF_4 was transferred to the refinery to recover the uranium values. The uranium was recovered by dissolving it in nitric acid, followed by extraction and denitration. The insoluble materials left over after the acid digestion were filtered out, reslurried, mixed with lime (calcium oxide) to a pH of around 11, and pumped to the waste pits. This material was deposited in Waste Pit 3 from 1965 until Waste Pit 5 was completed in October 1968, and in Waste Pit 5 thereafter.

  The composition of slag leach (dry basis) is approximately 96.5 percent MgF_2, 3 percent filter aid (diatomaceous earth), and 0.5 percent uranium, with some amount of calcium compounds from the neutralization step as well as nitrates. The material was white to gray in color and granular, with 100 percent less than 0.03 inch and 90 percent smaller than 50 microns.

- Other Waste Streams: Other waste known to have been deposited in the waste pits in significant quantities or whose presence may be of concern from an environmental standpoint include:

  - *Depleted Residues*: Various residues were generated from the processing of depleted materials. These residues included wastes from the packaging of depleted products in Plant 4, reduction and casting in Plant 5, and machining in Plant 6. A wide variety of material size, density, and uranium content are represented in these residues.

    The materials include the following (taken from actual records of discards):

    Contaminated rags, paper and polyethylene
    Contaminated asbestos material
    Dust collector bags
    Scrap salts (high in fluoride), including floor sweepings
    Off-spec UF_4 or thorium tetraflouride (ThF_4)
    Contaminated soil, rocks, sand, brick, and ceramics

Furnace salt (solidified, nonchloride)
Dust collector residues (high fluoride, pyrophoric)
Dry crushed slag from furnace pot blowouts
Partially oxidized metal (containing no metl-x fire retardant)
Bad reductions (no derby)
Unrecycled slag (ball mill product)
Dirty prill (magnesium metal, high uranium content)
Reject UO_3
Drum decontamination residues
Magnesium oxide and magnesium zirconate from crucible cleanout
Sludges (oily, high free metal)
Sludges (salt, soft, chloride)
Sludges (nonoily, low or high free metal)
Wet sump of filter cake (with and without oil)
Scrap uranium oxide, U_3O_8
Chips and turnings
Solid metal (other than cores) U_3O_8
Contaminated asbestos materials

In total, these residues contain an average of approximately 47 percent uranium, with a range of 0 percent to nearly 95 percent. They range in density from 400 kg/cubic meters (m^3) (25 lb/cubic feet [ft^3]) to 8000 kg/m^3 (500 lb/ft^3), with an average of approximately 1440 kg/m^3 (90 lb/ft^3).

These residues were deposited in Waste Pits 1, 2, 4, and 6. Appendix F.6.7 of the RI Report details the amount of these residues generated and deposited in the waste pits.

- *Water Treatment Sludge*: Sludge from the softening of water for use in the production process was placed in the waste pits to further neutralize and solidify the contents. A total of approximately 300 tons per year of this material was placed in Waste Pits 3 and 5 for a 20-year period beginning in the mid-1960s. This material contains precipitated calcium and magnesium as well as excess lime. It is white to gray in color and pasty to granular.

  Appendix F.6.9 of the RI Report details the amount of this sludge that was generated and deposited in the waste pits.

- *Graphite and Ceramics*: Graphite was used in various places in the production process, including crucibles and ingot molds. This graphite was regularly replaced. The waste graphite from the processing of normal and enriched uranium was burned in the graphite burner to concentrate the uranium. Waste graphite from the processing of depleted uranium was deposited in Waste Pits 1, 2, and 4.

Ceramic brick was used to line the reduction furnaces and ceramic refractory was used in the remelt furnaces in Plant 5. These ceramics were periodically replaced, with the old ones deposited in Waste Pits 1, 2, and 4.

Appendix F.6.6 of the RI Report details the amount of graphite/ceramics generated and deposited in the waste pits.

- *Uranyl Ammonium Phosphate Filtrate*: Uranyl ammonium phosphate (UAP) filtrate was generated from 1953 through 1964 in the UAP process in Plant 8. This process was a method of recovering uranium from magnesium fluoride slag. The neutralized UAP filtrate was deposited in Waste Pits 1 and 2. Although not a major contributor to the contents of these waste pits, the filtrate did contain various impurities. Appendix F.6.8 of the RI Report details the amount of filtrate generated, its disposition in the waste pits, and its primary constituents.

- *Thorium Wastes*: Thorium wastes were generated at the site from two sources: an impurity in the ore concentrates and thorium processing. Total thorium in the concentrates ranged from 0.001 percent to 1.06 percent (Appendix F.6.2 of the RI Report). The impurities in the ore concentrates were concentrated up to three times in the raffinate by virtue of removing the uranium. Therefore, depending on the ore concentrate and the associated impurities, significant concentrations of thorium may be expected in Waste Pits 2, 3, and 5 associated with the raffinate.

  The production of thorium metal generated residues for disposal. In the early 1950s, these residues were stored and later transported to Maxey Flats in Moorehead, Kentucky, and Mallinckrodt. Some of these residues, however, were deposited in the waste pits as raffinates (Waste Pits 1, 3, and 5), solids (Waste Pit 4), and liquid wastes (Waste Pits 2, 3, and 5 through the general sump).

  Appendix F.6.10 of the RI Report details the amount of thorium residues disposed of in the waste pits.

- *Ash*: As illustrated in Table 1-1 and Figure 1-9, all contaminated combustibles, such as wooden pallets, paper, general trash, graphite, oils, etc. were burned or incinerated on site. The purpose of this activity was to reduce the volume to be ultimately disposed and to concentrate any recoverable uranium. The incinerators included the Sewage Treatment Plant incinerator, the security incinerator, and the Trane incinerator. The burners included the graphite Burner, the Oil Burner, and the Burn Pit.

  The ash from these burning activities was collected and sampled for uranium content and isotopic level. If these levels were above the Economic Discard Limit (EDL),

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TABLE 1-1
DISPOSITION OF ASH FROM ON-SITE INCINERATORS

Combustion Device	Materials Burned	Uranium Level	Disposition of Ash
Incinerator at Sewage Treatment Plant	Paper, rags, wood, etc.	Above Economic Discard Limit (EDL): 0.2 - 0.42% uranium	Ash was reprocessed to recover uranium at refinery (Plant 8). Ash (and associated contaminants) entered raffinate waste stream. During 1954-1959, raffinate was heat dried (calcined) and disposed of in Waste Pit 2. After that, raffinate slurry was pumped to Waste Pits 3 and 5.
Security Incinerator	Classified documents (paper)		
Trane Incinerator	Miscellaneous contaminated combustibles		
Graphite Burner	Graphite molds (normal and enriched contamination)		
Oil Burner	Miscellaneous waste oils	Below EDL	Disposed in Waste Pit 1, 2, or 4.
Coal Fired Boilers	Coal	Testing undocumented.	Disposed of in flyash piles (majority), Waste Pit 3, and the Burn Pit.
Burn Pit	Waste oils, laboratory waste, railroad ties, pyrophorics, etc.	Above EDL	Reprocessed to recover uranium (see disposition of reprocessed ash above).
		Below EDL	Remained in Burn Pit or disposed of in Waste Pit 1, 2, or 4.

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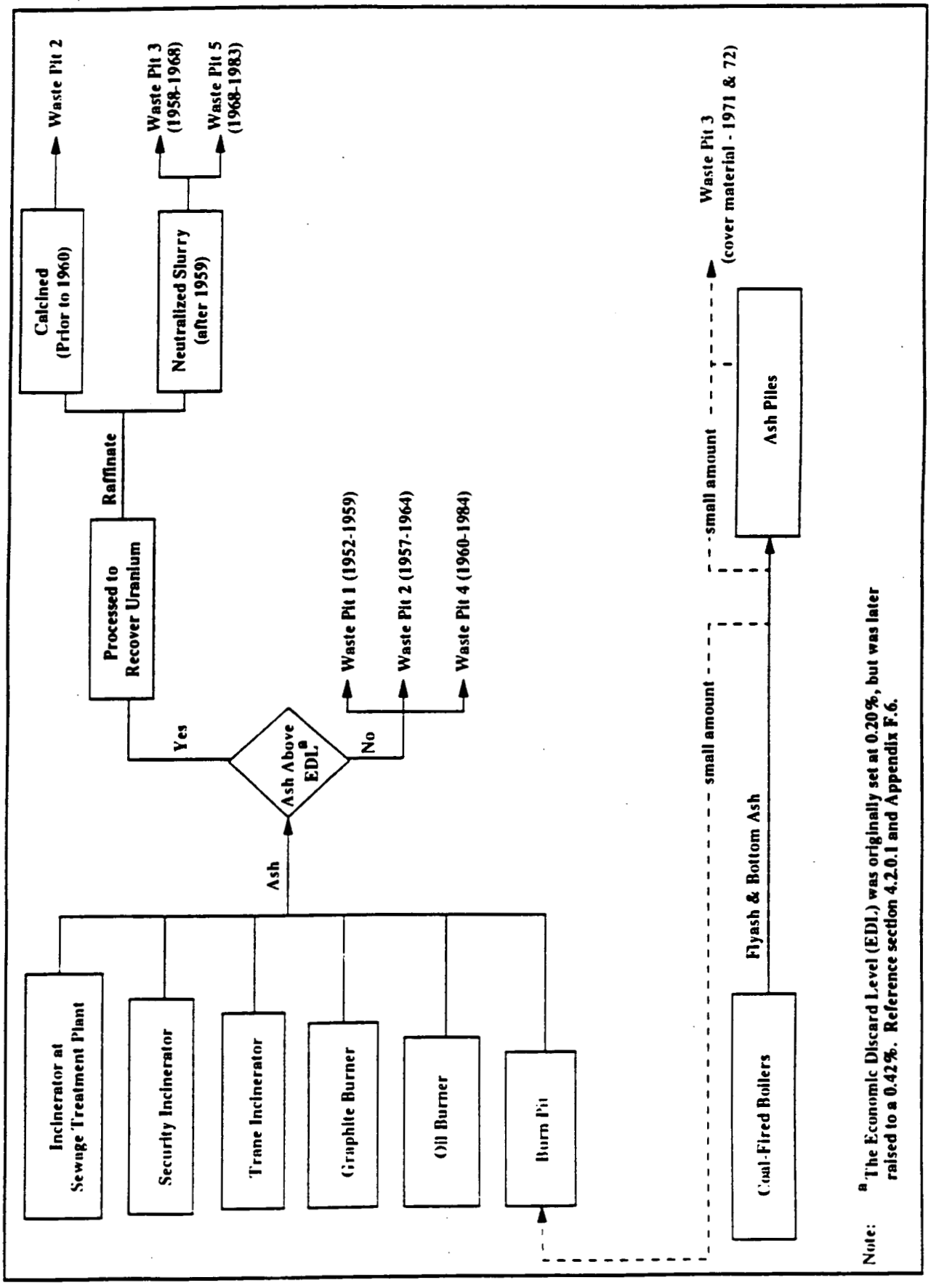


Note: [a] The Economic Discard Level (EDL) was originally set at 0.20%, but was later raised to a 0.42%. Reference section 4.2.0.1 and Appendix F.6.

FIGURE 1-9. DISTRIBUTION OF ASH TO WASTE PITS

the ash was processed to recover the uranium. In this case, the ash would have become part of the raffinate, and been deposited in Waste Pits 2, 3, or 5. If the uranium content was below the EDL, the ash would have been deposited directly in Waste Pits 1, 2, or 4.

Records indicate that approximately 25 MT of incinerator ash was received from the K-25 Plant at Oak Ridge, Tennessee from FY 70 through FY 82. This ash had uranium contents of 2 percent to 85 percent and contained 0.8 percent to 10 percent uranium (U)-235. Because of the uranium content, this material was processed to recover the uranium, with the residue becoming part of the neutralized raffinate and discarded in Waste Pit 5.

Flyash: Flyash was generated from the onsite, coal-fired boiler. This material generally was deposited in one of two ash storage piles. However, as discussed in Section 1.2.1.3, some of the flyash was used as cover material for Waste Pit 3. In addition, records indicate that some of this flyash was deposited in the Burn Pit prior to 1959.

Table 1-1 summarizes the combustion equipment and disposition of the ash generated and Figure 1-9 shows the distribution of the various ashes to the waste pits.

1.1.4 Operating History of the FEMP

The Atomic Energy Commission (AEC), predecessor to the U.S. Energy Research and Development Administration (ERDA) and then DOE, established the FMPC in conformance with AEC orders in the early 1950s. In 1951, National Lead Company of Ohio, Inc., (now NLO) entered into a contract with the AEC as the Management and Operations Contractor for the facility. This contractual relationship lasted until January 1, 1986. Westinghouse Materials Company of Ohio (WMCO), a wholly owned subsidiary of Westinghouse Electric Corporation, then assumed management responsibilities for the site operations and facilities. In 1991, Westinghouse renamed this subsidiary the Westinghouse Environmental Management Company of Ohio (WEMCO). During that same year, DOE renamed the site the Fernald Environmental Management Project (FEMP) to reflect the site's revised mission. On December 1, 1992, Fernald Environmental Restoration Management Company (FERMCO) assumed responsibility for the site as the first Environmental Restoration Management Contractor (ERMC) for DOE.

The FEMP began operations in 1952 upon completion of the Pilot Plant, the site's first operational facility. Plant 1, Plant 2/3, Plant 4, Plant 5, and Plant 8 began operations in 1953. Plant 6 began operations in 1952. Plant 7 (where UF_6 was processed) and Plant 9 became operational in 1954.

Production peaked in 1960 at approximately 12,000 MTU per year. A product decline began in 1964 and reached a low in 1975 of about 1230 MTU. During the 1970s, consideration was given to closing the FEMP. Thus, capital improvements and staffing were minimized. The staffing level, which peaked at 2891 personnel in 1956, slowly declined to 538 personnel in 1979. In 1981, the FEMP began planning to accommodate increased production requirements. Production levels significantly increased and there was a rapid staff buildup for several years. The renewed need for uranium metal resulted in the implementation of a major facilities restoration program. Production ceased in July 1989, and plant resources were focused on environmental cleanup activities. In June 1991, the site was officially closed as a federal production facility.

1.2 DESCRIPTION AND HISTORY OF OPERABLE UNIT 1

This section provides a brief physical description of each of the waste units that comprise Operable Unit 1 and a summary of the operational history pertinent to these facilities. The operational history focuses primarily on the operational activities conducted prior to the initiation of the site-wide RI/FS in 1986.

1.2.1 Description of Operable Unit 1

Operable Unit 1 contains six waste pits, the Burn Pit, and the Clearwell. Operable Unit 1 (Figure 1-4) is located west of the former production area and includes approximately 37.7 acres. The area is relatively flat with gentle slopes resulting from the emplacement of soil covers over buried wastes and topographical modifications to control surface runoff. Paddy's Run, an intermittent tributary of the Great Miami River, runs along the west side of the FEMP property between the waste storage area and the site boundary. The geographic area constituting Operable Unit 1 is bounded by the Ohio State Planar Coordinates shown in Figure 1-4. Figure 1-10 shows a cross section profile of the waste pit area; Figure 1-11 shows cross sections of each waste pit.

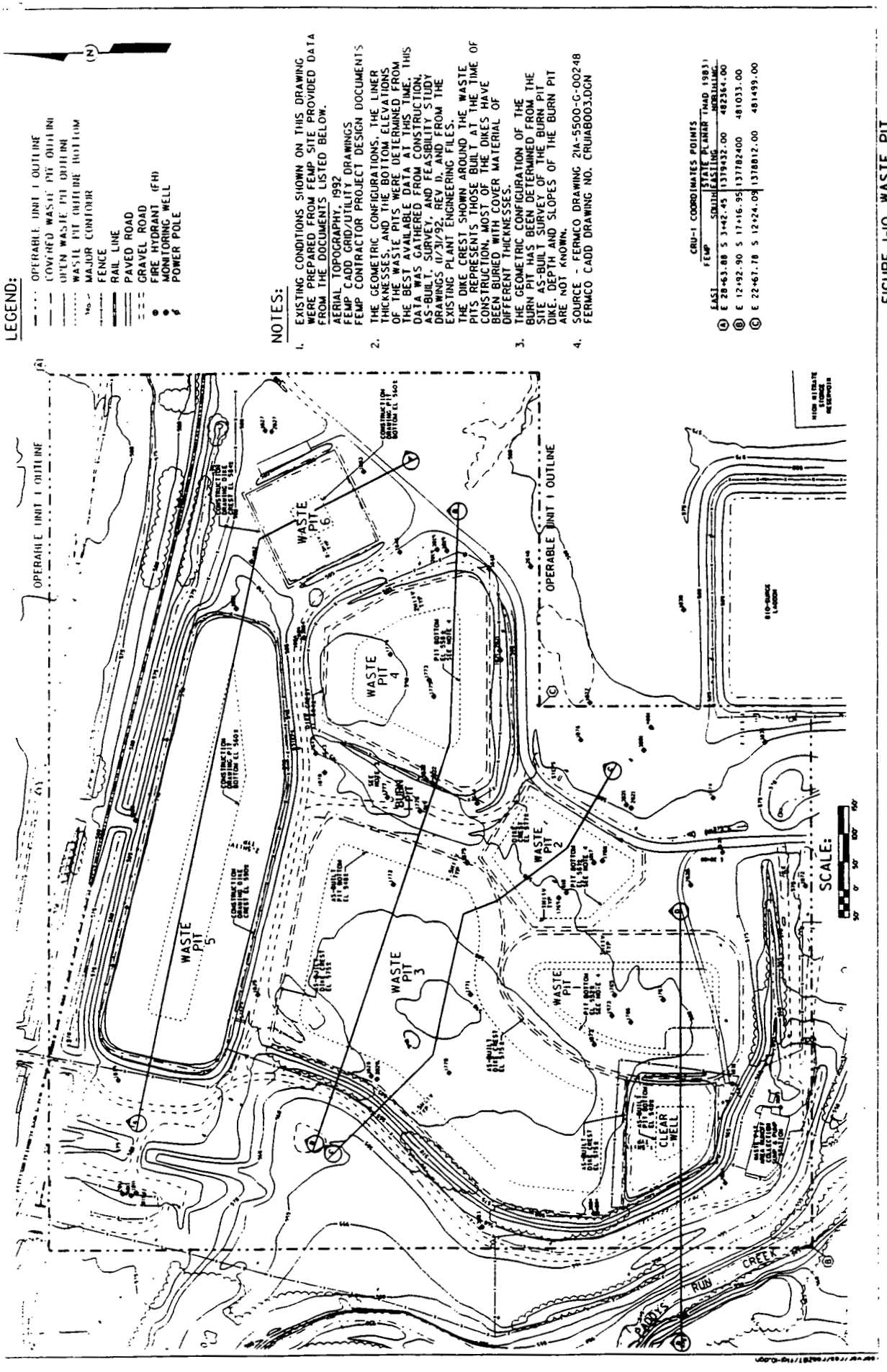
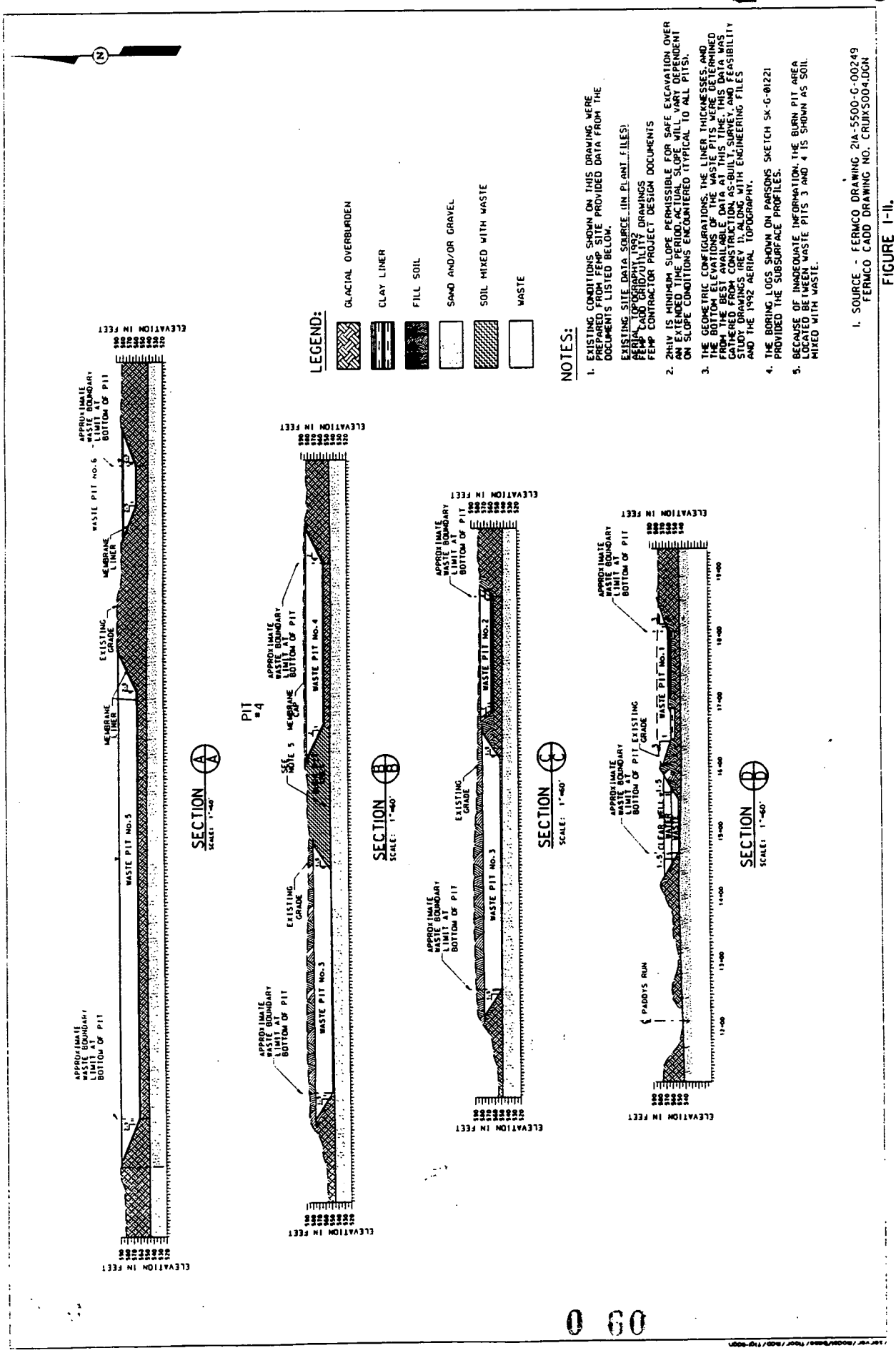


FIGURE 1-10. WASTE PIT CROSS SECTION PLAN


LEGEND:
GLACIAL OVERBURDEN
CLAY LINER
FILL SOIL
SAND AND/OR GRAVEL
SOIL MIXED WITH WASTE
WASTE
NOTES:
1. EXISTING CONDITIONS SHOWN ON THIS DRAWING WERE PREPARED FROM FEMP SITE PROVIDED DATA FROM THE DOCUMENTS LISTED BELOW.
EXISTING SITE DATA SOURCE (IN PLANT FILES)
AERIAL TOPOGRAPHY, 1992
FEMP CADD GRID/UTILITY DRAWINGS
FEMP CONTRACTOR PROJECT DESIGN DOCUMENTS
2. 2H:1V IS MINIMUM SLOPE PERMISSIBLE FOR SAFE EXCAVATION OVER AN EXTENDED TIME PERIOD. ACTUAL SLOPE WILL VARY DEPENDENT ON SLOPE CONDITIONS ENCOUNTERED (TYPICAL TO ALL PITS).
3. THE GEOMETRIC CONFIGURATIONS, THE LINER THICKNESSES, AND THE BOTTOM ELEVATIONS OF THE WASTE PITS WERE DETERMINED FROM THE BEST AVAILABLE DATA AT THIS TIME. THIS DATA WAS GATHERED FROM CONSTRUCTION AS-BUILT, SURVEY, AND FEASIBILITY STUDY DRAWINGS (REV 1), ALONG WITH ENGINEERING FILES AND THE 1992 AERIAL TOPOGRAPHY.
4. THE BORING LOGS SHOWN ON PARSONS SKETCH SK-G-01221 PROVIDED THE SUBSURFACE PROFILES.
5. BECAUSE OF INADEQUATE INFORMATION, THE BURN PIT AREA LOCATED BETWEEN WASTE PITS 3 AND 4 IS SHOWN AS SOIL MIXED WITH WASTE.
1. SOURCE - FERMCO DRAWING 21A-5500-G-00249
FERMCO CADD DRAWING NO. CRUIXS004.DGN
FIGURE 1-11.
WASTE PIT AREA CROSS SECTIONS
SECTION A
SCALE: 1"=40'
SECTION B
SCALE: 1"=40'
SECTION C
SCALE: 1"=40'
SECTION D
SCALE: 1"=40'
WASTE PIT NO. 5
WASTE PIT NO. 6
WASTE PIT NO. 4
WASTE PIT NO. 3
WASTE PIT NO. 2
WASTE PIT NO. 1
PIT #4
MEMBRANE LINER
EXISTING GRADE
APPROXIMATE WASTE BOUNDARY LIMIT AT BOTTOM OF PIT
ELEVATION IN FEET
PADDYS RUN

0 60

The following is a summary of information pertaining to waste pit construction and closure.

1.2.1.1 Waste Pit 1

Waste Pit 1 was constructed in 1952 by excavating into an existing clay lens, and then lining the waste pit with clay excavated from an area to the northeast of the waste pit, which later became the Burn Pit. The waste pit surface area is oval-shaped; the dimensions at the bottom are approximately 165 feet wide by 347 feet long. The waste pit is an average 29.5 feet deep, including approximately 18 feet of wastes, 11 feet of lining, and a 6-inch cover. The bottom of Waste Pit 1 slopes approximately 1 foot from east to west. Four feet of excavated clay was placed in the southeast corner of Waste Pit 1 and a berm was constructed on the west side of the waste pit. This berm is elevated approximately 20 feet above the ground surface. The sides of Waste Pit 1 were constructed with 3:1 slopes and then seeded. Figure 1-12 presents a physical description of Waste Pit 1.

A trench, 11 to 12 feet wide and 10 feet deep, was excavated around the bottom of Waste Pit 1 and backfilled with low permeability material (clay). A sump area, lined with approximately 6 feet of low permeability material (clay), was also constructed in the southwest corner. The trench fed rainwater and other liquids to the sump, where they could be removed as necessary.

A 2-inch asphalt dumping pad was constructed over a 6-inch macadam base on the east side of Waste Pit 1. A concrete apron was extended from the pad toward the bottom of the waste pit to facilitate sliding wastes into the waste pit. A fire hydrant was located near the center of the dumping pad to wash materials down into the waste pit.

Water drained from Waste Pit 1 through a series of three pipes located in the west dike. Eight-inch decant lines were constructed through the west berm of Waste Pit 1 but were rarely used. Rainwater from the pipe trench in the K-65 area was pumped into the south end of Waste Pit 1 through an existing pump.

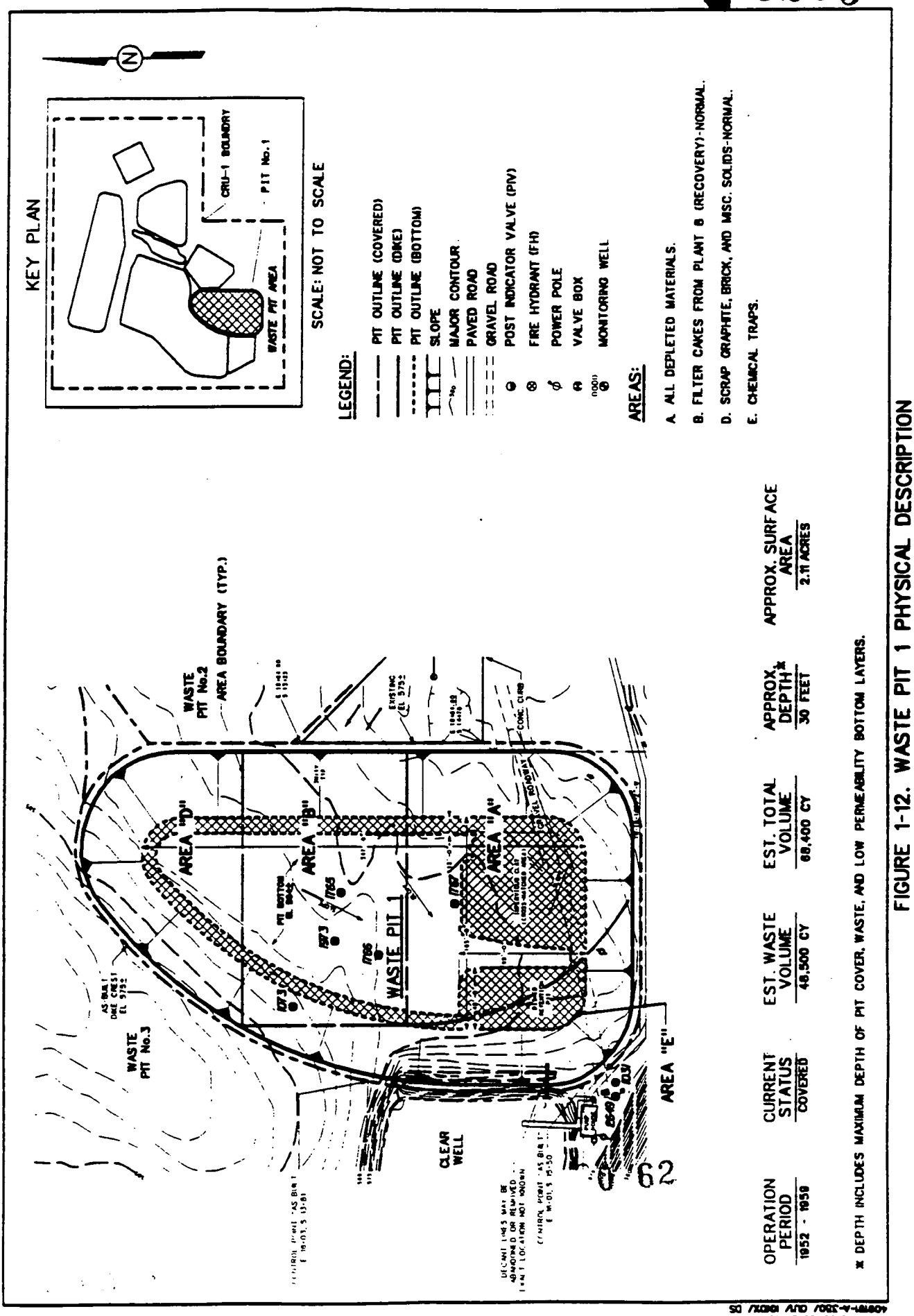


FIGURE 1-12. WASTE PIT 1 PHYSICAL DESCRIPTION

In 1954, the dumping pad on the east side of the waste pit was enlarged and a curb constructed of reinforced concrete was added. Materials used in constructing the pad included a 6-inch asphalt macadam base course and a 2-inch surface treatment.

In 1957, additional storage space was created when excavated material from the construction of Waste Pit 2 was used to increase the berm height by 5 feet on the west side of the waste pit. Because of this increase in height, the slope of the dike near the top edge is approximately 1.5:1 (Figure 1-11).

In 1959, a channel at least 5 feet wide was excavated between the residues and the outer berm to facilitate the proper flow of rainwater to the sump.

Waste Pit 1 was closed and covered with clean fill soil in mid-1959. A portion of this cover was removed in 1972 as a source of cover material for Waste Pit 3. Also, a gravel roadway is constructed on top of the existing cover in the southern portion of the waste pit. The roadway leads to the clearwell pumphouse.

The waste pit is classified as a solid waste management unit (SWMU) under the RCRA.

The results of material volume calculations are presented in Table 1-2:

TABLE 1-2
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 1

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	0.5	1700	
Waste	18 (maximum)	48,500	37,083
Low Permeability Material	11 (maximum)	18,200	
TOTAL	29.5 (maximum)	68,400	

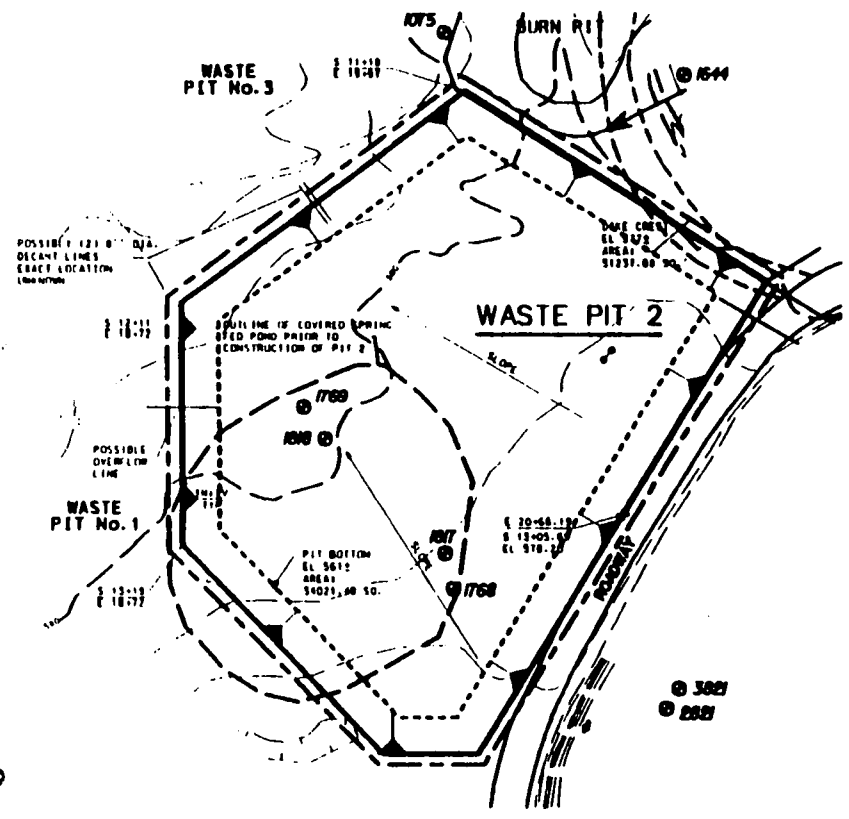
1.2.1.2 Waste Pit 2

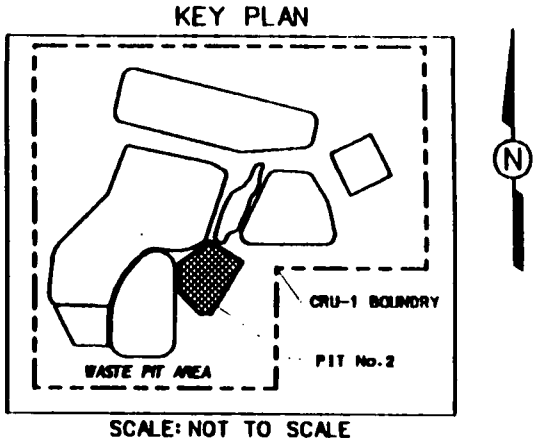
In 1957, Waste Pit 2 was constructed northeast of Waste Pit 1. An existing spring-fed pond (water level elevation 574±1 feet) existed on what became the southern portion of the waste pit. The waste pit was constructed by draining the pond and excavating into the existing native clay. Trees, stumps, and roots had to be removed from the north end. The bottom and side slopes were then lined with 4.5 feet of additional clay from an area immediately northeast of the waste pit, which later became the Burn Pit.

The surface area boundary of the waste pit resembles a six-sided polygon with dimensions at the top of approximately 190 feet wide by 270 feet long. The waste pit is approximately 23.5 feet deep, including 15 feet of wastes, 4.5 feet of lining, and 1 to 4 feet of cover. Log records from Borings Nos. 1768 and 1769 conducted during the RI/FS activities indicate that the top of the low permeability material for Waste Pit 2 is encountered at an elevation of 561 feet. There are two 8-inch cast iron decant pipes installed through the northwest berm of the waste pit. Like Waste Pit 1, the decant lines were rarely used. Figure 1-13 presents a physical description of Waste Pit 2.

A road was built only 4 feet from the east edge of the waste pit. With roadway improvements over the years, the current road could lie over a portion of Waste Pit 2.

Waste Pit 2 was closed and covered with clean fill in mid-1964. A portion of this cover was removed in 1972 as a source of cover material for Waste Pit 3. The cover material varies from approximately 1 to 4 feet in thickness over the waste pit. In 1975, a test area for the above-grade storage of raffinate filter cake was constructed on Waste Pit 2. The test area was 60 feet by 60 feet and was constructed of earth and coal cinders. The height of the test area is unknown. An unloading area, about 20 feet in diameter, was constructed inside the test pit and roadfill gravel and sand were placed on the edge of the area. Raffinate cake from Plant 8 was dumped by truck into the unloading area, and the cake was moved into the southern half of the waste storage area with the use of a crane. From May 22 to June 9, 1975, 29 truckloads (275 tons) of filter cake were placed in the waste storage area. The filter cake was generated by the filtration of a lime neutralized raffinate stream and had a moisture content of about 70 percent. The filter cake was allowed to dry in the sun to remove





SCALE: NOT TO SCALE

LEGEND:

- PIT OUTLINE (COVERED)
- PIT OUTLINE (DIKE)
- PIT OUTLINE (BOTTOM)
- SLOPE
- MAJOR CONTOUR
- PAVED ROAD
- GRAVEL ROAD
- POST INDICATOR VALVE (PIV)
- FIRE HYDRANT (FH)
- POWER POLE
- VALVE BOX
- MONITORING WELL

OPERATION PERIOD	CURRENT STATUS	EST. WASTE VOLUME	EST. TOTAL VOLUME	APPROX. DEPTH *	APPROX. SURFACE AREA
1957 - 1984	COVERED	24,200 CY	37,400 CY	25 FEET	0.90 ACRES

* DEPTH INCLUDES MAXIMUM DEPTH OF PIT COVER, WASTE, AND LOW PERMEABILITY BOTTOM LAYERS.

FIGURE 1-13. WASTE PIT 2 PHYSICAL DESCRIPTION

0 65

some of the moisture for volume reduction. The experiment was deemed unsuccessful and material from the test was deposited into Waste Pit 3.

Waste Pit 2 is classified as a SWMU under RCRA.

The results of material volume calculations are presented in Table 1-3:

TABLE 1-3
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 2

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	1 to 4	4200	
Waste	15.1 (maximum)	24,200	18,503
Low Permeability Material	4.5 (approx.)	9000	
TOTAL	23.5 (maximum)	37,400	

1.2.1.3 Waste Pit 3

Waste Pit 3 was placed in service in December 1958 and was constructed by excavating into the underlying naturally occurring clay lens. To construct Waste Pit 3 and the Clearwell, a small creek that ran along the west embankment of Waste Pit 2 was relocated north of the Burn Pit and parallel to the railroad tracks. The surface area boundary of the waste pit is oval-shaped and has dimensions of approximately 450 feet wide by 720 feet long. The waste pit is approximately 42 feet deep, including 27 feet of wastes, 1 foot of liner, and 14 feet of cover.

A natural layer of low permeability clay forms the bottom of the waste pit, so the placement of additional clay material was not necessary. The bottom of Waste Pit 3 has an elevation of approximately 548 feet.

The sides of Waste Pit 3 were constructed with a 1.5:1 slope and lined with 12 inches of clay. The west berm of Waste Pit 3 was constructed approximately 20 feet above the 1958 ground level. Some

of the soil excavated from the waste pit itself was used to form the west wall. No berm was constructed on the north side of Waste Pit 3.

The east side of Waste Pit 3 was formed from the west sides of Waste Pits 1 and 2. An effluent line from the general sump was constructed through the north dike of Waste Pit 3. Spoil areas used during the construction of Waste Pit 3 were located due north and west of the waste pit. The spoil area due north of the waste pit was subsequently graded to an elevation of approximately 575 feet. Top soil was placed further north of the waste pit. Figure 1-14 presents a physical description of Waste Pit 3.

A 4-foot wide walkway of crushed stone was constructed on top of the berm between Waste Pit 3 and the Clearwell. In the middle of the berm, a 20-foot-long by 19-foot-wide reinforced concrete weir was constructed. The weir allowed water to decant from Waste Pit 3 to the Clearwell. The height of the weir was adjusted using 10-foot-long two-by-fours and two-by-sixes, which were laminated to achieve the appropriate thickness. In the early 1970s, the weir was removed and the area was filled with soil to create a wider berm between Waste Pit 3 and the Clearwell.

In 1965, the capacity of Waste Pit 3 was increased by adding 2 feet of additional material onto the berms. In the late 1960s, an area in the north end of Waste Pit 3 was excavated and wooden pallets were placed in this area and crushed with a bulldozer.

In 1970, when the waste pit could no longer be used as a settling basin, solid materials were placed in the waste pit starting from the northeast corner. A bulldozer was used to initially push flyash into the waste pit.

Prior to June 1, 1971, approximately 5000 cubic yards of dry materials consisting of broken concrete and soil excavated from nearby areas were dumped into Waste Pit 3. Because of the hazards involved in placing these materials on the unstable sludge, it was decided to limit operations to the east side of the waste pit, which was believed to be more stable. In November 1972, a considerable amount of soil was pushed from Waste Pits 1 and 2 into Waste Pit 3. From June 1971 through December 1972,

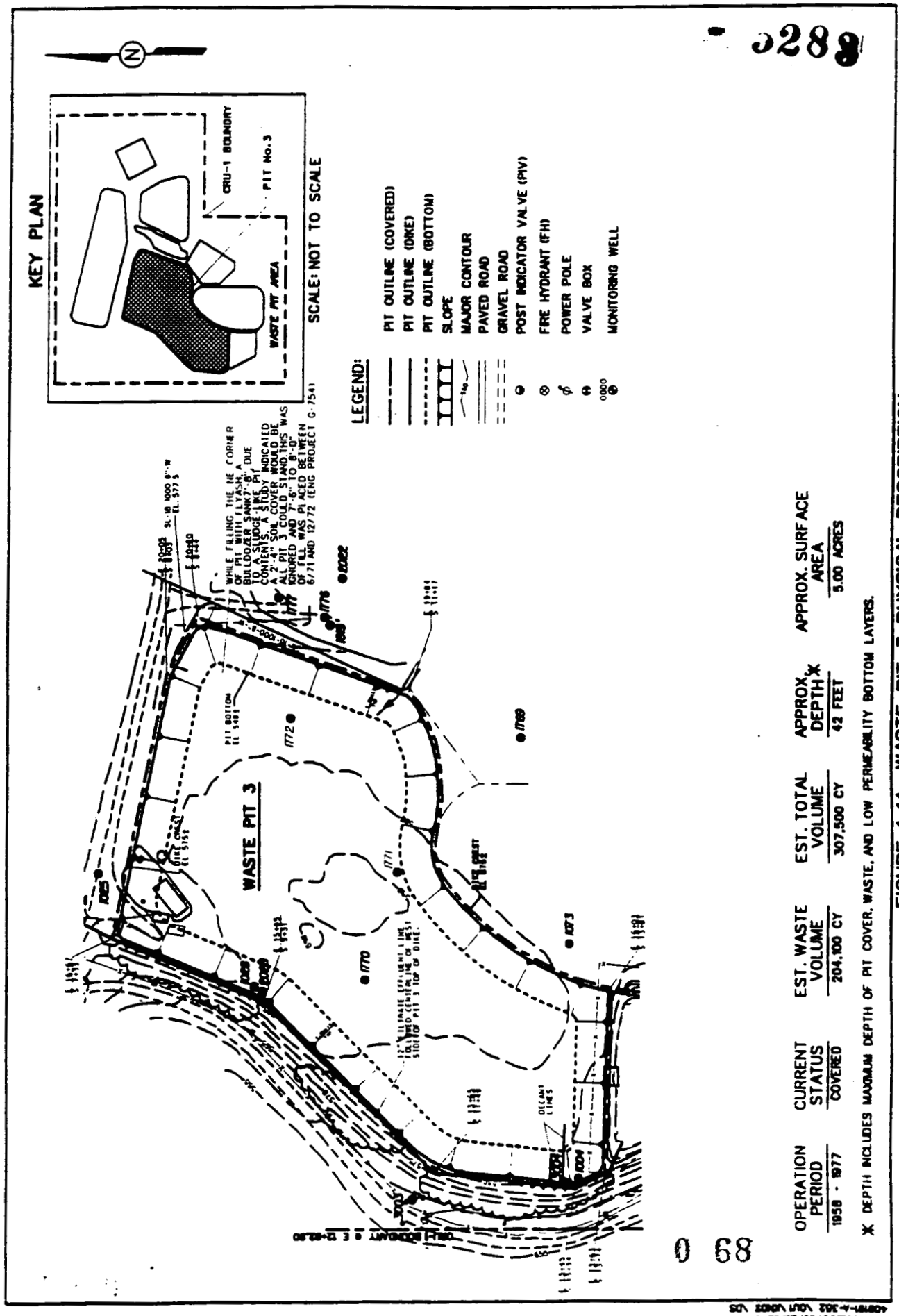


FIGURE 1-14. WASTE PIT 3 PHYSICAL DESCRIPTION

the engineering department kept records of how many truckloads of cinders from the south pit, silo cinders, dirt from the field, and coal fines from the coal storage area were placed in Waste Pit 3. The engineering department assumed that each truckload was equivalent to 10 cubic yards. Table 1-4 shows the amount of each material placed into Waste Pit 3 per month.

From 1975 to 1977, slag leach residue, filter cakes, flyash, soil, and lime sludges were deposited into the waste pit. From 1975 until 1984, some of the filter cakes from Plant 8 sludges accumulated in the general sump tanks, and recycled slurries from Waste Pit 5 were classified as dry waste and deposited into Waste Pit 3. A road between Waste Pits 2 and 4 was used to bring material to the waste pit by truck. The waste would then be placed into the waste pit using a bulldozer with a 15-foot extension.

In 1975, when Waste Pit 3 was partially covered, the drainage patterns were changed to channel surface water from Waste Pits 1, 2, and 3 to the Clearwell and Waste Pit 4. The surface water from Waste Pit 4 was pumped into Waste Pit 5 to settle suspended solids.

In 1975, a field demonstration was held on top of Waste Pit 3 to test the use of a drag scraper for dispersing raffinate and Waste Pit 5 sludge filter cake into the waste pit from a truck dumping point. The test proved this method was feasible, and the drag scraper was further used to prepare Waste Pit 3 for more filter cake dumping.

In 1975, filter cake was placed into Waste Pit 3 by using a transfer truck to dump the filter cake into a prepared depression on the edge of the waste pit. The solids were in a slurry form when first dumped but quickly came to rest. When the depression filled, a clamshell bucket shoveled the solids and piled them further into the waste pit. Often the solids would form a conical pile.

In 1975, Waste Pit 5 was almost full so several hundred thousand gallons of sludge were removed, combined with other waste streams, and pressed into filter cake. The resulting filter cakes were primarily discarded into Waste Pit 3. None of the materials deposited in Waste Pit 3 as part of the

TABLE 1-4
MATERIAL PLACED IN WASTE PIT 3 AS COVER

Month	Cover Materials (m^3)[a]			Totals
	Flyash	Coal Fines	Dirt	
Prior to Jun-71	---	---	---	3,823
Jun-71	283	0	1,254	1,537
Jul & Aug-71	749	0	6,087	6,836
Sep-71	2,019	0	3,127	5,146
Oct-71	505	0	5,735	6,240
Nov-71	566	0	5,796	6,362
Dec-71	2,485	0	0	2,485
Jan-72	1,537	596	0	2,133
Feb-72	2,187	84	329	2,600
Mar-72	2,982	0	153	3,135
Apr-72	2,309	0	765	3,074
May-72	1,002	0	1,713	2,715
Jun-72	436	0	3,257	3,693
Jul-72	390	0	2,072	2,462
Aug-72	390	0	5,368	5,758
Sep-72	---	---	---	2,133
Oct-72	2,133	0	0	2,133
Nov-72	688	0	0	688
Dec-72	535	0	0	535
Totals	21,196	680	35,656	63,488

a The volume does not include unknown volumes of slag leach, filter cakes, flyash, lime sludges, or soil from the cover of Waste Pits 1 and 2, all of which are known to have been deposited in Waste Pit 3 after 1974.

activities to construct the cover are accounted for as wastes in the waste pit. However, it is known that many of these materials became mixed into the wastes.

In 1977, Waste Pit 3 was closed for disposal purposes and completely covered with clean fill.

Waste Pit 3 is classified as a SWMU under RCRA.

The results of material volume calculations are presented in Table 1-5:

TABLE 1-5
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 3

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	14 (maximum)	93,700	
Waste	27 (maximum)	204,100	156,055
Low Permeability Material	1	9700	
TOTAL	42 (maximum)	307,500	

1.2.1.4 Waste Pit 4

Waste Pit 4 was constructed in 1960. The waste pit sides and bottom are lined with 1 to 2 feet of low permeability clay. The surface area boundary of the waste pit is trapezoidal in shape and has maximum dimensions of approximately 380 feet wide by 310 feet long. The waste pit is approximately 32 feet deep, including 25 feet of waste, 1 to 2 feet of liner, and 6 feet of cover. The waste pit was constructed with side slopes of 2:1. The top of the waste pit has an elevation of 584 feet above mean sea level (MSL) with the existing ground elevation at 584 feet to 588 feet above MSL.

There is a concrete pad on the northeast edge of Waste Pit 4, which served as a temporary storage area for drummed material to be emptied into the waste pit. There was a fire hydrant located at the pad to wash contamination from vehicles and materials from the pad into the waste pit.

Disposal activities in Waste Pit 4 were terminated in 1985, and it was closed in May 1986. Figure 1-15 presents a physical description of Waste Pit 4.

Waste Pit 4 was classified as a Hazardous Waste Management Unit (HWMU) under RCRA in 1984. Interim RCRA closure, as certified by the OEPA, was completed in August 1989. Final closure of Waste Pit 4 has been deferred to the CERCLA program. At the time of the waste pit's closure, the surface of the waste pit was a shallow dome of soil surrounded by an earthen berm. To facilitate drainage, the cover was designed to extend a minimum of 3 feet, and an average 9.8 feet beyond the center line of the earthen berm. A ditch was excavated around the perimeter of the waste pit to collect runoff. Fill material was placed on the waste pit between the crown of the surface soil dome and the earthen berm.

Approximately 5000 cubic yards of fill material were required to provide sufficient slope to allow rain water to flow from the top of the dome outward in all directions. Soil and organic material excavated for the perimeter ditch were added to the fill material. Clay was combined with bentonite to achieve the required low permeability. Approximately 1000 cubic yards of clay was required to cover the waste pit to a depth of 2 feet while maintaining the necessary slope.

Because heavy earth moving equipment was expected to generate dust and cause surface contaminants to become airborne, the construction contractor was prohibited from performing any excavation or regrading on the waste pit surface. The cap was designed to place 0 to 3 feet of fill material over certain sections of the waste pit to minimize the addition of material while achieving the required slope.

Following installation of the fill and clay cover, a Hypalon cover was placed onto the waste pit in sheets that varied from 47.9 to 51.8 feet in length. Each sheet was thermally bonded to the adjacent sheets to provide an impermeable cover. An anchor system was designed to increase the cover's stability during high winds. At every other seam, one sheet's edge was placed into a trench that was excavated 1 foot into the clay. The trench was backfilled with clay and compacted. The adjoining sheet was then welded with adhesive to the exposed surface of the buried sheet. On the perimeter of

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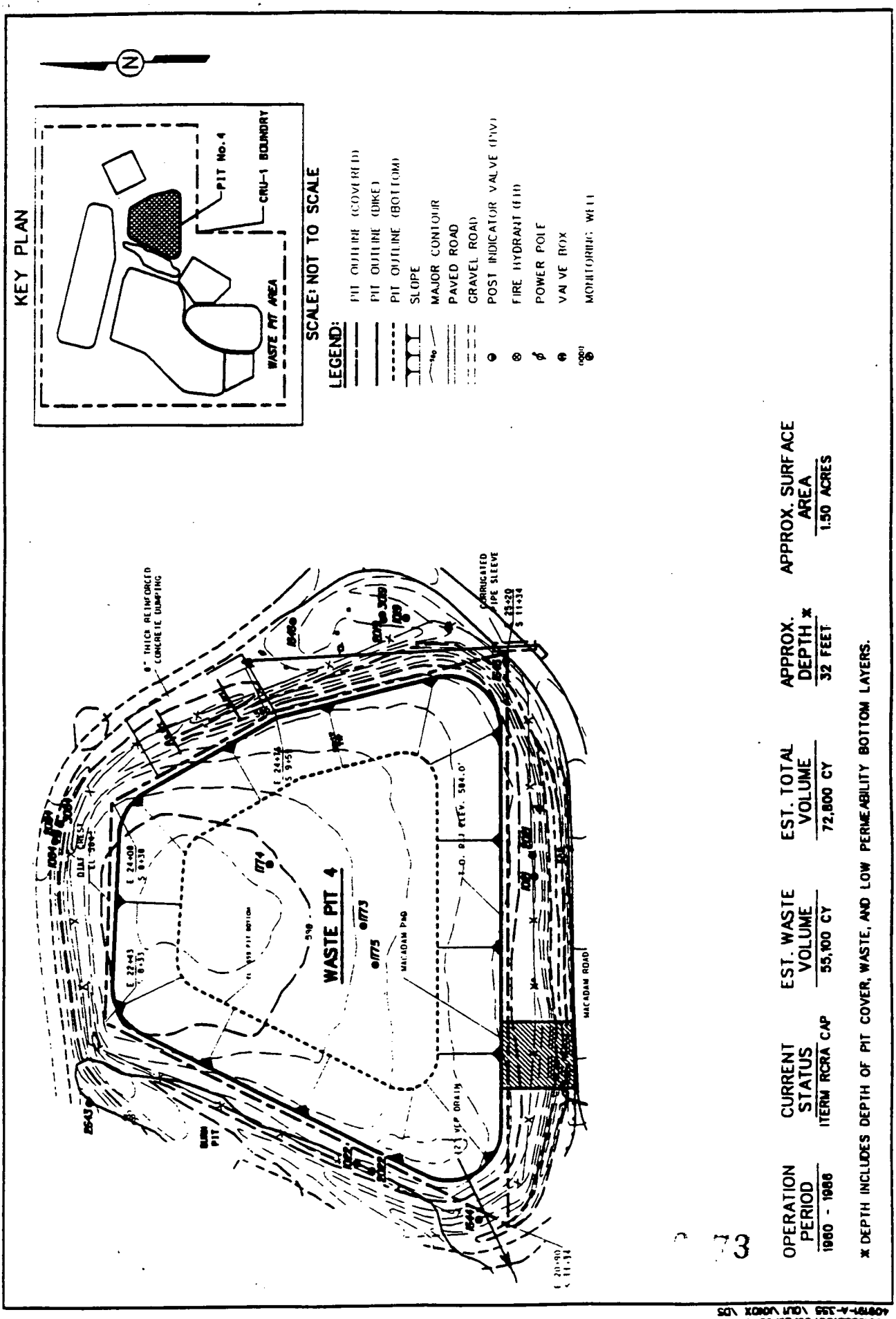

FIGURE 1-15. WASTE PIT 4 PHYSICAL DESCRIPTION

the waste pit, the cover was secured in a trench excavated to 4 feet below the frost line. Pillows made of Hypalon and filled with sand were welded to the cover surface at 50-foot intervals to act as weights.

A vent was installed through the Hypalon and clay to allow gas to escape. Rock channel protection was placed in the perimeter drainage ditch and the exposed soil was seeded to prevent erosion.

The results of material volume calculations are presented Table 1-6:

TABLE 1-6
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 4

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	6	14,600	
Waste	25	55,100	42,130
Low Permeability Material	1	1000	
TOTAL	32 (maximum)	72,800	

1.2.1.5 Waste Pit 5

Waste Pit 5 was constructed and placed into service in 1968. The Waste Pit 5 surface area boundary is rectangular in shape and is approximately 820 feet long by 240 feet wide. The waste pit is approximately 29 feet deep, including 28 to 29 feet of wastes, and a membrane liner. Waste Pit 5 was constructed with side slopes of 2.5:1. The waste pit berm extends about 10 feet above grade on the south side and 14 to 20 feet above grade on the north side. Excavated material was used to build the waste pit dike. The waste pit was lined with a 60-mil thick Royal-Seal ethylene propylene diene monomer (EPDM) elastomeric membrane. Figure 1-16 presents a physical description of Waste Pit 5.

Water percolation from porous native material was encountered during the original excavation of the waste pit. The porous seams were overexcavated and filled with compacted clay prior to installation of the liner. Perched water was encountered during excavation activities, but the majority of water

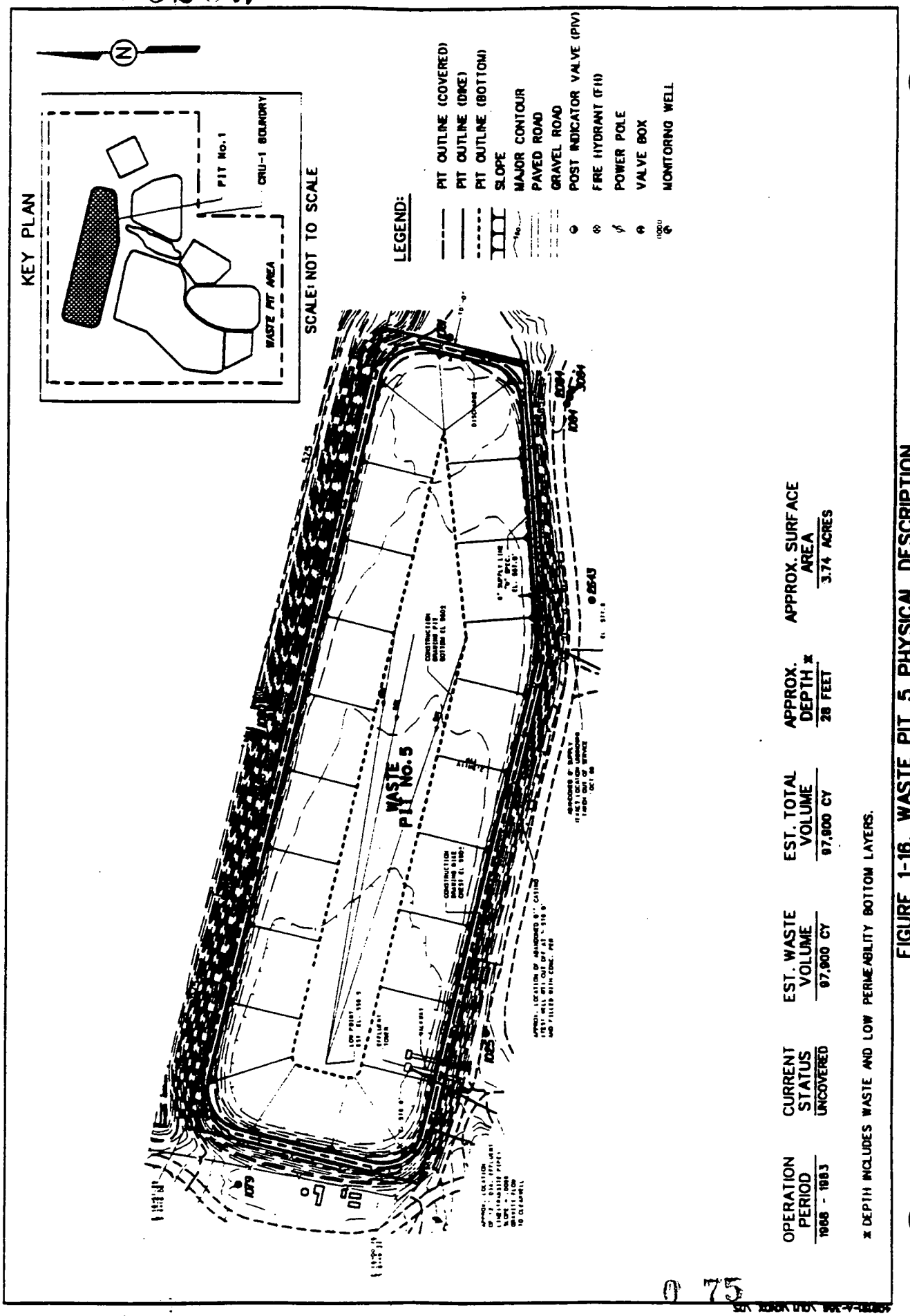

FIGURE 1-16. WASTE PIT 5 PHYSICAL DESCRIPTION

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originated from surface runoff into the waste pit. The waste pit bottom was sloped from east to west to allow for drainage. The perched water and runoff were pumped from the west end of the waste pit.

All liquid waste entered Waste Pit 5 through a 6-inch pipe in the eastern end. Supernatant overflowed through an effluent tower in the southwest corner of the waste pit. The tower included an adjustable overflow connected to a 12-inch transit pipe that routed the overflow to the Clearwell.

Two minor liner joint repairs were completed in December 1970. One failure was identified between the waste pit lining and effluent tower. The second failure was at a membrane field splice near the feed end of the waste pit. Because the failures were below the normal liquid operating level, some liquid release probably occurred. Waste Pit 5 stopped receiving slurried materials in 1983 and was discontinued for use as a settling basin in 1987.

Waste Pit 5 is classified as an HWMU under RCRA and a water cover is maintained.

Removal Action No. 11, Waste Pit 5 Experimental Treatment Facility (ETF), began on December 13, 1991, and was completed on March 22, 1992. Approximately 350 cubic yards of waste material and contaminated media were removed following completion of the testing. This action served as an interim RCRA closure/response action. Removal Action No. 18, Control of Exposed Material in Waste Pit 5, resulted in the dredging of exposed material to restore the water cover to the entire waste pit.

Waste Pit 5 is classified as an HWMU under RCRA.

The results of material volume calculations are presented in Table 1-7:

TABLE 1-7
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 5

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	N/A	N/A	
Waste	28±1	97,900	74,854
Low Permeability	N/A	N/A	
TOTAL	29 (maximum)	97,900	

1.2.1.6 Waste Pit 6

Waste Pit 6 was constructed from September 1978 to June 1979. It is square shaped, measuring approximately 210 feet on both sides. The waste pit is approximately 24 feet deep, measured from the top of the berm to the liner, but the depth of the wastes in the waste pit is only 20 feet.

Waste Pit 6 was constructed in the same manner as Waste Pit 5 and lined with a 60-mil EPDM elastomeric liner. There is a berm around all sides except for the west side, which is adjacent to Waste Pit 4. The berm varies in height from approximately 4 to 8 feet above grade. Figure 1-17 presents a physical description of Waste Pit 6.

A concrete dumping pad was constructed on the west side of Waste Pit 6. Material was moved from the concrete pad into the waste pit with a crane or flushed in with water. Later, a concrete dumping pad was constructed on the east side of the waste pit.

Water percolation was encountered during excavation activities. Numerous pockets of perched groundwater were encountered during the construction of Waste Pit 6.

Preventing water from entering the waste pit during construction was difficult. The liner continued floating on water entering the waste pit, so holes were cut in the liner. A pump was inserted under

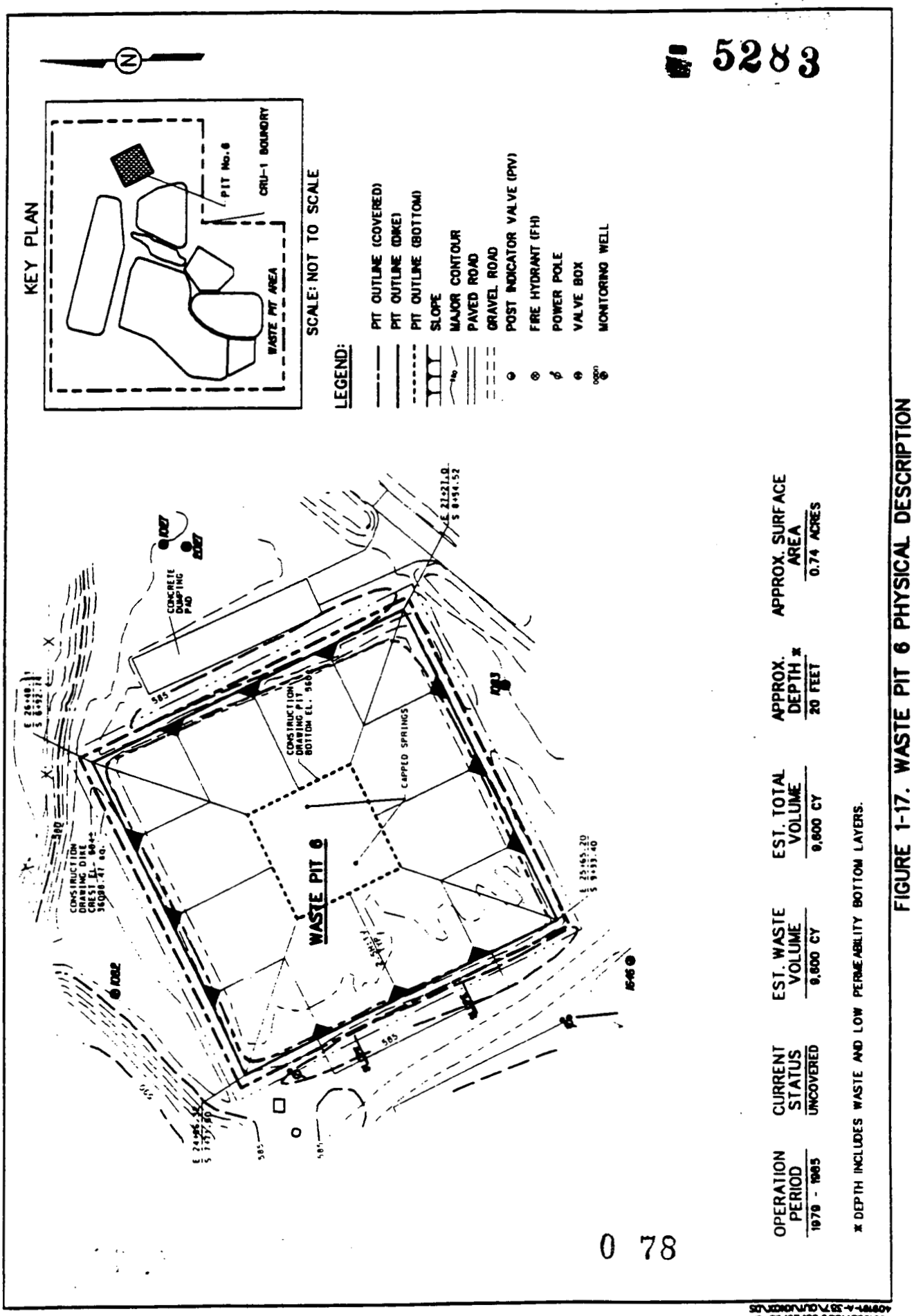

FIGURE 1-17. WASTE PIT 6 PHYSICAL DESCRIPTION

the liner and the perched groundwater was removed. Before cutting holes in the liner, pieces of plastic reinforcement were fixed to the liner in those locations so that the liner would not tear extensively when the holes were cut. Once the water was removed, patches were welded over the holes to complete the integrity of the impervious liner. Sand bags were also placed on the liner to keep it from floating. Because of the small size, the waste pit bottom was not sloped during construction. Waste Pit 6 is currently water covered.

The use of Waste Pit 6 ceased on March 11, 1985. Removal Action No. 6, Control of Exposed Material in Waste Pit 6, was completed in December 1990. This action involved the redistribution of exposed material in the waste pit so that it would be completely covered with water. The water cover continues to be maintained.

Waste Pit 6 is classified as a SWMU under RCRA.

The results of material volume calculations are presented in Table 1-8:

TABLE 1-8
MATERIAL VOLUME CALCULATION RESULTS FOR WASTE PIT 6

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	N/A	N/A	
Waste	20	9600	7340
Low Permeability Material	N/A	N/A	
TOTAL	24 (maximum)[a]	9600	

[a]Distance from top of berm to liner.

1.2.1.7 Clearwell

The Clearwell was constructed in 1959 during Waste Pit 3 construction activities. To allow for construction of Waste Pit 3 and the Clearwell, a small creek that ran along the west embankment of

Waste Pit 2 was relocated north of the existing Burn Pit and parallel to the railroad tracks. The Clearwell was excavated into existing low permeability material to an elevation of 548±1 feet above MSL. The Clearwell is approximately 200 feet long by 180 feet wide, with a maximum depth of 27 feet. The east, west, and south sides of the Clearwell were constructed with a 1.5:1 slope and lined with 12 inches of clay. The north side was constructed with a 2:1 slope and also lined with 12 inches of clay. The west berm of the Clearwell was constructed approximately 20 feet above grade in 1958. The north side is adjacent to the south side of Waste Pit 3. The east side was formed from the west side of Waste Pit 1. A natural layer of low permeability material forms the bottom of the Clearwell, and additional clay material was not placed in the bottom. The bottom of the Clearwell is at elevation of 548±1 feet above MSL. Figure 1-18 presents a physical description of the Clearwell.

Spoil areas for the construction of the Clearwell were due north of Waste Pit 3 and west of Waste Pit 3. Top soil was placed farther north of Waste Pit 3. The spoil area due north of Waste Pit 3 was subsequently graded.

A series of three 8-inch pipes are located in the berm between Waste Pit 1 and the Clearwell, but these decant lines were rarely used. Also, a weir was constructed on the north side of the Clearwell to drain Waste Pit 3. Finally, the 12-inch line from the overflow of Waste Pit 5 extends through the east berm of the Clearwell.

The Clearwell is classified as a SWMU under RCRA.

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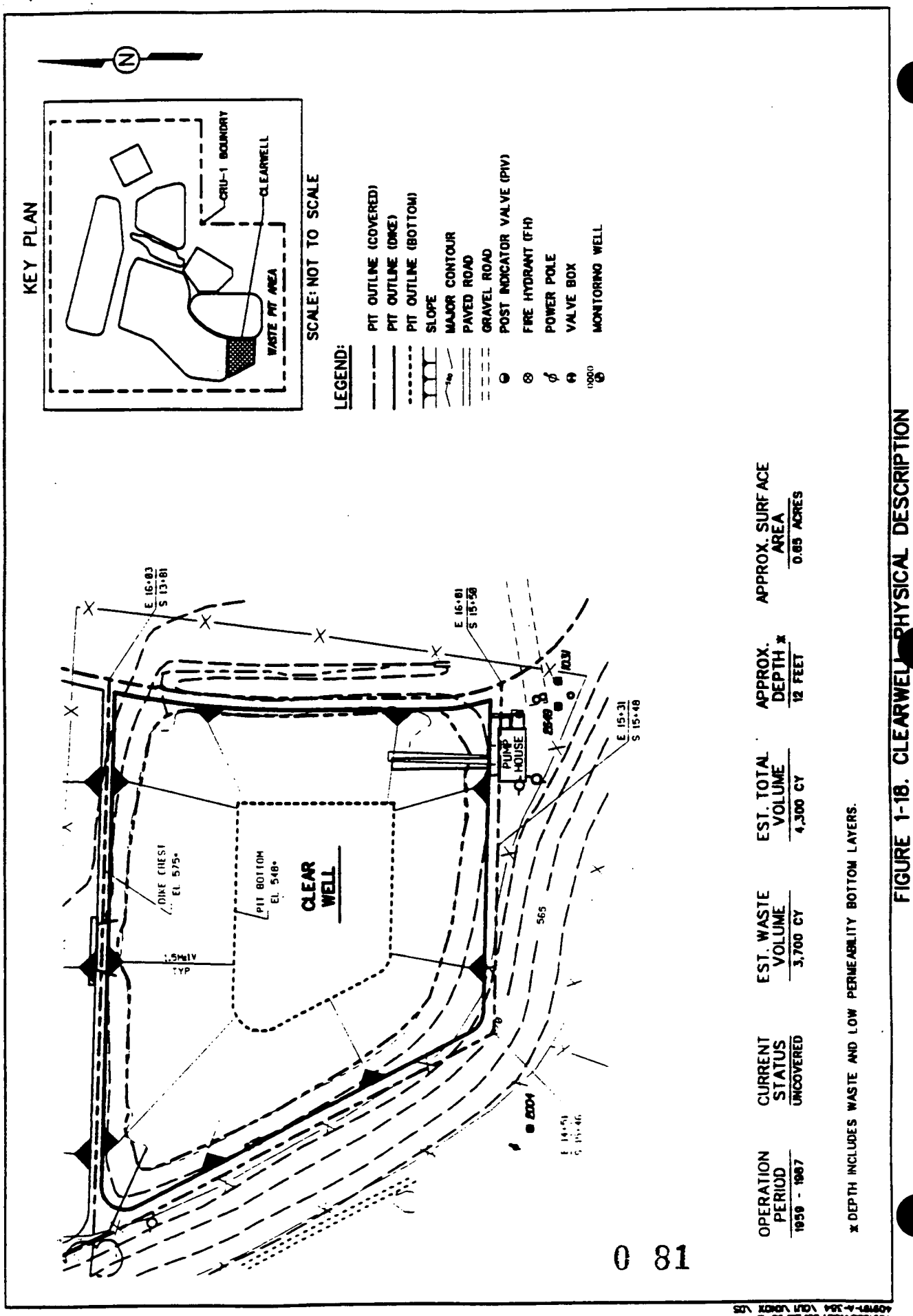

FIGURE 1-18. CLEARWELL PHYSICAL DESCRIPTION

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The results of material volume calculations are presented in Table 1-9:

TABLE 1-9
MATERIAL VOLUME CALCULATION RESULTS FOR THE CLEARWELL

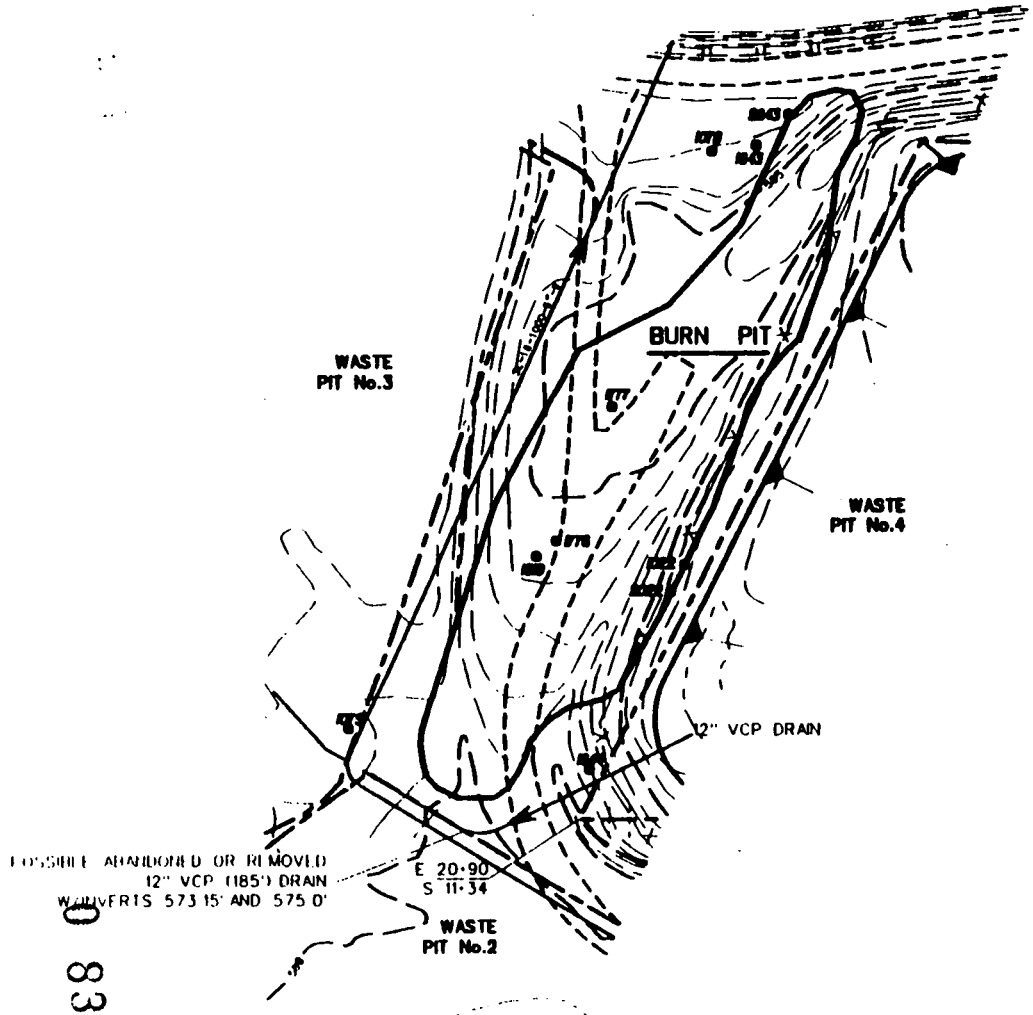
Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	N/A	N/A	
Waste	11	3700	2829
Low Permeability Material	1	600	
TOTAL	27 (maximum)[a]	4300	

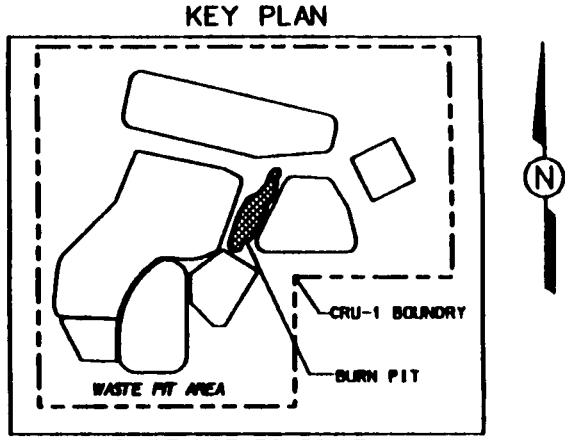
[a]Distance from top of berm to bottom of Clearwell.

1.2.1.8 Burn Pit

Clay to line Waste Pits 1 and 2 during their construction was obtained from an area immediately northeast of Waste Pit 2, which at that time was called the clay pit. A gravel dumping pad was eventually built up on the north end of the resulting excavation so that trucks could back into the deepest part of the waste pit to dump combustible wastes. Thus, the waste pit became known as the Burn Pit. Although records were not kept on all of the materials or amounts deposited, it is known that the Burn Pit was used primarily to burn combustible materials such as laboratory chemicals; pyrophoric and reactive chemicals; oils; low-level contaminated combustible material, such as pallets and skids; and cafeteria debris. In addition, several materials were deposited directly into the Burn Pit, including cans, bottles, general refuse, and laboratory glassware.

The Burn Pit was filled with cinders, concrete, ash, gravel, and soil in 1968, during the construction of Waste Pit 5. Figure 1-11 shows a cross section of the Burn Pit. Figure 1-19 presents a physical description of the Burn Pit.





SCALE: NOT TO SCALE

LEGEND:

- PIT OUTLINE (COVERED)
- PIT OUTLINE (DIKE)
- PIT OUTLINE (BOTTOM)
- SLOPE
- MAJOR CONTOUR
- PAVED ROAD
- GRAVEL ROAD
- POST INDICATOR VALVE (PIV)
- FIRE HYDRANT (FH)
- POWER POLE
- VALVE BOX
- MONITORING WELL

OPERATION PERIOD	CURRENT STATUS	EST. WASTE VOLUME	EST. TOTAL VOLUME	APPROX. DEPTH ✱	APPROX. SURFACE AREA
1957 - 1968	BACKFILLED	30,300 CY †	30,300 CY †	28 FEET †	0.50 ACRES †

† BOUNDARIES OF THE BURN PIT ARE NOT CLEARLY IDENTIFIED. QUANTITIES ARE ASSUMED TO BE WITHIN +/- 30% ACCURACY.
✱ DEPTH INCLUDES APPROXIMATE DEPTH OF PIT COVER, WASTE, AND LOW PERMEABILITY BOTTOM LAYERS.

FIGURE 1-19. BURN PIT PHYSICAL DESCRIPTION

The results of material volume calculations are presented in Table 1-10:

TABLE 1-10
MATERIAL VOLUME CALCULATION RESULTS FOR THE BURN PIT

Material	Depth (ft)	Volume (yd^3)	Volume (m^3)
Cover	N/A	N/A	
Waste	26	30,300	23,167
Low Permeability Material	N/A	N/A	
TOTAL	26 (maximum)	30,300	

1.2.2 History of Operable Unit 1

With few exceptions, FEMP storage facilities were used for storing all wastes generated at the facility since the beginning of uranium production operations in 1951. The waste pits were constructed to store waste material generated at the site as well as some materials imported from other facilities.

Section 1.1.3.2 describes how these materials were generated. The following paragraphs describe how the wastes were transferred to the waste pits and, based upon knowledge of the operations, the characteristics of the various waste pits.

The FEMP refinery processed two basic classes of materials: (1) pitchblende ores as they were mined and shipped to the FEMP, and (2) other uranium concentrates that had already been refined to some degree. This second class of materials included uranium concentrates that had already undergone a preliminary refining process at an off-site mill and residues recovered at various stages of FEMP operations.

Uranium-bearing ores, as they are mined, contain not only uranium, but also equilibrium concentrations of uranium progeny (i.e., the isotopes of other elements formed through the sequential radioactive decay chains that begin with U-235 and U-238). The concepts of radioactive decay chains and progeny products are discussed in detail in Section 4.0 of the RI Report. These progeny, which include radium, are removed in either a preliminary milling process or in the refining process (if the ores are not preprocessed through a mill). Thus, when the FEMP refinery processed pitchblende ores

(non-K-65 material), the refinery wastes were known as "hot" raffinates. The term "hot" was used to indicate that the material contained a high concentration of the gamma-emitting radionuclide radium (Ra)-226 and progeny that result in a significant direct penetrating radiation exposure rate. When the FEMP processed uranium concentrates that had been preprocessed through a uranium mill, a significant portion of the Ra-226 and the gamma-emitting progeny had already been removed. The thorium progeny of uranium (i.e., thorium [Th]-230, etc.) remained with the uranium concentrates due to the inefficiency of the mill in removing this metal, and were thus termed "cold" metal oxides.

The six waste pits are numbered based on the chronology of their construction. They are further identified as dry or wet pits on the basis of the physical characteristics of the waste materials intended to be placed in them. Waste Pits 3 and 5 were classified as wet pits and received pumped slurries. Waste Pits 1, 2, 4, and 6 were generally identified as dry pits because they received primarily dry solids, but they may have received liquid waste streams as well.

In general, the process plant and type of residue dictated the type of container, mode of transportation, and method of depositing the materials in the waste pits (NLO 1977):

- With four exceptions, liquid residues were normally neutralized in the general sump and pumped to the waste pits. The exceptions were Zirnlo slurry, heat-treat quench water, UAP neutralized filtrate, and slag leach slurry, which were routed directly to the waste pits. The volume of the Zirnlo slurry and heat-treat quench water was minor and contributed insignificant amounts to the solids in the waste pits. Also, feed sump residues from the water treatment and boiler plants and cooling water from the heat treating operation were hauled directly to the waste pits in tank trucks.

- Drummed materials were transported on semi-flatbed trailers and, in the case of pyrophoric metals, by four-wheeled flatbed trailers pulled by a tow tractor. With few exceptions, as discussed below, the drums were unloaded and the contents dumped onto the edge of the respective waste pit with a fork truck equipped with a drum rotator.

- Metal dumpsters and hoppers were transported to the waste pits and the residues emptied directly onto the edge of the respective waste pit.

- Bulk materials were hauled by dump trucks and dump trailers, which also deposited materials onto the edge of the respective waste pit.

Material deposited on the edges of the waste pits was pushed into the waste pits by either a bulldozer or a drag line scraper. Loose contamination was washed from the bulldozers, drag line, scraper, vehicles, dumpsters, and fork trucks at one of two hydrants. One of these hydrants was located near the center of the concrete pad for Waste Pit 1 and the second at the southeast corner of the concrete pad for Waste Pit 4. Empty drums were transported to Plant 8 and cleaned in the drum washing facility, and (as necessary) containers and equipment were cleaned at the decontamination facility.

The following section describes the operating history of each of the structures in Operable Unit 1, including the types of materials deposited in each and the expected constituents. Figure 1-20 presents a time line showing the period of operation for each of the waste pits. Table 1-11 shows the distribution of the waste streams in the waste pits and Table 1-12 summarizes the major constituents in each waste pit.

1.2.2.1 Waste Pit 1

Waste Pit 1 was in operation from 1952 to mid-1959. For most of this period, there was no need for a settling lagoon because waste slurries, other than effluent from the general sump, were filtered or calcined to remove water. Therefore, Waste Pit 1 has been considered a dry pit. It was, however, used as a clearwell for Waste Pit 2 in 1958 and 1959 (NLO 1985).

Waste Pit 1 is divided into four sections: depleted materials; filter (trailer) cakes from Plant 8; graphite from Plant 5 along with bricks, stones, and miscellaneous solids; and chemical trap material and other miscellaneous drummed materials (Carvitti 1959). The first three sections are approximately equal in size and arranged, respectively, from south to north. The fourth section is located in the southwest corner of the waste pit.

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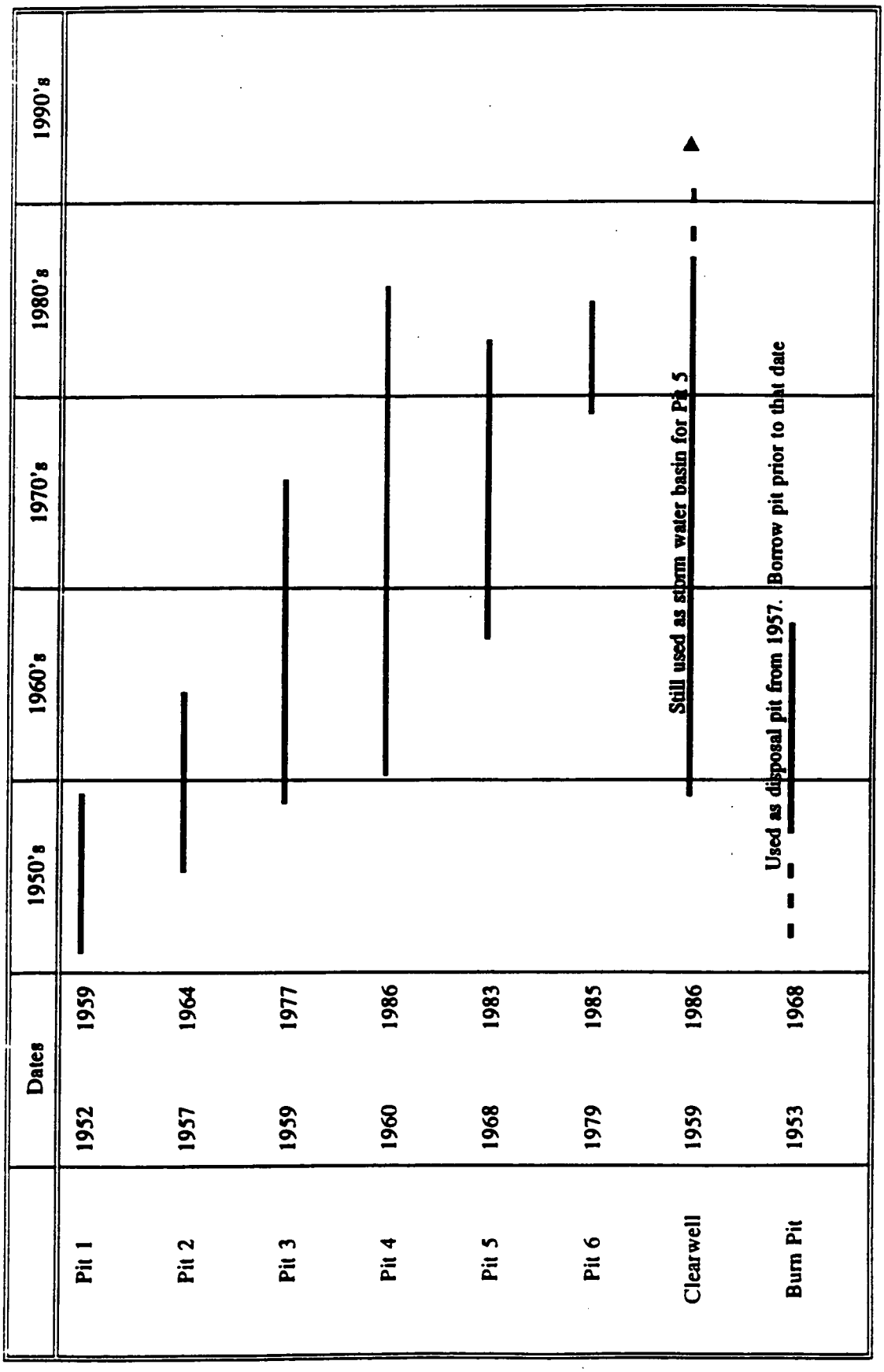

FIGURE 1-20. HISTORICAL TIMELINE OF PIT USAGE

TABLE 1-11

SUMMARY OF OPERABLE UNIT 1 WASTE PIT CONTENTS BASED ON PROCESS KNOWLEDGE

Source	Solids to Waste Pits[i]																	
	Waste Pit 1			Waste Pit 2			Waste Pit 3			Waste Pit 4			Waste Pit 5			Waste Pit 6		
	Uranium (MTU)	Mass (MT)	Volume (m^3)	Uranium (MTU)	Mass (MT)	Volume (m^3)	Uranium (MTU)	Mass (MT)	Volume (m^3)	Uranium (MTU)	Mass (MT)	Volume (m^3)	Uranium (MTU)	Mass (MT)	Volume (m^3)	Uranium (MTU)	Mass (MT)	Volume (m^3)
General Sump Sludge[a]	2	10,764	7,500	1	6,578	4,600	12	41,720	29,000				20	53,493	37,100			
Raffinate[b]				7	433	500	633	39,754	41,400				501	30,070	31,300			
Magnesium Flouride																		
Depleted Slag[c]	636	6,783	4,700	59	634	400				329	7,845	5,300				332	8,082	5,500
Trailer Cake[d]	92	18,401	13,000	71	14,208	9,900	150	30,072	20,900	55	11,137	7,700						
Slag Leach[d]							63	12,605	8,700				26	5,239	3,600			
UAP Filtrate[e]	3	1,712	1,200	8	3,763	2,600												
Depleted Residues[e]	339	2,163	1,500	32	202	100				1,818	3,590	2,500				1,100	1,853	1,200
Graphite/Ceramics[f]	3	150	60	0	13	5				1	450	230						
Water Treatment Sludge[g]							0	2,669	1,900				0	3,857	2,700			
Thorium Wastes[h]		80	100		0	0		89	100		1,093	800		1,007	1,000		0	0
Totals	1,075	40,054	28,060	178	25,832	18,105	858	126,909	102,000	2,203	24,115	16,530	547	93,666	75,700	1,432	9,935	6,700

Notes: a) See Appendix F.6.3.
b) See Appendix F.6.4.
c) See Appendix F.6.7.
d) See Appendix F.6.5.
e) See Appendix F.6.8.
f) See Appendix F.6.6.
g) See Appendix F.6.9.
h) See Appendix F.6.10. Note that the thorium values are not included in the uranium column totals and do not include thorium deposited in the waste pits through the general sump.
i) See Appendix F.6.11.

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TABLE 1-12
SUMMARY OF OPERABLE UNIT 1 WASTE PIT CONSTITUENTS BASED ON PROCESS KNOWLEDGE

Constituent	Solids to Waste Pits (MT)[a]					
	Waste Pit 1	Waste Pit 2	Waste Pit 3	Waste Pit 4	Waste Pit 5	Waste Pit 6
Uranium (U)	1,075	178	858	2203	547	1432
Aluminum (Al)	52	120	710	0	420	0
Antimony (Sb)	0	0	1	0	0	0
Arsenic (As)	0	1	64	0	41	0
Barium (Ba)	5	12	75	0	45	0
Boron (B)	0	0	1	0	0	0
Bismuth (Bi)	0	0	0	0	0	0
Cadmium (Cd)	0	0	4	0	3	0
Calcium (Ca)	3,776	2,524	31,585	0	36,800	0
Chloride (Cl)	316	695	39	0	25	0
Chromium (Cr)	0	0	4	0	2	0
Cobalt (Co)	0	0	1	0	1	0
Copper (Cu)	2	4	22	0	13	0
Dysprosium (Dy)	0	0	2	0	1	0
Erbrium (Er)	0	0	0	0	0	0
Europium (Eu)	0	0	0	0	0	0
Flouride (F)	18	39	81	0	38	0
Gadolinium (Gd)	0	0	1	0	1	0
Holmium (Ho)	0	0	0	0	0	0
Iron (Fe)	18	49	812	0	513	0

TABLE 1-12
(Continued)

Constituent	Solids to Waste Pits (MT)[a]					
	Waste Pit 1	Waste Pit 2	Waste Pit 3	Waste Pit 4	Waste Pit 5	Waste Pit 6
Lead (Pb)	0	0	4	0	3	0
Lutetium (Lu)	0	0	0	0	0	0
Magnesium (Mg)	10	30	673	0	430	0
Manganese (Mn)	4	9	26	0	14	0
Molybdenum (Mo)	0	1	54	0	35	0
Nickel (Ni)	0	0	1	0	0	0
Samarium (Sm)	0	0	0	0	0	0
Sodium (Na)	485	1,078	960	0	624	0
Terbium (Tb)	0	0	0	0	0	0
Thorium (Th)	1	2	97	74	72	0
Thulium (Tm)	0	0	0	0	0	0
Tin (Sn)	1	2	7	0	4	0
Vanadium (V)	0	5	395	0	257	0
Yttrium (Y0)	0	0	3	0	2	0
Ytterbium (Yb)	0	0	0	0	0	0
Zinc (Zn)	0	0	9	0	6	0
NH3	0	1	50	0	32	0
CO3	0	3	238	0	155	0
MgF2	11,952	10,694	41,183	18,263	5,056	7,750
PO4	592	1,338	6,491	0	3,516	0
P2O5	0	8	623	0	405	0
SiO2	757	889	3,092	334	1,169	0

TABLE 1-12
(Continued)

Constituent	Solids to Waste Pits (MT)[a]					
	Waste Pit 1	Waste Pit 2	Waste Pit 3	Waste Pit 4	Waste Pit 5	Waste Pit 6
SO4	0	36	2,915	0	1,896	0
V2O5	0	4	310	0	202	0
NO3	0	66	7,529	0	4,475	0
Dolomite	11,953	3,592	0	0	0	0
Unaccounted	9,037	4,452	27,959	3,241	36,860	753
		0				
Totals	40,054	25,832	126,909	24,115	93,666	9,935

Notes: a) See Appendix F.6.10 of the RI Report for further details.

A pad was located on the east side of Waste Pit 1. Waste materials were dumped on the pad and either pushed into the waste pit by a bulldozer or washed into the waste pit using the fire hydrant on the pad.

Approximately 28,100 m^3 of wastes have been accounted for in Waste Pit 1, compared to 37,086 m^3 (76 percent accounted for) based on survey data and boring logs (Parsons 1993). As indicated in Table 1-11, the most significant portion of the volume accounted for is trailer cake (46 percent), with less significant amounts of general sump sludge (27 percent), and depleted materials (slag and residues - 22 percent). The average density of the materials accounted for in the waste pit is 1400 kg/m^3 (90 lb/ft^3), with a range from 400 kg/m^3 (25 lb/ft^3) to 8000 kg/m^3 (500 lb/ft^3) associated with the depleted residues.

Waste Pit 1 contains an estimated total of 1075 MTU. The most significant sources of the uranium are depleted slag (59 percent) and depleted residues (32 percent). The uranium content of the waste pit is expected to range from 0 percent to nearly 95 percent, both associated with depleted residues.

Waste Pit 1 contains significant amounts (12,000 MT each) of dolomite and MgF_2, (both associated with C-liner and trailer cake), and calcium (3800 MT, associated with the general sump sludge).

1.2.2.2 Waste Pit 2

Waste Pit 2 was used from 1957 through mid-1964. Waste Pit 2 was used briefly as a settling waste pit for neutralized raffinate during 1958 and 1959, prior to completion of Waste Pit 3 (NLO 1985). It was used as a settling waste pit because the drying equipment available at that time could not process all of the raffinate.

Approximately 18,100 m^3 of waste have been accounted for in Waste Pit 2, compared to 18,505 m^3 (98 percent accounted for) based on survey data and boring logs (Parsons 1993). As indicated in Table 1-11, the most significant portions of the accounted volume for are trailer cake (55 percent) and general sump sludge (25 percent), with a less significant amount of UAP filtrate (14 percent). The

average density of the materials accounted for in the waste pit is 1400 kg/m^3 (90 lb/ft^3), with a range from 400 kg/m^3 (25 lb/ft^3) to 8000 kg/m^3 (500 lb/ft^3) associated with the depleted residues.

Waste Pit 2 contains an estimated total of 178 MTU. The most significant sources of the uranium are trailer cake (40 percent), depleted slag (33 percent), and depleted residues (18 percent). The uranium content of the waste pit is expected to range from 0 percent to nearly 95 percent, both associated with depleted residues.

More than 40 percent of the estimated mass in Waste Pit 2 is MgF_2 (14,842 MT) from both C-liner and trailer cake. Waste Pit 2 contains significant amounts of dolomite (3600 MT) and calcium (2500 MT), associated with general sump sludge and neutralized raffinate. The relatively small amount of neutralized raffinate in Waste Pit 2 contributes small amounts of impurities associated with raffinates.

1.2.2.3 Waste Pit 3

Waste Pit 3 was the first waste pit built specifically for settling solids from liquid waste streams. It was used as such from December 1958 through October 1968. Liquid wastes, including contaminated storm water from the Burn Pit, were pumped to Waste Pit 3 (Carvitti 1959). Waste Pit 3 also received dry residues after Waste Pit 2 was filled. The liquid wastes were pumped to the north end of the waste pit and solid materials settled as the liquid flowed toward the overflow weir at the south end.

Beginning in the late 1960s, solid materials were placed in the waste pit in an attempt to stabilize it. These efforts included the deposition of approximately 5000 cubic yards of broken concrete and excavated earth prior to June 1, 1971 (Nelson 1972), as well as placement of wooden pallets in the north end (Parsons 1993) and a considerable amount of soil from Waste Pits 1 and 2 into the waste pit in November 1972 (Engineering File [EF] 1958). Finally, filter cake, slag leach residue, lime sludge, and flyash were used to complete the filling of the waste pit from 1975 to 1977 (NLO 1985a). Also in 1975, several hundred thousand gallons of sludge were removed from Waste Pit 5, filtered, and most of the sludge deposited in Waste Pit 3. All of these residues have been accounted for as cover material and not as part of the waste inventory.

Approximately 102,000 m^3 of waste have been accounted for in Waste Pit 3 compared to 156,066 m^3 (65 percent accounted for) based on survey data and boring logs (Parsons 1993). Part of this difference is associated with the estimated bulk densities of the residues in the waste pit; unaccounted for materials that were deposited in the waste pit as part of the cover; and compounds, such as lime, sodium hydroxide, potassium hydroxide, magnesium oxide, filter aid, and soda ash that were associated with neutralization of the materials deposited in the waste pit but not accounted for separately. As indicated in Table 1-11, the most significant portions of the accounted for volume are neutralized raffinate (40 percent), general sump sludge (28 percent) and trailer cake (20 percent). The average density of the materials accounted for in the waste pit is approximately 1200 kg/m^3 (75 lb/ft^3). Because most of the residues in Waste Pit 3 were slurries, the density is not expected to vary significantly from this average.

Waste Pit 3 contains an estimated total of 858 MTU. The most significant source of the uranium is the neutralized raffinate (74 percent), with trailer cake also contributing a significant amount (17 percent). The uranium content of the waste pit is expected to range from 0 percent in the water treatment sludge to 0.5 percent (wet basis) in the neutralized raffinate.

More than 32 percent of the estimated mass in Waste Pit 3 is MgF_2 (41,183 MT) from trailer cake and slag leach, which also contributed nearly 25 percent of the mass as calcium. Waste Pit 3 contains significant amounts of arsenic and barium, associated with the neutralized raffinate, as well as thorium, (97 MT - Table 1-12) associated with general sump sludge.

1.2.2.4 Waste Pit 4

Solid wastes were deposited in Waste Pit 4 from August 1960 until May 1986. The solid wastes were dumped onto a concrete pad on the northeast edge and pushed into the waste pit with a bulldozer.

In some cases, these wastes were hauled to the waste pits in drums. These drums were generally emptied into the waste pit and the drums returned to Plant 8 for cleaning prior to reuse. At least 100

of the drums, however, were deposited on the west side of the waste pit (Diehl 1980). These drums probably contained spent heat treatment salts that had solidified in the drums, although definitive records in this regard are not available.

In 1975, some of the filter cake from the dredging of Waste Pit 5 was placed in Waste Pit 4 (Pennak et al. 1976). Barium chloride was reportedly deposited in Waste Pit 4 (WMCO 1986). The 1986 report indicates that 23,500 pounds of low-level radioactive waste containing barium chloride heat treatment salt were deposited in the waste pit from May 1981 and April 1983. Review of records during the RI phase indicates that the material deposited in the waste pit was contaminated with barium chloride (floor sweepings, etc.) and that the salts were stored in the RCRA warehouse.

Only 16,500 m^3 of waste have been accounted for in Waste Pit 4, compared to 42,133 m^3 (39 percent accounted for) based on survey data and boring logs (Parsons 1993). The remainder of the material in the waste pit is assumed to be trash from the site that could be deposited without documentation. These materials included cans, laboratory glass and plastic, concrete, asbestos, construction rubble, and general trash (Parsons 1993). The general trash included nonrecoverable metal refuse, glass, plastic, wood, and noncombustible cafeteria waste (prior to 1974 when the sanitary landfill was opened). The Burn Pit may include similar general trash. Lime was occasionally added to Waste Pit 4 to maintain a pH suitable for uranium precipitation (NLO 1977).

As indicated in Table 1-11, the most significant portions of the accounted for volume are trailer cake (47 percent) and depleted materials (slag and residues - 47 percent). The average density of the materials accounted for in the waste pit is approximately 1500 kg/m^3 (90 lb/ft^3), with a range from 400 kg/m^3 (25 lb/ft^3) to 8000 kg/m^3 (500 lb/ft^3) associated with the depleted residues.

Waste Pit 4 contains an estimated total of 2203 MT of uranium. The most significant source of the uranium is the depleted residues (83 percent), with depleted slag also contributing a significant amount (15 percent). The uranium content of the waste pit is expected to range from 0 percent to nearly 95 percent, both associated with depleted residues.

More than 75 percent of the estimated mass in Waste Pit 4 is MgF_2 (18,263 MT) from depleted slag. Aside from the uranium and MgF_2, Waste Pit 4 contains approximately 1093 MT of wastes from thorium processing, 74 MT of which is thorium (Table 1-12).

1.2.2.5 Waste Pit 5

Waste Pit 5 served as a settling basin for thin slurries pumped from the refinery (Plant 8) and the general sump from October 1968 through August 1983, as well as supernatant from Waste Pits 4 and 6. The waste pit also received supernatant from the general sump from August 1983 into 1987.

In 1975, several hundred thousand gallons of sludge were removed from Waste Pit 5 (because it was filling up) and filtered; the majority of the sludge was deposited in Waste Pit 3, with some going to Waste Pit 4.

Approximately 75,700 m^3 of wastes have been accounted for in Waste Pit 5 compared to 74,860 m^3 (100 percent accounted for) based on survey data and boring logs (Parsons 1993). As indicated in Table 1-11, the most significant portions of the accounted for volume are general sump sludge (49 percent) and neutralized raffinate (41 percent). The average density of the materials accounted for in the waste pit is approximately 1200 kg/m^3 (75 lb/ft^3). Because all of the residues in Waste Pit 5 were slurries, the density is not expected to vary significantly from this average.

Waste Pit 5 contains an estimated total of 547 MTU. The most significant source of the uranium is the neutralized raffinate (92 percent). The uranium content of the waste pit is expected to range from 0 percent in the water treatment sludge to 0.5 percent (wet basis) in the neutralized raffinate. Waste Pit 5 also contains approximately 72 MT of thorium (Table 1-12) from the periods when thorium was processed.

Over 39 percent of the estimated mass in Waste Pit 5 is calcium associated with the general sump sludge and the neutralized raffinate. It also contains 5056 MT of MgF_2 from slag leach. Waste Pit 5 contains significant amounts of arsenic and barium, associated with the neutralized raffinate.

1.2.2.6 Waste Pit 6

Waste Pit 6 received wastes from June 1979 through March 1985. Generally, to protect the membrane liner, the waste pit received only noncoarse, nonpyrophoric materials.

Approximately 6700 m^3 of waste have been accounted for in Waste Pit 6, compared to 7341 cubic meters (91 percent accounted for) based on survey data and boring logs (Parsons 1993). As indicated in Table 1-11, the only wastes that Waste Pit 6 received were depleted slag (82 percent by volume) and depleted residues (18 percent by volume). The average density of the materials accounted for in the waste pit is approximately 1500 kg/m^3 (90 lb/ft^3), with a range from 400 kg/m^3 (25 lb/ft^3) to 6480 kg/m^3 (400 lb/ft^3) associated with the depleted residues.

Waste Pit 6 contains an estimated total of 1432 MT of uranium. The depleted residues account for 77 percent of this amount. The uranium content of the waste pit is expected to range from 0 percent to nearly 95 percent, both associated with depleted residues.

Nearly 80 percent of the estimated mass in Waste Pit 6 is MgF_2 (7750 MT) from the depleted slag.

1.2.2.7 Clearwell

The Clearwell received surface water runoff from the waste pits and supernatant from Waste Pits 3 and 5. It acted as a final settling basin prior to periodic pumping to the Great Miami River. The Clearwell was dredged in the late 1960s or early 1970s, but has never been emptied or dredged again. Measurements indicate the presence of approximately 11 feet of sludge in the bottom of the Clearwell.

1.2.2.8 Burn Pit

The Burn Pit was used from before 1957 to 1968 to burn materials such as laboratory chemicals; pyrophoric and reactive chemicals; oils; low-level contaminated combustible material, such as pallets and skids; cafeteria debris; and general refuse, such as cans, bottles, and laboratory glassware.

The actual inventory of materials disposed of in the Burn Pit is unknown. Boring logs 1776 and 1777 indicate debris such as glass, ceramics, metal, wood, etc., down to an elevation of 558±1 feet. This information is consistent with its known use. Because of its use, the Burn Pit is expected to contain a wide variety of unburned materials as well as products of complete and incomplete combustion.

1.2.3 Operable Unit 1 Study Area Removal Actions

1.2.3.1 Removal Actions

Removal actions, as described in 40 CFR Part 300.415, are primarily intended to abate, minimize, stabilize, mitigate, or eliminate a release or threat of release of hazardous substances, pollutants, or contaminants before a final remedial action, if there is a threat to public health and welfare or the environment. These actions are initiated to accelerate cleanup activities to address releases or potential releases of hazardous substances. Five removal actions have been conducted within Operable Unit 1:

- Removal Action No. 2: Waste Pit Area Runoff Control
- Removal Action No. 6: Control of Exposed Material in Pit 6
- Removal Action No. 11: Waste Pit 5 Experimental Treatment Facility
- Removal Action No. 18: Control of Exposed Material in Pit 5
- Removal Action No. 22: Waste Pit Area Containment Improvement (Operable Unit 1).

1.2.3.2 Waste Pit Area Runoff Control: Removal Action No. 2

This removal action can be broadly defined as management of radioactively contaminated storm water runoff from Operable Unit 1. Waste storage units within Operable Unit 1 included in this removal action are the six waste pits, the Burn Pit, and the Clearwell. Runoff from the concrete storage silos in Operable Unit 4 also was included in this removal action. Implementation of the removal action entailed a site evaluation, work plan preparation, and the execution of the recommended measures. The eight-phase removal action was completed June 15, 1992 (DOE 1992c).

This project included installing concrete drainage ditches, dikes, and culverts, which, along with existing topographic features, collect the waste pit area storm water runoff. A concrete collection sump was installed south of the Clearwell to collect contaminated storm water runoff and pump it to

the Bioderelrification Surge Lagoon (BSL). The storm water runoff from uncontaminated portions of the waste pit area is routed from the perimeter drainage areas to Paddy's Run.

This removal action continues to provide runoff control and collection. The potentially-contaminated storm water runoff is collected and pumped to the BSL and the effluent treatment system before discharge to the Great Miami River. Thus, the potential for release of contaminants to the environment has been reduced.

1.2.3.3 Control of Exposed Material in Pit 6: Removal Action No. 6

This removal action involved redistributing the exposed material such that all solids were below the water level in Waste Pit 6 to reduce particulate emissions to the environment. Field activities for the removal action began on December 17, 1990 and were completed on December 19, 1990.

Approximately 125 cubic yards of the waste pit contents were exposed above the water cover of the 29,000-square-foot Waste Pit 6 surface area. This exposed waste pit material was subject to wind erosion and was estimated to be a contributor to the airborne dose received by the maximally exposed off-site individual from all sources of radiation at the FEMP. The removal action entailed using a crane with a clamshell attachment to remove the exposed material and redistribute the material to deeper portions of the waste pit.

Air sampling equipment was set up and air monitoring was initiated during late November 1990, approximately 3 weeks prior to any waste pit material movement. The air was sampled to provide quantitative measurements before, during, and after the waste pit material relocation.

A procedure was jointly agreed to by DOE and EPA to ensure that none of the material will be exposed. This procedure provides that the water level on the waste pit will be maintained (i.e., lowered after heavy rainfall or increased to compensate for losses, such as those due to evaporation). As a result of this removal action, Waste Pit 6 is no longer a significant source of particulate emissions.

1.2.3.4 Waste Pit 5 ETF: Removal Action No. 11

This removal action involved dismantling the ETF, removing the surrounding soils to prevent any potential spread of contamination beyond the immediate area, and packaging the waste materials generated during the removal action for storage pending final disposition.

The ETF was built in 1984 to test the feasibility of thermally drying sludge material from Waste Pit 5. This facility included a sand and gravel filter bed installed over a plastic liner. Six-foot wooden walls surrounded the filter bed and the structure was covered with a "greenhouse-type" enclosure. The drying experiment entailed spreading the wet material on the filter bed to facilitate drainage and evaporation; however, in February 1988, high winds removed the plastic roof from the facility and some of the sludge material was deposited on nearby surrounding soil. As an interim measure, water was applied to the remaining residues and a tarpaulin was placed over the filter bed to prevent further escape of material.

Field activities for this removal action began in December 1991 and was completed in March 1992. All of the potentially contaminated material was packaged and temporarily stored pending final disposition. The demolished site has been backfilled and capped with clay. Decontamination and rinsate waters from this removal action are being stored on site pending final disposition. Completion of this activity has resulted in the elimination of one of the particulate sources in Operable Unit 1.

1.2.3.5 Control of Exposed Material in Pit 5: Removal Action No. 18

This removal action involved dredging the exposed material below the waterline. Waste Pit 5 was removed from service in 1983. From 1983 to 1987, it received only decant water from the general sump, filtrate from the recovery plant, and nonradioactive slurries from the boiler plant and water treatment plant. Solids built up in the east end of the waste pit to the point that they were exposed and became a concern in regard to airborne contaminants.

Prior to starting the field activities in September 1992, the exposed materials were sprayed with water to soften them. Following this activity, a dredge was used to move the exposed materials to the west end of the waste pit.

Ambient air monitoring was conducted prior to this action, during the action, and after its completion in December 1992. The results indicate that the concentration of particulates in the ambient air in the vicinity of the FEMP were significantly reduced.

1.2.3.6 Waste Pit Area Containment Improvement (Operable Unit 1): Removal Action No. 22

This removal action involved minimizing the potential for wind and water erosion of contaminated materials from access roads and exposed surfaces in the Operable Unit 1 study area. A work plan was submitted to the EPA on August 31, 1992. Prior to work plan approval, exposed or stressed areas were seeded with grass. EPA and OEPA were notified of this, and in September and October 1992 seeding commenced to ensure that the schedule for completion of the removal action can be maintained (Craig 1992). Field activities for the remainder of this removal action were completed on June 30, 1993.

1.3 POLLUTANTS/CHEMICALS

Analysis of the RI data and data from previous studies show releases to the environment from Operable Unit 1 have occurred. Surface soils, the glacial overburden, and the groundwater beneath the waste pits are contaminated. The principal environmental concern associated with Operable Unit 1 is contaminant migration and transport in ground water. Radiological and chemical Contaminants of Potential Concern (CPC) were evaluated in the RI as part of the Operable Unit 1 Baseline Risk Assessment and are presented in Tables 5-1 and 5-2. Tables 5-3 through 5-25 list the CPCs in Operable Unit 1 surface soils, waste pit subsurface soils, and waste pit surface water (Pits 5, 6, and the Clearwell). Information on the methodology used for determining the CPCs can be obtained in the Operable Unit 1 Baseline Risk Assessment.

In general, the major radioactive chemicals of concern are limited mainly to the isotopes of uranium, thorium, technicium, and radium. Among non-radioactive chemicals, the constituents of concern are limited mainly to metals, volatile organics, and dioxins/furans.

1.4 TREATMENT TECHNOLOGY DESCRIPTION

1.4.1 Identification of Technologies

Several remediation technologies are being considered for the Operable Unit 1 RI/FS. The dissimilarity of materials in the pits may preclude the selection of only one remediation technology for all waste pits. These alternatives are described in detail in the DOE report "Initial Screening of Alternatives (ISA) for Operable Unit 1, Task 12 Report, January 1991." The ISA evaluated the following seven remediation alternatives in addition to the no-action alternative.

Alternative 0 - No Action

The no-action alternative provides no remediation and leaves the waste pits in their present condition. This is the baseline alternative.

Alternative 1- Nonremoval, Slurry Wall, and Cap

This alternative is intended to isolate the waste from the environment and to minimize the generation and release of contaminated leachate to the underlying Great Miami Aquifer. This alternative includes removing and treating any standing water, installing subsurface flow control measures, building a closure cap, and providing storm water runoff and run-on control measures. The subsurface flow control measures combine a slurry wall, subsurface drains, and a temporary groundwater extraction system.

Alternative 2 - Nonremoval, Physical Solidification, Slurry Wall, and Cap

This alternative is identical to Alternative 1 with the addition of a waste solidification step. The purpose of this additional process is to promote the compaction (densification) of the waste to minimize both the potential for long-term settlement and the release of contaminated waste pit water into the underlying till. The need for continuing maintenance of the cap due to settling will be correspondingly reduced.

Alternative 3 - Nonremoval, In-Situ Vitrification, and Cap

Because a waste immobilization step has been incorporated into the nonremoval scenario, this alternative is similar to alternative 2. However, this solidification step specifies vitrification technology rather than physical solidification technologies. In addition, subsurface control measures are not included in this alternative. It is reasoned the resultant vitrified mass precludes future releases of contaminated water from the waste.

Alternative 4 - Removal, Waste Treatment, and On-Property Disposal

The waste material is removed to completely eliminate the waste source from its current location above the Great Miami Aquifer and to obviate future problems through treatment and disposal of the wastes. This alternative utilizes technologies which include removing and treating the standing water, removing the waste, waste segregation and treatment, and on-property disposal. The waste treatment portion of this alternative retains two distinct process options: cement solidification and continuous vitrification. Treatment of residual water will be handled by the existing FEMP wastewater treatment facility and the advanced wastewater treatment (AWWT) facility. Any pretreatment will consist of waste segregation/separation.

Alternative 5 - Removal, Waste Treatment, and Off-Site Disposal

This alternative is identical to alternative 4 except the treated and packaged waste is transported to and disposed of at an approved off-site location.

Alternative 6 - Waste Removal, Treatment, On-Property Disposal, and Cap

This alternative, like alternative 4, addresses the removal and treatment of the waste pit caps (or standing surface water on those pits without caps) and pit wastes from each waste pit including the Burn Pit and Clearwell. However, in this alternative, contaminated soils that make up and surround the pits will be left in place and fitted with a closure cap. The treated and packaged waste will be housed on site in an engineered waste management facility.

Alternative 7 - Waste Removal, Treatment, On-Property Disposal, Soil Treatment, and Cap

This alternative is identical to Alternative 6, except soils in the surrounding waste pits are treated by in-situ technologies following the excavation of the waste pit contents.

After evaluating each alternative, Alternatives 0, 1, and 3 were removed from further consideration due to concerns about technology, implementability, and reliability. No treatability testing has been performed on these alternatives. Alternative 6 was initially chosen as the Leading Remedial Alternative (LRA) based on effectiveness and ability to meet risk assessment requirements.

Because the comprehensive base of information contained in the RI report was not available at the time the ISA was completed, it is possible the FS screening process will produce different results. If this is the case, the basis of such differences will be explained in detail in the Feasibility Study.

Based on Alternative 6, two primary technologies were identified for treatment of the waste pit material. These two treatment alternatives were vitrification and cement solidification. A treatability study program was initiated to assess the feasibility of these technologies. Under Alternative 6, treated material would be disposed of on-site. The criteria established for this program were based on meeting potential on-site risk based disposal criteria. A Treatability Study Work Plan was developed by IT Corporation. and testing was initiated.

In December 1992 Westinghouse Environmental Management Corp. was replaced by Fernald Environmental Restoration Management Company as manager of the remediation activities for the site. Under FERMCO management remediation alternatives were reassessed and revised. Off-site disposal was determined to be a viable option. Treatment alternatives to support off-site shipment and disposal were assessed. The primary treatment alternative identified for off-site disposal was thermal processing potentially followed by particle agglomeration, if required, to control dust or to reduce cost of containers for shipment. A determination was made that sufficient information exists from previous site operations and general industrial experience to support the evaluation of thermal processing as a treatment alternative for the waste pit material. Because thermal processing is also being considered as a pre-treatment option for cement solidification and vitrification, and is therefore

included in all of the alternatives currently under consideration in the FS, additional treatability studies to develop baseline characterization and thermal processing data were initiated. These treatability studies which include thermal processing and particle agglomeration, will provide the baseline information needed to support remedial design and scale-up for whichever alternative is selected in the OU1 FS and Proposed Plan.

All of the studies included in this report assess treatment for the contents within the waste pits themselves and do not address the treatment of the contaminated soils in the waste pit area. Operable Unit 5 has taken the lead for development of treatment methods for contaminated soil throughout the FEMP site. A short description of the OU5 treatability work is included here as a supporting technology for Operable Unit 1 remediation. The following sections describe the individual technologies studied.

1.4.2 Vitrification

Vitrification is a thermal treatment process that converts contaminated materials into a chemically inert and stable glass and crystalline product. The vitrification process can destroy combustible and some toxic portions of hazardous waste (ie. organics, nitrates, etc.) and simultaneously incorporate and immobilize residuals, such as ash and nonvolatile heavy metals, into a geologically stable glass form. The final product is reduced in volume and mass by driving moisture from the waste permanently, destroying portions of the waste thermally, and consolidating the residuals into a dense glass and crystalline product. Glass-former additions are sometimes necessary to produce an acceptable product.

Molten-glass processes are viewed as permanent treatment measures producing a waste form which is reduced in volume and is highly leach resistant. The processes reduce the volume of the waste by factors of between 2 and 100, depending on the composition, destructibility, and density of the waste. Volume reduction generally reduces overall disposal costs significantly.

Molten-glass processes operate by the principle of joule-heating. Electrodes placed in the molten glass apply an electrical voltage to the molten glass, passing electrical current through alkaline ionic components in the glass. The electrical resistance of the molten glass creates heat within the confines of the electrodes when voltage is applied. The heat is distributed evenly within the molten glass by natural, convective currents in the fluid.

1.4.3 Cement Solidificationn

Solidification and stabilization are treatment processes designed to either (1) improve waste-handling and physical characteristics, (2) decrease surface area across which pollutants can transfer or leach, or (3) limit the solubility of or detoxify the hazardous constituents.

Solidification implies these results are obtained primarily by production of a monolithic block of treated waste with high structural integrity. It is a process in which materials are added to the waste to produce a solid. It may or may not involve a chemical bonding between the toxic containment and the additive.

Stabilization describes processes which limit the solubility of or detoxify the contaminant; the physical characteristics may or may not be improved or changed. Stabilization refers to a process by which a waste is converted to a more chemically stable form. The term includes solidification, but also includes use of a chemical reaction to transform the toxic component to a new, nontoxic compound or substance.

Solidification and stabilization technology may be characterized by the binder used or by the binding or containment mechanism; or it may be categorized by the process type.

The use of cements as a binder matrix for the containment of mixed or hazardous waste falls under the broad category of inorganic based solidification/stabilization (S/S) techniques. In this process portland cement is combined with flyash or other pozzolans to produce a relatively high strength,

dimensionally stable, waste-and-concrete matrix. Waste containment is primarily by entrapment of waste particles. Soluble silicates may be added to aid processing and to assist in containment of metals through the formation of silicate gels. Water is removed in the hydration of the portland cement. Characteristics of this process are the following:

- Pozzolan products added to portland cement react with free calcium hydroxide to improve strength and chemical resistance of the solidified waste product.
- Portland cement types are available and can be selected to enhance a specific desirable reaction.
- A variety of materials (e.g., clays, hydrated silica gels, etc.) have been added to change a desired performance.
- Cement-based processes can be formulated for exceptional strength and have been found to retain selected contaminants effectively.
- Certain waste components may interfere with the setting and stability of cement-based processes (e.g., acids,, borates, oil, etc.).

1.4.4 Thermal Processing

Thermal processing is broken out into several phases (drying/mechanical dewatering, calcining, and clinkering) to determine the effects of various temperature ranges on the waste material. Testing is accomplished in a phased approach, with each new phase building on information obtained from the previous phase.

Thermal treatment has been employed for the disposal of industrial wastes (hazardous wastes) for over 50 years. The most common equipment for used for thermal treatment of hazardous waste in the U.S. is the rotary kiln. Substantial design and operational experience exists for rotary kilns and a wide variety of commercial systems are available. Since extensive information exists on thermal treatment technology and rotary kilns, both at the FEMP and industrywide, full treatability testing of kiln technology on the pit wastes was not performed. Because of EPA's recent research efforts, more

is known about thermal treatment/kiln technology and its effects on the environment than virtually any other waste management alternative. Benefits of thermal treatment include the destruction of toxic organics, volume reduction, low public health risk, potential energy recovery, and a wide range of applications. Because of these benefits, EPA has embraced thermal treatment as the preferred treatment method for a wide range of waste streams.

Thermal treatment of residues and wastes occurred as part of normal site operations for the majority of the site history (see Section 1.5).

Drying and Mechanical Dewatering. Various techniques are available to reduce the volume of waste through physical treatment. Such techniques usually remove a non-hazardous portion of the waste, such as water. Available concentration methods include gravity and vacuum filtration, ultra-filtration, reverse osmosis, freeze vaporization, filter press, heat drying and compaction.

Drying may be used as either the primary treatment for waste material or as a pretreatment for another treatment process. Thermal drying is the process of removing free water from solids by heat and evaporation. Drying may be accomplished in varying ways and is highly dependent on the properties of the waste material. These properties include particle size, moisture content, chemical composition, etc. Thermal dryers may be direct fired or indirect heated rotary or fluid bed dryers among other varieties. The choice of the dryers is dependent on the degree of dryness desired, throughput capabilities, temperature requirements and energy efficiency. The off-gas from drying processes generally requires additional treatment dependent on the nature of the waste and the temperature at which it is processed.

Calcining. Calcining is the process of heating of a solid to a temperature below its melting point to bring about a state of thermal decomposition or a phase transition other than melting, so that hydrates and other compounds are decomposed and the volatile material is expelled. Calcining takes place in a rotary kiln or calciner. Calcination may be considered as taking place in stages as the waste advances down the kiln. The water is driven off in the first zone followed by devolatilization in the calcination

zone of the kiln. The calcined material is then cooled. The calciner is installed at a slight angle to permit the solids to advance by gravity as the kiln rotates.

Clinkering. Clinkering is the process of fusing controlled feed materials together to form chemically stable compounds. Clinkering for the production of cement-like materials takes place at high temperatures in rotary kilns. During the clinkering process, any water is driven off first, followed by devolatilization (calcination), and then the fusing of the materials at elevated temperatures to form clinkers. The clinker is then cooled and either disposed of directly or, if the composition is suitable, ground into cement-like material.

1.4.5 Particle Agglomeration

Agglomeration/Pelletization. Agglomeration is the process of particle size enlargement in which small, fine particles (such as dusts or powders) are gathered into larger masses, clusters, granules, pellets, or briquettes for use as end products or in secondary processing steps. A binder may be added to the material being agglomerated to provide bonding strength in the final product. A binder can be a liquid or solid that forms a bridge, film, or matrix filler or that causes a chemical reaction. This process minimizes dusting, increases density, and improves handleability.

Polymer Encapsulation (PE). Encapsulation is a process involving the complete coating or enclosure of a toxic particle or waste agglomerizate with a new substance. For these preliminary studies, polymer encapsulation has been selected as the polymer for screening purposes. The use of polyethylene as a binder matrix for the containment of mixed or hazardous waste falls under the broad category of organic-based Solidification/Stabilization (S/S) techniques. PE can be used as a containment mechanism for two types of treatment under this broader category, microencapsulation and macroencapsulation.

Microencapsulation is commonly a thermoplastic process in which a thermoplastic material such as polyethylene, bitumen, or paraffin is used to bind the wastes into a S/S mass. In this case there is not a chemical interaction between the waste and binder. The thermoplastic material is heated and the

waste is mixed with the material at this higher temperature. Upon cooling the mass sets and becomes a solid mass thus trapping the contaminants in the matrix.

Macroencapsulation is a process that places the waste in a drum (Usually steel or PE) or some type of sizeable and sealable container. Usually the waste is S/S or otherwise microencapsulated prior to macroencapsulation.

Some characteristics of polyethylene encapsulation processes are the following:

- Thermoplastic fixation methods result in lower contaminant mobility than most other techniques.
- Thermoplastic materials are relatively resistant to most aqueous solutions.
- Incorporated wastes adhere well to thermoplastics.
- Thermoplastics require specialized equipment and skilled labor.
- Some contaminants may mobilize at processing temperatures.
- Thermoplastics are flammable.
- Wastes must be dry prior to mixing.
- Some organics and solvents may cause deterioration of thermoplastic material.
- The end product can behave in a plastic manner and usually requires macroencapsulation prior to transportation.

1.4.6 Supporting Technologies

The emphasis of the treatability program for Operable Unit 1 has been for the waste contained in the waste pits themselves. Operable Unit 1 also contains a significant quantity of potentially contaminated soils. Operable Unit 5 has taken the responsibility to develop effective treatment methods for contaminated soils throughout the FEMP. Soil Washing has been identified as an effective treatment for contaminated FEMP soils in laboratory tests and pilot testing is currently ongoing. A brief description of the soil washing processes is provided here. The process developed from the Operable Unit 5 program will support the final remediation of the Operable Unit 1 soils.

Other technologies which may support final remediation of the waste pit materials are Long Term Durability Testing and Non-Destructive Test Methods. One of the significant concerns raised in the initial consideration of cement stabilization for on-site disposal of the waste pit materials was the long term durability of the product. A test program was initiated in cooperation with the EPA Risk Reduction Engineering Laboratory (RREL in Cincinnati, Ohio), to develop test procedures to predict the long term durability of cement stabilized wastes. A short description of that project is included here. To date only surrogate wastes have been tested in the program.

Another need identified during development of treatment alternatives was the need to be able to test potential waste forms for physical stability and homogeneity (for disposal/stacking in an on-site disposal cell). Non-destructive test methods were developed as part of the long term durability test program using acoustical methods. These tests proved to be cost effective and relatively simple to perform and have a wide application to a variety of waste form types. A short description of the test methods is also included in this section.

Soil Washing

Technology Description. Soil washing is an ex situ treatment process which incorporates the separation of chemical contaminants from the soil matrix by a combination of physical and chemical treatments. The initial operation in the process is to reduce soil aggregates to single grain composition (i.e., clay, silt, sand, gravel, etc.). This is accomplished by either mechanical means (e.g., high pressure water or mixers) and/or chemical dispersing agents (e.g., sodium salts). This is followed by various physical/chemical processes which aid in the extraction of inorganic, organic and radiological chemical contaminants from the discrete soil particles. Spent washing (extracting) solution is then regenerated through precipitation and/or ion exchange processes and recycled back through the soil washing process. The remaining contaminated residue fraction is collected, containerized and stored for either disposal or subsequent treatment (e.g., vitrification, solidification, stabilization, etc.). The clean soil fraction can be stored and subsequently used for backfill.

Physical Separation. Many organic and inorganic contaminants tend to bind primarily to clay and fine silt soil particles. The attraction of chemicals to this soil size fraction (especially in ionic form) is

primarily a function of the negative exchange sites associated with the surface of clays. However, there may be those soil/chemical matrices in which the chemical contaminants are associated with the coarse silts and sands as well as the clays. Soil washing can be more universally applied to all soils as a combination of both physical and chemical processes which not only separate the soil into discrete size fractions, but also separates the chemical contaminants from each of these size fractions.

Physical separation operations in soil washing have included high pressure water, screening, attrition scrubbing, froth flotation, hydrogravimetric separation (including hydrocyclones, mineral jigs and spiral classifiers), and multigravity separation.

Chemical Extraction. Water-based chemical reagent processes can also be considered as providing two primary functions - dispersion and extraction. Chemical reagents (especially sodium salts) can be employed to breakdown soil aggregates into discrete soil particles. In addition, chemical reagents (e.g., surfactants, chelators, acids and bases) can be used as extraction reagents (including those used for dispersion) to separate the chemical contaminants from the surface of individual soil particles. The use of these water-soluble chemicals. The incorporation of chemicals in an aqueous solution is used to physicochemically enhance the removal of ions and compounds (collectively to be referred to as chemicals) from soil particles. Physicochemical separation of chemicals may be via mass action, substitution or complexation.

Process Water Treatment. A final operation in the soil washing system is the regeneration of the spent washing solution. In many operations, the amount of spent wash water generated during the soil washing operation may equal anywhere from three to 10 times the initial volume of soil being processed through the system. Therefore, regeneration of spent wash water is mandatory. Two primary processes for waste water treatment are ion exchange and precipitation.

Waste Form Testing

Current regulatory and other test procedures evaluate one or more aspects of a stabilized waste, but provide little or no information to predict the long term behavior of the waste form. Evaluation of the long-term behavior of a waste form is necessary to show the waste form will continue to isolate

the hazardous contaminants from the environment after disposal. Test protocols for Accelerated Aging of Cement Solidification Stabilization (CSS) waste samples are being developed by the University of Cincinnati Accelerated Life Testing and Environmental Research (A.L.T.E.R.) Facility to assess the long term durability of solidified/stabilized waste forms.

Accelerated Aging. The University of Cincinnati is developing a test protocol for accelerated aging of stabilized waste samples to assess their long term durability in the environment. The test protocol is based on the Arrhenius aging models. Considerable work was completed toward development of this protocol especially in determination of accurate activation energies for use in the Arrhenius model.

Non-destructive testing (NDT). The assessment of physical degradation in stabilized waste forms may significantly affect the leaching potential of the waste form. Few standards exist for these measurements and they provide little information to quantify the degradation. A NDT method using acoustical methods was modified from ASTM standards for testing of structural concrete and applied to S/S waste cylinders in the lab. This test provides a better indication of internal structural deterioration and long-term durability potential than Unconfined Compressive Strength (UCS).

1.5 PREVIOUS TREATABILITY STUDIES AT THE SITE

Previous treatability studies under CERCLA have not been performed on Operable Unit 1 wastes. However, process residues from uranium production were treated as part of normal site operations prior to disposal in the waste pits or shipment to the Nevada Test Site (NTS). Residue or waste treatment processes included processing for uranium removal, dewatering, drying, calcining, and other thermal treatments. The majority of these treatment processes were performed in Plant 8. Although these operations were not performed as treatability studies, valuable information may be derived from this historical process data. A search for operating records has been initiated and discussions are being held with retired and former employees (operators and engineers) involved with these processes to develop information for evaluating treatment technologies. The following is a description of several former waste treatment operations being examined. The following are

descriptions of past plant operations involving thermal treatment of process residues similar to those which may be found in the waste pits:

1.5.1 Residue Recovery Operations: Plant 8.

The Recovery Plant (Plant 8) began production in November 1953. Impure metal and residues from the sites production plants were sent to the Recovery Plant for processing, to quickly return uranium to the production stream where it was urgently needed. In about 1963, when the supply of uranium became adequate, residues were processed to reduce the amount stored in drums. Figure 1-21 shows the FMPC Waste Handling Operations.

High-grade residues such as machining chips and turnings were processed in automatically rabbled furnaces. There, the metallic uranium particles were burned to U_3O_8. A vibrating screening operation separated the +8 mesh (U.S. standard) fraction which contained most of the unoxidized metal to be recycled for further oxidation. The -8 mesh fraction was drummed as product and sent to Plant 2/3 for additional processing. Low-grade residues, such as sump cakes, floor sweepings and dust collector residues were also processed through automatically rabbled furnaces vented to Venturi-type scrubbers. The individual processes in the Recovery Plant for converting the impure metal scrap and low-grade residues included hydrometallurgical and miscellaneous operations. Following are descriptions of some of the major Plant 8 residue treatment operations.

1.5.2 Oxidation Furnace No. 1

Oxidation furnace No. 1 was a six-hearth, 54" ID, automatically rabbled furnace with a total hearth area of 85 square feet. Three open-flame gas burners were used for combustion of feed materials. It was used to oxidize high grade scrap, such as uranium metal fines and "sawdust", from metal machining operations, to U_3O_8. The product contained essentially no free metal. Inside the furnace, the feed was mechanically rabbled to the outer edge of one hearth, dropped through port holes, and rabbled to the center of the hearth below. Feed continued to pass from hearth to hearth in this manner until black oxide was discharged from the sixth hearth. (See Figure 1-22 for flow diagram.) Product from the furnace was drummed for disposal in the packaging station.

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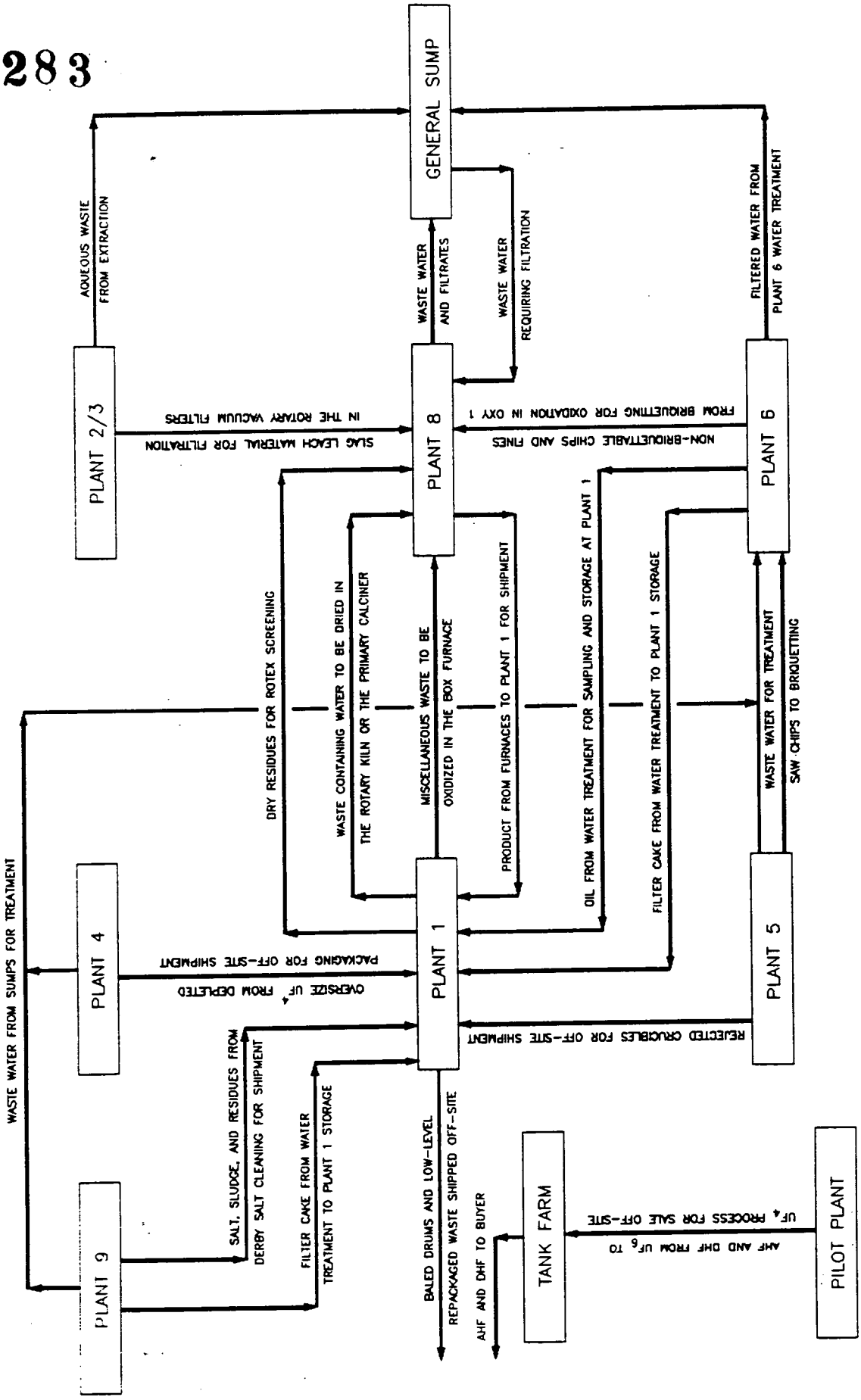

FMPC WASTE HANDLING OPERATIONS

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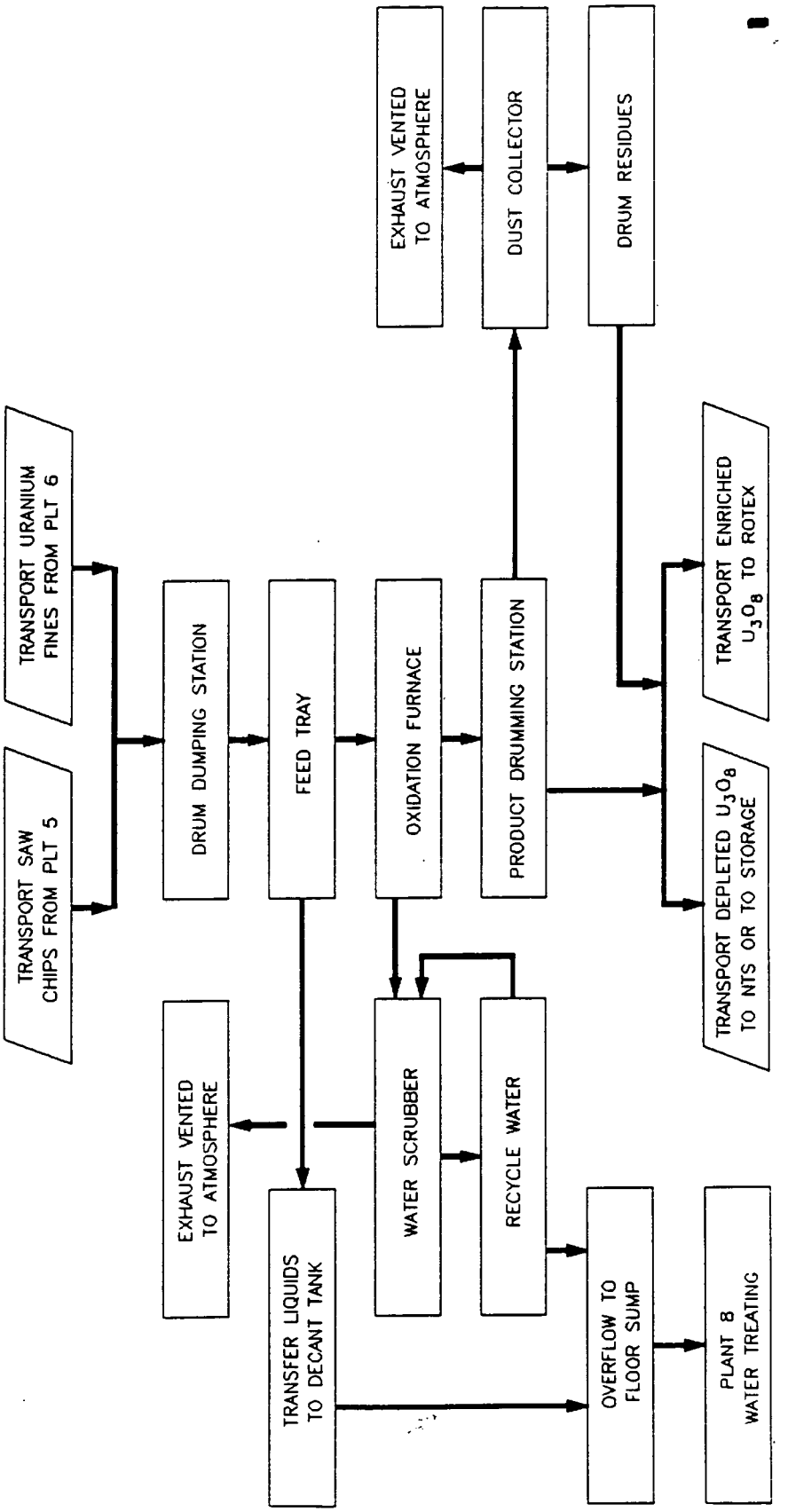

PLANT 8 OXY 1

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Typical annual production from Oxidation Furnace Number 1 was 12 metric tons of uranium per month. This was a production rate in the early to mid-1980s; no historical production records are available.

1.5.3 Oxidation Furnace No. 2.

Oxidation No. 2 furnace was a six-hearth furnace most recently used to convert uranium tetrafluoride to calcium uranate and calcium fluoride using calcium hydroxide (lime). Originally, it was used to oxidize dust collector residues and to reoxidize scrap or impure U_3O_8 to U_3O_8 which could be used as refinery feed. No production records are available. Operation of the furnace was essentially the same as Oxidation Furnace No. 1.

1.5.4 Primary Calciner.

The Primary Calciner (Figure 1-23) was a natural gas fired unit 13 ft. 6 in. in diameter consisting of a steel shell and eight lined hearths with three burners. Burners were located on hearths 3, 5, and 6. The Calciner was an automatically rabbled furnace used to process low grade residues. No production records are available.

1.5.5 Rotary Kiln.

The Rotary Kiln consisted of a horizontal steel cylinder, 66 in. ID and 50 ft. long. It was lined with 6 in. refractory bricks backed by insulating blocks (Figure 1-24). The kiln was slightly inclined from the horizontal. The cylinder rotated at speeds of 0.45, 0.60, 0.90, and 1.23 rpm. The kiln processed low-grade residues such as nonbriquettable turnings and pyrophoric finely-sized residues. During the later years, the kiln was used to dry waste materials before shipment off-site for burial.

Wet materials were fed to the kiln from a feed tray into a chute equipped with a valve operated by a foot lever, whereas dry materials were fed by means of a drum dumper and feed screw. The rotation and incline of the kiln caused the material to move from the feed through the combustion chamber to the exit, where it was discharged into a water-cooled screw conveyor which conveyed the material to

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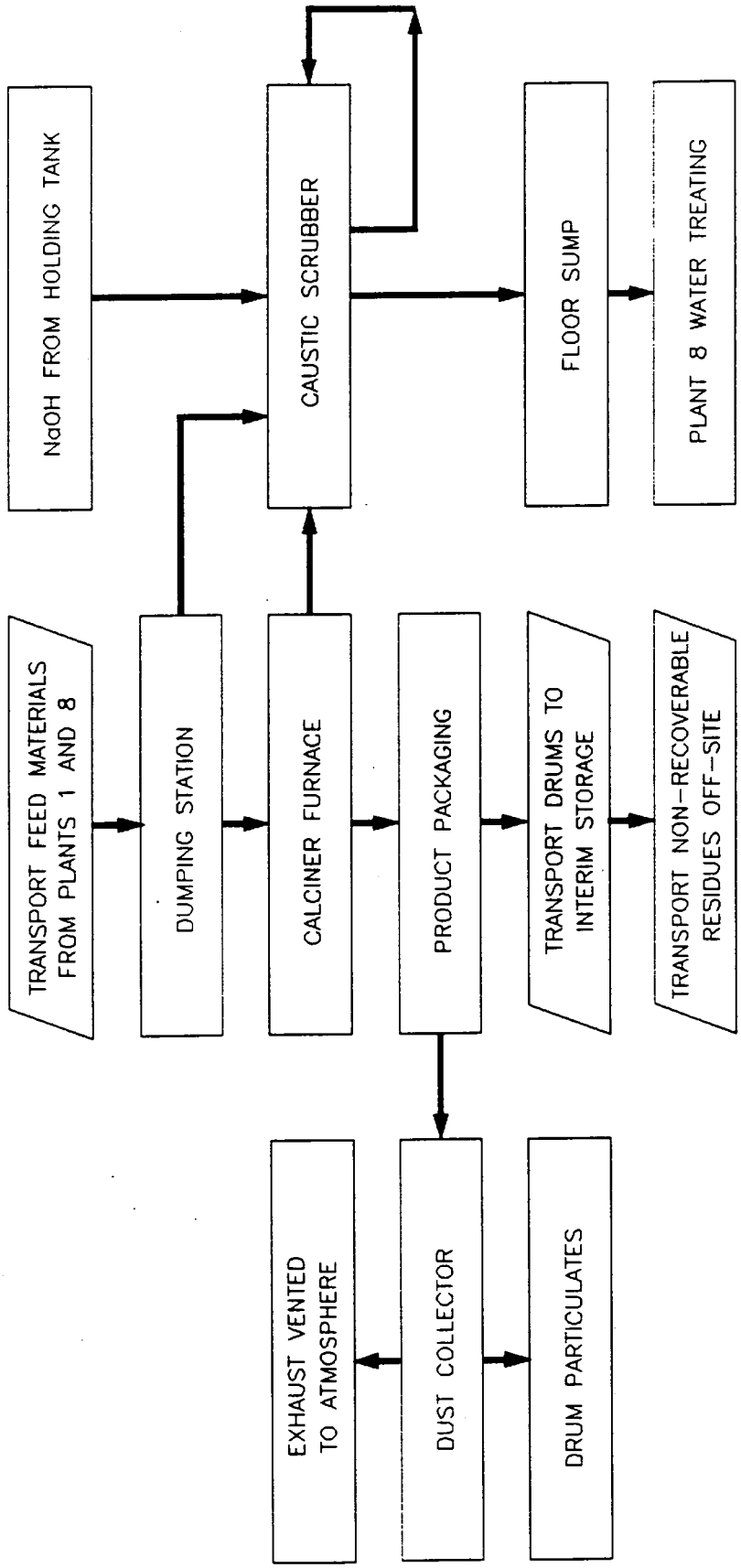

PLANT 8 CALCINER

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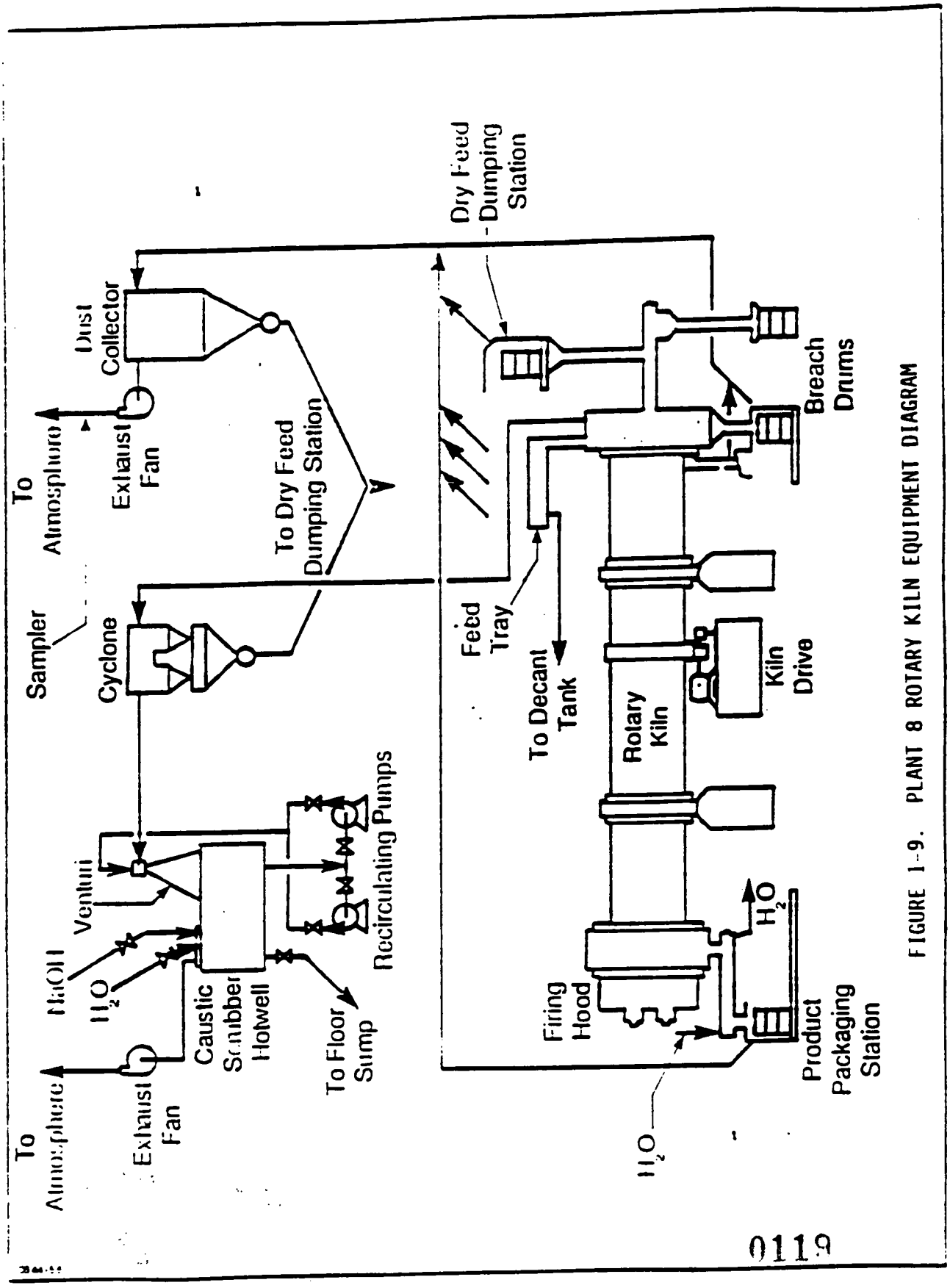

FIGURE 1-9. PLANT 8 ROTARY KILN EQUIPMENT DIAGRAM

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a packaging station. Materials passing through the kiln were dried, roasted, or oxidized depending upon the characteristics of the feed materials and the desired product. Typical feed to the rotary kiln was 77.3 metric tons of uranium per month.

1.5.6 Box Furnace

The Box Furnace (Figure 1-25) was a refractory-lined steel fire-box. It was fed in batches and rabbled (furnace contents are agitated to ensure complete combustion) manually until the charge was completely oxidized. After oxidation was complete, the furnace charge was manually transferred into a product drum. The Box Furnace was used to oxidize gloves, filters, rags, and other contaminated burnables to recover their uranium content, as well as to oxidize miscellaneous metallic uranium scrap to U_3O_8 (black oxide). Product from the furnace was screened to remove non-oxidized material which was sent back for reprocessing.

The Box Furnace produced about one kilogram of uranium per month due to the low uranium content of the feed material.

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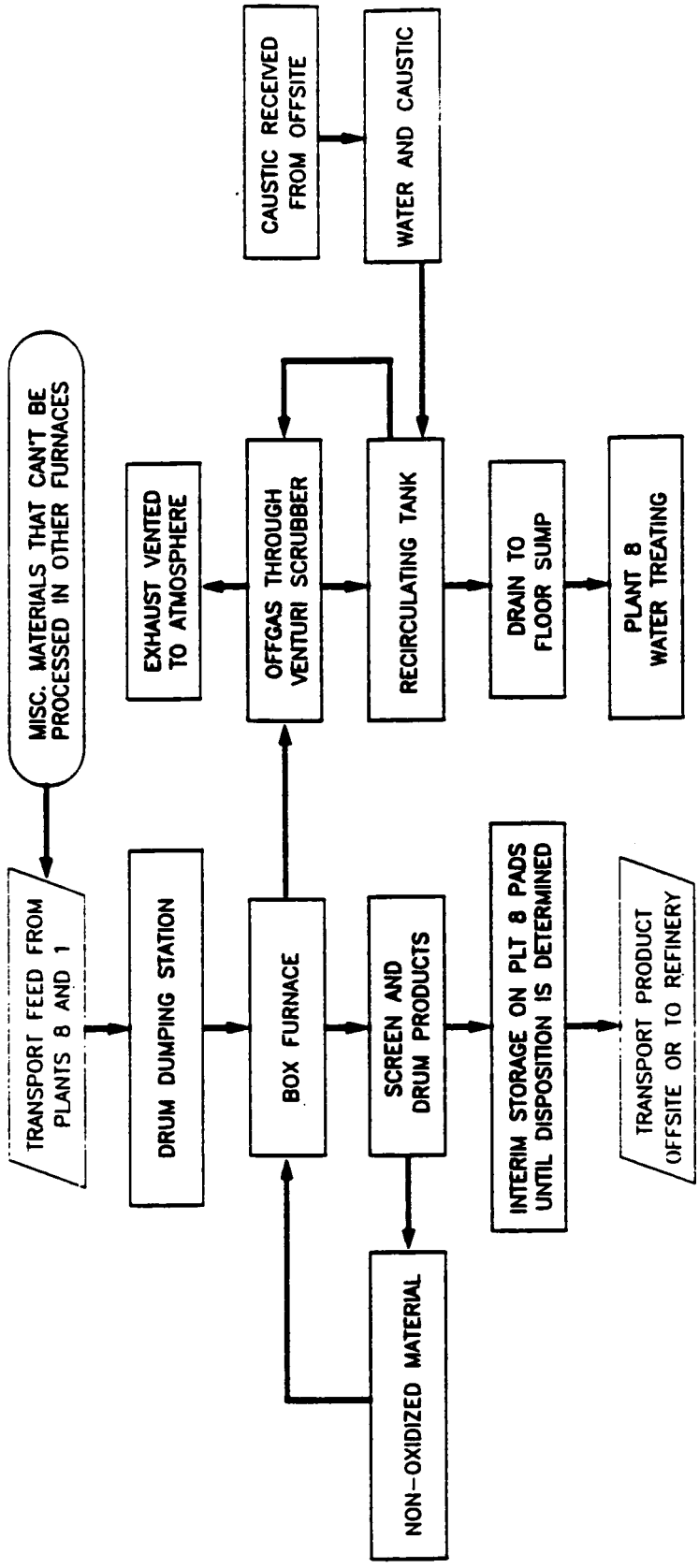

PLANT 8 BOX FURNACE

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SECTION 2.0 RECOMMENDATIONS AND CONCLUSIONS

Three main types of treatment were studied as part of the OU1 treatability study program, vitrification, cement solidification and thermal treatment followed by possible particle agglomeration. The conclusions and recommendations made for each of these technologies based on the treatability studies are presented in this section. The potential robustness of a process is perhaps the most important consideration for evaluation of these treatment processes because the waste pit contents are extremely heterogenic in nature. Full characterization prior to excavation is not possible. The treatment process chosen must be robust enough to handle the wide variety of materials to be processed.

2.1 Vitrification

These treatability studies have evaluated the use of vitrification for treatment of the OU1 pit wastes. Waste from each of the waste pits has been characterized for glass forming constituents. Crucible melts have been performed for a broad range of potential vitrification formulas. More in-depth crucible studies have been performed to evaluate process parameters such as conductivity and viscosity. In addition several small continuous process melter runs have been made with material from Waste Pit 5. The vitrified products from these experiments have been analyzed and tested for leach resistance. The results from these experiments are summarized in Section 4.0 of this report. The conclusions reached regarding vitrification as a treatment alternative for the waste pit materials are as follows:

(1) Waste Pit material can be vitrified (i.e. a non-crystalline glass product can be formed) with the proper formulation and use of additives. Variations in chemical composition within the waste pit material significantly impact the required formulation and amount of additives required.

(2) Vitrification was very effective in reducing the mobility of the contaminants. Leach test results from the TCLP and the PCT demonstrated that the glass matrix effectively prevents uranium, thorium and other contaminants from leaching.

(3) A significant reduction in volume of waste was also achieved by vitrification. The amount of volume reduction was greatly dependent on the waste pit material and the required amount of additives to achieve a vitrified product.

(4) Preliminary results show that fluoride can be captured in an off-gas system and recycled into the feed batch.

(5) Heavy metals and radionuclides appear to be retained in the glass melt minimizing off-gas problems.

Recommendations

Sufficient data has been developed from the treatability work performed to date to evaluate vitrification as a treatment alternative as part of the RI/FS process. Should vitrification be selected as the treatment alternative for all or part of the waste pit material, additional and extensive pilot testing would be required to support design and operations planning. Although fairly extensive laboratory data has been developed for vitrification of the waste pit materials, no body of industrial data or experience is available to support the evaluation of this treatment option. Vitrification has in the past been applied almost exclusively to high level nuclear waste. Processes for producing this glass are generally small melters and highly controlled processes which have undergone intensive testing. Vitrification of large volumes of low-level radioactive waste has not been previously attempted. Since no vitrification processes of this scale have ever been operated for radioactive waste, cost data must be extrapolated from smaller scale studies.

Pretreatment alternatives would also need to be investigated to reduce the impact of the waste heterogeneity if robust enough formulations could not be developed to handle the wide variations in the waste pit's chemical composition.

2.2 Cement Solidification

Cement solidification testing was performed on waste from each of the waste pits. A broad range of potential formulations were tested. Portland cement (Type I and II) and blast furnace slag (BFS) were tested as binders. Additives tested included Type F flyash, site flyash, absorbents and sodium silicate. Solidified samples were allowed to cure and were tested for Unconfined Compressive Strength (UCS), leach resistance (TCLP and 5 day static), permeability and durability. Results of the cement solidification testing are summarized in Section 4.0 of this report.

The conclusions reached regarding cement solidification as a treatment alternative for the waste pit material based on these treatability studies are as follows:

(1) Cement solidification was effective in controlling leachability as tested by the TCLP. All formulations pass the TC regulatory criteria in the TCLP leachate.

(2) The leachability of uranium was effectively controlled in the stabilization process with the exception of Waste Pit 4 due to the large quantity present in the raw waste.

(3) Formulations developed would appear to be capable of scale-up without significant problems. No significant increase in temperatures were observed during mixing and no observable gases were released during mixing.

(4) Typically formulations with greater than 43 percent portland cement Type II were effective in meeting the UCS requirements of 500 psi set for an on-site retrievable waste form and controlling the leaching of uranium and gross alpha and beta.

(5) The typical bulking factor for the cement stabilization was relatively high. The increase in volume may significantly impact the cost of disposal both on or off-site.

(6) Waste Pit 4 showed significant uranium in the TCLP leachate. Due to the high uranium content in the Waste Pit 4 samples, Waste Pit 4 may require pretreatment or treatment with an alternative technology.

(7) No significant problems were encountered with "setting" of the waste mixtures in Waste Pits 1, 3, 4, 5, 6, and the Clearwell. The Burn Pit would not set with the addition of cement but did set with the addition of blast furnace slag to the mixture. Waste Pit 2 also experienced problems with setting in the preliminary, stage most probably due to the presence of organics in the waste.

(8) Permeabilities of all of the solidified samples were low.

(9) Solidified samples passed the criteria set for durability testing (Wet/Dry and Freeze/Thaw). The addition of blast furnace slag to the solidification mixtures had a detrimental effect on their durability.

Recommendations

Sufficient data exists at this stage of the RI/FS process to evaluate cement stabilization as a treatment option. Cement stabilization is a widely utilized technology for treatment of predominately inorganic wastes. Cement stabilization has often been used for stabilization of low level radioactive wastes and is in common use today. Cost and implementability data are available from the literature.

If cement stabilization is selected in the FS/PP as a treatment option for any of the waste pit material, additional testing would be required to refine formulations and develop operational data for remedial design. The waste contained in the waste pits is extremely heterogeneous. The waste contains many elements which are considered "set retarders" and "set accelerators". The impact on each individual batch of waste may be difficult to predict. If the cement mixture were to be placed in monoliths or in lifts in a disposal cell the impact of a removing and reworking a failed batch would be significant in terms of cost and time. Additional testing in the laboratory would be required to develop more refined formulations to carry forward this option. An alternate treatment method may be required for material in Waste Pit 4 if blending of the waste could not be performed to reduce the uranium concentration on a batch basis.

Due to the extreme heterogeneity of the waste pits, pretreatment alternatives to reduce the possibility of spikes or pockets of high concentrations of contaminants should be investigated. These may include blending and/or drying of the waste prior to solidification.

Cement stabilization is relatively inexpensive based on the cost of equipment and reagents, however careful formulation and stringent quality control is required for a successful process. The extreme heterogeneity of the waste pit material may make both successful formulation and quality control extremely difficult.

The creation of a low strength cement material was also considered but no testing was performed. The low strength, possibly soil-like material would require considerably less quantities of cement and would lower the volume increase. Also by creating a soil-like material the problems associated with gel and set of the cement would be eliminated. The higher pH of the mixture would likely be effective in reducing the leach potential of the metals and uranium. The effect of the heterogeneity of the waste would be somewhat mitigated, but spikes could still easily occur which could affect product performance.

2.3 Thermal Processing and Particle Agglomeration

Thermal Treatment

Thermal treatment studies were initiated in 1993 to develop data on waste drying. Drying may be used as a primary treatment for the waste pit material before shipment to an off-site disposal facility. Drying may also be used as a pretreatment for either vitrification or cement solidification treatment alternatives.

Baseline testing has only recently begun. Physical characterization and baseline crucible studies are underway to determine the effects of temperature on the waste material. Data from these studies will be included in an addendum to this report in Spring 1994.

Thermal treatment has been used to treat residues from the processing of uranium for many years at the FEMP. Based on this experience and the extensive information available from industry on thermal treatment of residues the following conclusions were reached:

(1) Waste from the waste pits can be effectively dried and packaged for shipment to an off-site disposal facility.

(2) Thermal treatment of the waste will significantly reduce the volume.

(3) High temperature drying (above the calcining temperature) will require more complex off-gas treatment due to the decomposition of organics and salts.

(4) The dried waste will pass TCLP leach criteria (based on evaluation of the raw waste characterization).

(5) A wide variation in the feed material will not significantly affect the thermal process at lower temperatures (below the calcining temperature).

Recommendations

The pit wastes contain large amounts of free water. It is expected water will be removed during the retrieval and feed preparation operations by selective excavation, pit dewatering, settling and decantation of the retrieved waste, and by mechanical removal. It is expected that the feed to the treatment plant will have a moisture content of 30 to 35% (dry weight basis) as a result of these operations.

To ensure full-scale implementability, the entire process would need to be tested in a pilot-scale test program. This program should include testing of dewatering during retrieval and feed preparation, and to establish parameters for drying and off-gas treatment. The advantages and disadvantages of higher temperature drying (ie. creation of a clinkered material (to about 2600° F)) should also be evaluated.

To fully assess the process parameters for a drying process, the test program must determine the drying behavior of the waste (i.e., a drying profile as a function of time and temperature). This program will determine what the actual operating temperature, residence time, and dryer size should be for the materials to be dried. It will also provide data for determining off-gas treatment parameters.

Testing would also be required to determine the raw mixes that may produce stable clinkers for the production of low-quality Portland cement and magnesium-oxychloride cement from the waste pit material. Tests and a separate study should be performed to determine if the OU2 lime sludge could be used as an additive for thermal treatment.

Particle Agglomeration

If drying is used as a primary treatment alternative, the dried material may pose a dusting problem for handling and shipping. Several methods for agglomeration of the dried waste have been investigated. These include pelletizing and polymer encapsulation.

This option is a combination of the previously described drying process followed by an agglomeration step using water or other additives as binders. Agglomeration technology is a process of size enlargement or upgrading of otherwise finer particles. The forms of product, depending on the reason for agglomeration, can be spheres, pellets, irregular extrusions, or merely loosely bound aggregates or clusters.

To date only tests with a surrogate material have been performed. Based on these surrogate tests and information available from studies at other DOE sites the following conclusions were reached:

(1) This technology is implementable. There is a long industrial history of agglomeration. The agglomeration equipment is reliable and easy to construct, operate, and maintain. Prospective technologies are readily available as are equipment vendors and specialists.

(2) The agglomeration process may require the addition of water or other binders.

(3) Agglomeration can successfully reduce the dusting hazard for dried waste.

(4) Waste does not need to be completely dry for successful encapsulation or agglomeration.

(5) High waste loadings in proportion to the binder can be achieved.

(6) Chemical variations in the feed material have little or no effect on the polymer encapsulation process since the waste particles are microencapsulated and no chemical interaction occurs.

Recommendations

To prove technology applicability and implementability, further test work would be necessary. The testing should identify the appropriate technology and develop basic process parameters, including:

(1) Feed size
(2) Moisture content
(3) Surface Requirements (ft^2/ton of feed)
(4) Additives

This technology could be used to decrease dusting when handling and shipping the end product. The energy required for drying and encapsulation is moderately high, and depending on the amount of polymer required for treatment, the operation and maintenance costs could impact cost.

Further testing should be performed to define the agglomeration process parameters and the agglomerated waste form requirements for transportation. Tests with actual pit waste would need to be performed at a bench scale. Additional pilot studies would also need to be performed.

2.4 Summary

All of the technologies tested are capable of treating the waste materials in OU1. The engineering and implementation risk and cost associated with the options may vary significantly. Cement stabilization is a well proven technology but is extremely waste specific and significant variations in the waste material may cause difficulty in implementation. Vitrification may provide increased protection against leachability and reduced volume but the process is unproven at scale.

Vitrification, cement solidification, and thermal treatment will be evaluated in the OU1 Feasibility Study. Further testing of a treatment process to support remedial design will be based on the alternative chosen in the OU1 FS and Proposed Plan.

3.0 TREATABILITY STUDY APPROACH

The EPA's Guide for Conducting Treatability Studies Under CERCLA (EPA 1989a) outlines a three-tiered approach to conducting treatability studies for a Superfund site. The original interpretation of the approach can be seen in Figure 3-1. The remedy evaluation phase of the RI/FS, in accordance with proposed revised EPA guidance, may require a maximum of three tiers of treatability testing:

- Remedy screening
- Remedy selection
- Remedy design

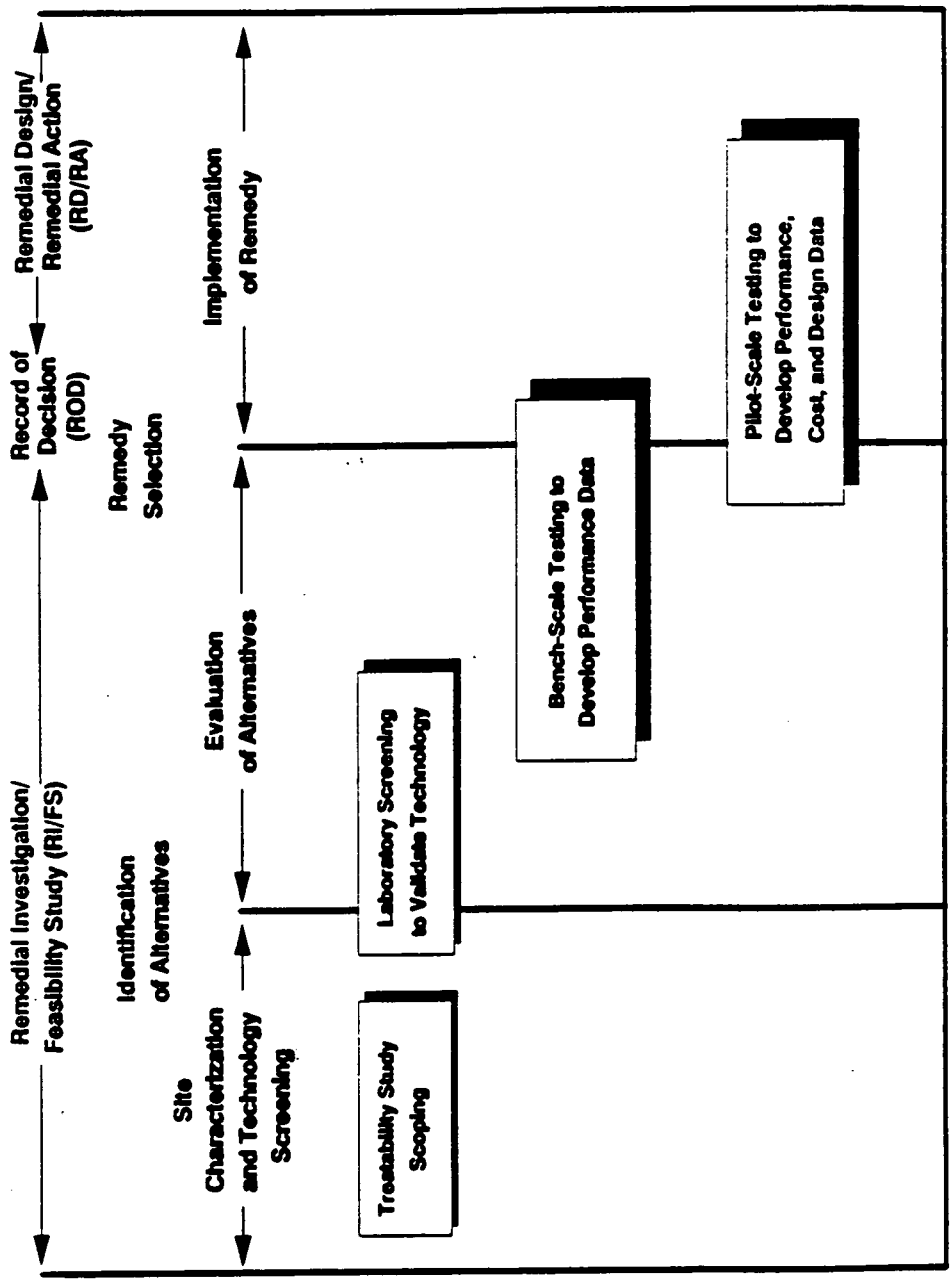
Treatment methods considered for remediation may require full, limited, or no treatability testing based on the amount of previous information available which is directly applicable to the waste. Figure 3-2 reflects the modified approach to treatability studies outlined in the EPA's "Guide for Conducting Treatability Studies Under CERCLA" Final (EPA 1992).

The three levels of treatability testing are divided into pre-Record of Decision (ROD) and post-ROD studies. The remedy screening and remedy selection testing are pre-ROD studies, and the remedy design studies are post-ROD.

Pre-ROD treatability studies provide critical performance and cost data needed to (1) evaluate all potentially applicable treatment alternatives and (2) select an alternative for remedial action based on the nine RI/FS evaluation criteria. The detailed analysis of alternatives phase of the RI/FS follows the development and screening of alternatives and precedes the actual selection of a remedy in the ROD.

During the detailed analysis, all remedial alternatives are evaluated based on nine RI/FS evaluation criteria. These criteria are as follows:

- Overall protection of human health and the environment
- Compliance with ARARs
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility, or volume through treatment



Source: Guide for Conducting Treatability Studies Under CERCLA. Interim Final 12/89.

FIGURE 3-1 THE ROLE OF TREATABILITY STUDIES IN THE RI/FS AND RD/RA PROCESS

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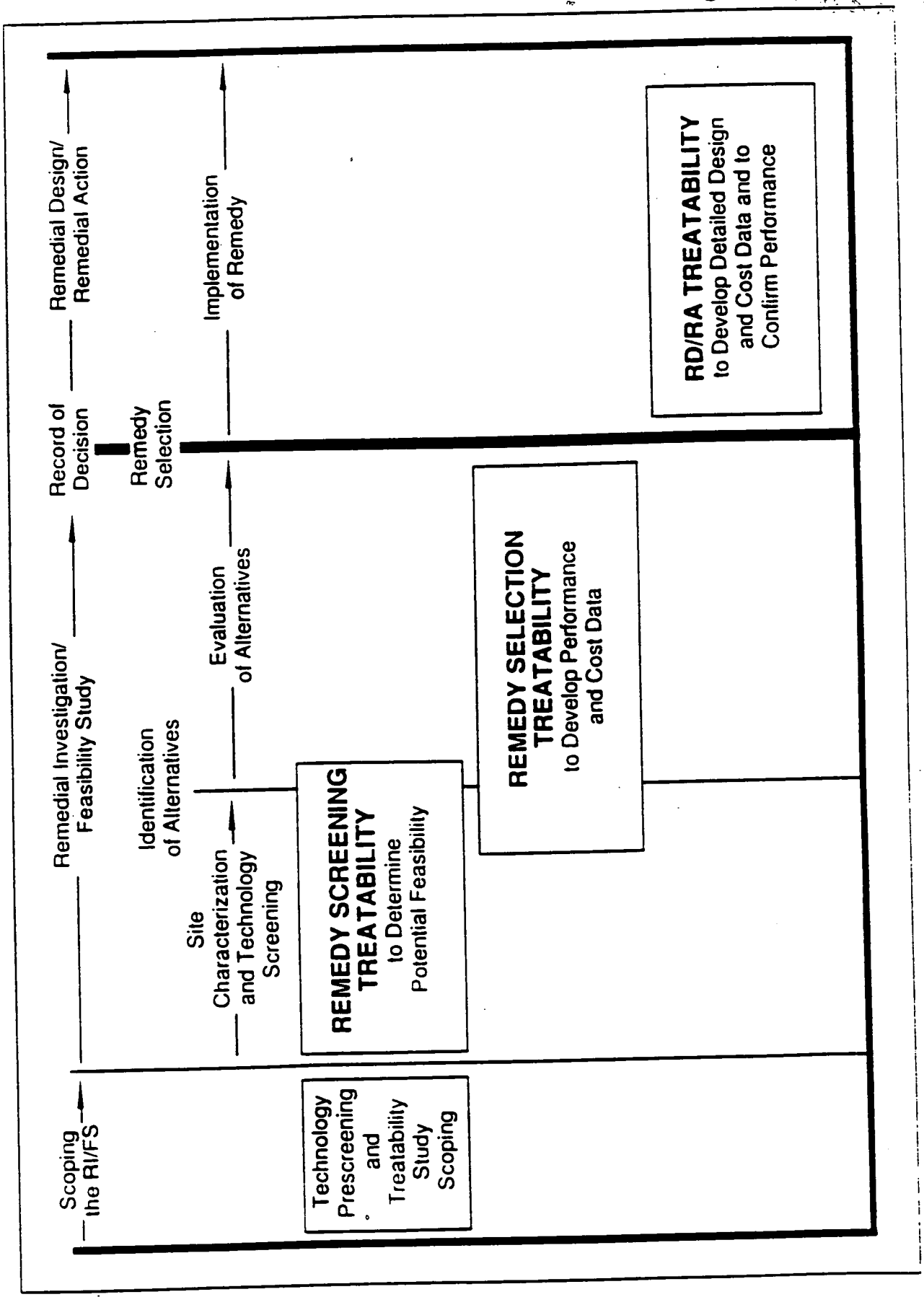


Figure 3-2 The role of treatability studies in the RI/FS and RD/RA process.

- Short-term effectiveness
- Implementability
- Cost
- State acceptance
- Community acceptance

Remedy screening is the first step in the tiered approach. Its purpose is to determine the feasibility of a treatment alternative for the contaminants/matrix of interest. These tests are typically conducted under conditions favorable to the technology. These small-scale studies are designed to provide a qualitative evaluation of the technology and are conducted with minimal levels of Quality Assurance/Quality Control (QA/QC). Tests conducted under this tier are generic in nature (not vendor specific). If the feasibility of the treatment cannot be demonstrated, the alternative should generally be screened out at this time.

The remedy selection tier of the treatability study program is designed to determine whether a treatment alternative can meet the operable unit's cleanup criteria and at what cost. The purpose of this tier is to generate the performance and cost data necessary for remedy evaluation in the detailed analysis of alternatives phase of the Feasibility Study (FS). The cost data developed in this tier should support costs estimates of +50 percent/-30 percent accuracy. The performance data will be used to determine if the technology will meet ARARs or cleanup goals. Remedy selection studies are typically small-scale, incorporating generic tests using bench- or pilot-scale equipment in either the laboratory or field. The study costs are higher than those encountered in the remedy screening tier and require longer durations to complete. The levels of QA/QC are moderate to high because the data from these studies will be used to support the ROD.

In the remedy design tier treatability study, detailed scale-up, design, performance, and cost data are generated to implement and optimize the selected remedy. Remedy design studies are performed, usually as part of the remedy implementation. These studies are performed with the purpose of generating detailed, scale-up design and cost data; they require moderate levels of QA and are vendor-specific.

All treatability work was performed based on work plans prepared in accordance with the EPA's Guide for Conducting Treatability Studies Under CERCLA Interim Final (EPA 1988) and Final (EPA 1992).

Remedial Action Objectives

The overall program goals, (i.e., remedial action objectives [RAOs]), are medium-specific cleanup goals for protecting human health and the environment. They address the contaminants of concern as well as exposure routes and receptors identified in the baseline risk assessment. The primary purposes of RAOs are to ensure site-wide compliance with:

- Chemical-specific ARARs and to be considered (TBC) guidelines
- EPA guidance for risk to public health from hazardous chemicals
- Regulatory standards for control of radiation and radioactivity in the environment

The RAOs for Operable Unit 1 must cover all constituents (radiological and chemical) which contribute to a reasonable maximum exposure (RME) scenario. Alternatives for remediation must meet airborne RAOs at a point immediately adjacent to the waste pits or at a location determined by an RME scenario to be of greatest risk to human and environmental receptors, as well as drinking water RAOs in the aquifer which might be encountered directly below Operable Unit 1.

RAOs are developed based on chemical-specific and radionuclide-specific criteria. The media for which RAOs will be developed include: air, soils, sediments and surface water, groundwater, and pit waste.

Overview

As described in Section 1.0, several technologies were chosen for investigation in the treatability studies. The following sections provide a synopsis of the Operable Unit 1 Treatability Study Work Plans developed for these investigations. These work plan excerpts describe the approach taken for

each treatability study. Additional detail on the studies' approach may be found in the referenced Work Plans.

Studies on vitrification were performed under three separate work plans. Remedy Screening/Remedy Selection studies were performed by IT Corp. under the Treatability Study Work Plan for Operable Unit 1, Oct. 1990. Remedy design studies were and are being performed by GTS Duratek/Catholic University of America under the Remedy Design Laboratory Studies, Part I: Vitrification Work Plan, and the Minimum Additive Waste Stabilization (MAWS) Work Plan. The CERCLA guidance for conducting treatability studies makes provisions for emerging or new technologies which have a greater risk associated with implementability. For these technologies, additional studies and scale-up studies may be indicated pre-ROD to make a more detailed evaluation of cost, implementability, and effectiveness since historical data is not available to support their assessment. Vitrification at a large scale for low-level radioactive waste falls into this category and additional, more detailed treatability studies were initiated pre-ROD.

The initial Operable Unit 1 Treatability studies performed by IT Corp. were designed to support evaluation of on-site disposal. The cement stabilization portion of the studies was designed to create a dimensionally stable waste form capable of being disposed of in an on-site disposal vault and retrieved if necessary. Subsequent treatability studies on vitrification were also designed to support the on-site disposal alternative. While vitrification will produce a waste form which can potentially be disposed of on-site or bulk shipped for off-site disposal, other more potentially cost effective methods for off-site disposal needed to be evaluated.

The reassessment of the Leading Remedial Alternative for Operable Unit 1 when FERMCO became the ERMC for the site, necessitated a reassessment of treatability options late in 1992. This reassessment of off-site disposal as a potentially viable option for Operable Unit 1 wastes required additional treatability studies be performed to evaluate treatment methods aimed at creating a potentially bulk shippable waste form which would be capable of meeting Waste Acceptance Criteria at proposed off-site disposal sites.

The University of Cincinnati Cooperative Remedy Screening Program (CRSP) was developed in 1993 to address these needs and was designed to evaluate a wide variety of potential treatments. The primary goal of the study was to dry the waste to reduce moisture content and volume, agglomerate or solidify the waste to reduce dust, and package the waste for shipment without the need for expensive containers. Several technologies were included in this program for testing. These included drying by thermal methods at a variety of temperatures (rotary drying) preceded by mechanical dewatering to increase efficiency. Dependent on temperature and residence time, the material could be dried to various moisture contents, calcined, or clinkered. Also considered were agglomeration methods for the dried product to mitigate dust and handling problems. The particle size of the majority of the waste pit material is very fine (50-70 percent < 200 mesh) which could create a dusting and exposure hazard when dried. Methods under consideration are creation of a low strength cement or cement soil-like product, pelletizing using water or other binders, and polyethylene encapsulation.

Details of the experimental approach for these studies are provided in the following sections. No experimental data were available to date on low-strength cement. Conclusions and recommendations for this option will be extrapolated from the high strength cement stabilization work performed by IT Corp.

To facilitate evaluation of the different treatment technologies, Section 3.0 is grouped by technology and is organized as follows:

Section 3.1 - Vitrification

- Section 3.1.1 - Vitrification Remedy Screening/Remedy Selection Studies;

  Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1

- Section 3.1.2 - Vitrification Remedy Design - Laboratory Scale;

  Work Plan - GTS Duratek/CUA, Nov. 1992, Remedy Design Laboratory Studies, Part I: Vitrification

- Section 3.1.3 - Vitrification Remedy Design - Bench Scale (MAWS);

  Work Plan - R.M. Parsons, Nov. 1992, OU1 Minimum Additive Waste Stabilization Remedial Design Bench-Scale Treatability Study Work Plan

Section 3.2 - Cement Solidification/Stabilization (CSS)

- Section 3.2.1 - CSS Remedy Screening/Remedy Selection Studies;

  Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1

- Section 3.2.2 - Long Term Durability of S/S Hazardous Waste Forms;

  Work Plan - University of Cincinnati, Jan. 1993, Long-Term Durability Testing (Waste form testing)

Section 3.3 - Thermal Treatment & Particle Agglomeration

  Work Plan - University of Cincinnati, Nov. 1993, CRU1 CRSP Work Plan

Each section summarizes the listed work plan and includes the following:

- Test objectives and rationale
- Experimental design and procedures
- Sampling and analysis
- Deviations from the work plan which occurred during the course of performing the treatability study

3.1 VITRIFICATION

Vitrification treatability studies were preformed under three separate work plans and cover remedy screening/remedy selection (Section 3.1.1), laboratory remedy design (Section 3.1.2), and bench-scale remedy design (Section 3.1.3).

3.1.1 Vitrification Remedy Screening/Remedy Selection Studies

Vitrification and Cement Stabilization (Section 3.2) remedy screening/remedy selection treatability

studies were performed by IT Corporation per the EPA approved Treatability Study Work Plan For Operable Unit 1, dated October 10, 1991, by IT Corp..

3.1.1.1 Test Objectives and Rationale

The objective of the studies was to develop reagent formulations for vitrification of the waste materials by varying the ratios of waste to binder to minimize the amounts of binder required to produce an acceptable waste form. Glass formers and modifiers considered for vitrification were fly ash, soil, and sodium hydroxide. Acceptable formulations met TCLP leaching standards, formed a durable glass, and had a minimum volume increase.

The vitrification screening treatability study consisted of the following:

- Preliminary Phase for remedy screening
- Advanced Phase - Stages 1, 2, and Optional for detailed analysis of alternatives and remedy selection

The Preliminary Phase for vitrification was designed to take advantage of samples collected in 1989-1991. Composite samples were used in the remedy screening phase to minimize the total number of experiments, and minimize costs and the generation of laboratory waste. The first step of the vitrification screening was performed in a simple laboratory furnace to determine the glass-forming characteristics of the waste without the addition of vitrifying reagents. Following this test, glass-forming agents such as site fly ash (Operable Unit 2), site soil/sand, and modifiers such as sodium hydroxide were added separately to the waste and the mix vitrified to determine the best combination of waste and glass-forming/modifying agents. Where possible, these experiments were based on a statistically designed matrix to maximize the information gained in the fewest experiments. The general procedure of this work was an iterative process where the results the experimental matrices were used to determine the course of the next set of experiments.

The Advanced Phase applied the best formulations from the Preliminary Phase to strata samples. It was important to test the individual layers of the waste pits because much of the material was added in batch to the pits (i.e., truck loads) over an extended period of time, producing a very

heterogeneous mixture. The effect of waste material variability was tested in this stage.

Specific test objectives were established so the performance of vitrification reagent mixtures could be evaluated. These performance objectives were used to determine if a particular reagent mixture produced an acceptable waste form. The specific objectives of the treatability study were:

- To develop a database of vitrification reagents, and corresponding hazardous and radioactive materials leachability data for vitrified waste forms
- To determine vitrification reagents and relative quantities required to minimize leachable concentrations of radionuclides and HSL constituents from the final waste form
- To minimize the final volume of treated waste
- To estimate the volumes of treated waste generated by each process
- To provide leaching characteristics for use in fate and transport modeling
- To develop preliminary reagent mixtures for use in future treatability studies
- To develop process parameters, such as percent moisture in the raw waste for use in future treatability studies
- To provide chemical and radiological data as shown in Table 3-1
- To establish the proof of process and applicability of the selected stabilization technology
- To screen a large number of parameters and identify those critical to future bench-scale studies
- To provide data for evaluation of alternatives:

  - 4 -> Waste removal, treatment, and on-property disposal
  - 5 -> Waste removal, treatment, and off-site disposal
  - 6 -> Waste removal, treatment, on-property disposal, and cap
  - 7 -> Waste removal, treatment, on-property disposal, soil treatment, and cap

3.1.1.2 Experimental Design and Procedures

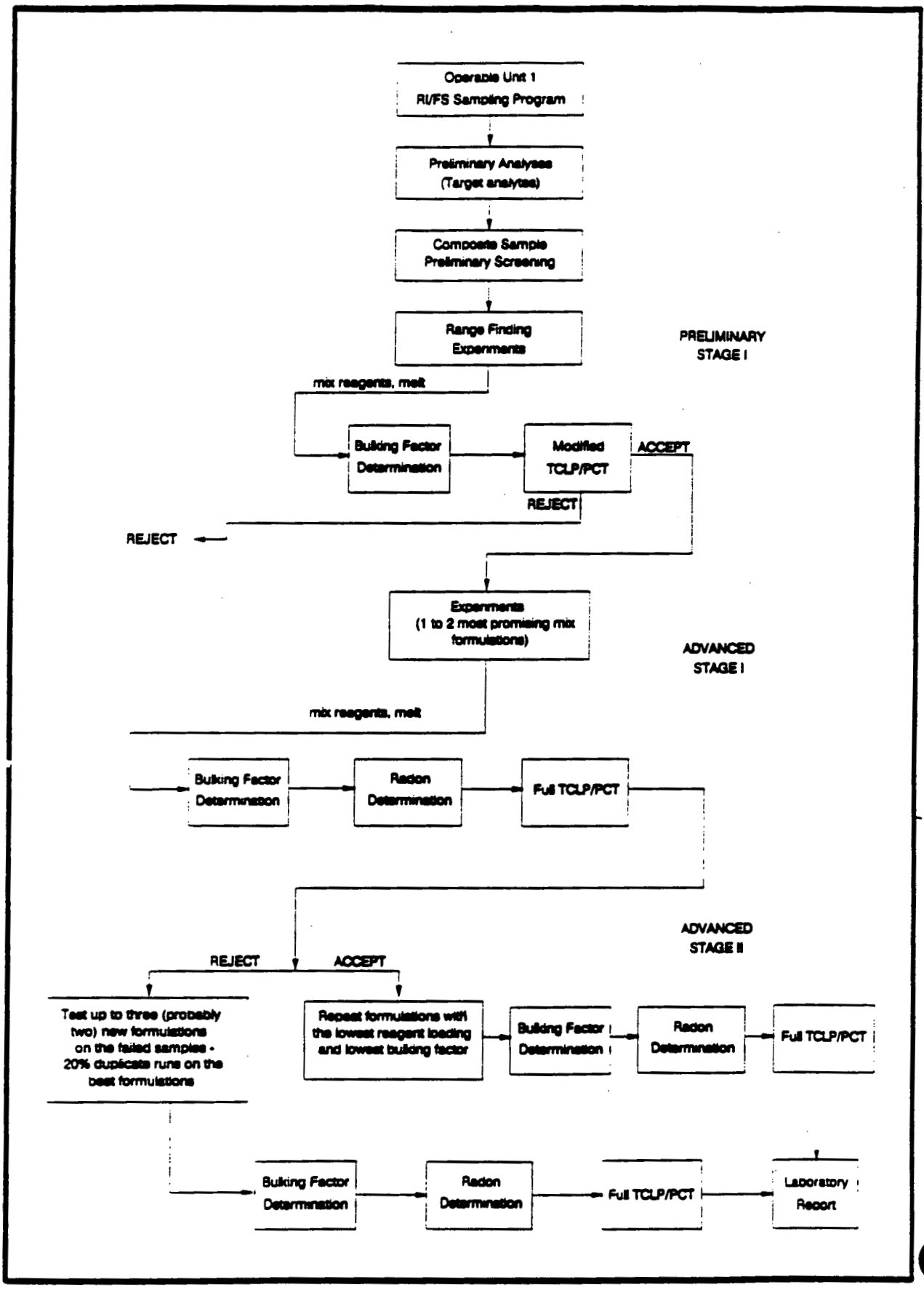
This Remedy Screening/Remedy Selection consisted of two phases: Preliminary Phase and Advanced Phase. The Advanced Phase was originally planned to be further broken down into Stage 1, Stage 2,

and an Optional Stage. Due to schedule constraints and an evaluation of data generated from the Advanced Phase - Stage 1, a decision was made that sufficient information had been developed to support Remedy Selection. Therefore, Advanced Phase - Stage II and the Optional Stage were not performed.

Approximately 48 experiments (8 composites samples x 6 experiments/sample) were planned in the Preliminary Phase, in addition to a series of initial range-findings experiments. The Advanced Phase applied the most promising mixtures from the Preliminary Phase to each of the samples. This determined if the successful formulations would work on the strata samples. These formulations were applied to each of 18 samples (1 strata composite each from Pits 1 through 4 and the Burn Pit x 3 strata per pit plus composite samples from Pits 5 and 6 and the Clearwell). See Figure 3-3 for the logic of the vitrification screening.

Preliminary Phase (Composite Samples)

During the Preliminary Phase, the effects of adding sodium hydroxide, site fly ash, and site soil were demonstrated. Except for tests on the raw waste, no experiments were conducted until chemical characterization of the soil and fly ash was completed. As a target, the reagent waste mixture was to have between 40 and 60 percent combined SiO_2 and Al_2O_3 content, and 10 to 20 percent sodium oxide content when dried. It was expected this range of SiO_2 and Al_2O_3 content would produce durable glass. The melting point of the glass mixture could be lowered by increasing the sodium oxide content of the glass. Sodium hydroxide could be added to the mixture before heating to increase the sodium oxide content of the vitrified waste. (Sodium hydroxide is converted to sodium oxide during the vitrification process.) Enough sodium hydroxide was added to cause the mixture to melt at 1250°C in a muffle furnace. This temperature was chosen to give a reasonable compromise between the cost of adding sodium oxide content to lower the melting point, the expected increase in leachability as the melting point of mixture is lowered, and the energy cost to melt and form the vitrified material. If this process is carried forward to the Remedy Design phase, the effect of metal temperature may be investigated.



VITRIFICATION LABORATORY SCREENING FLOWCHART

TABLE 3-1

CHEMICAL AND RADIOLOGICAL INFORMATION TO BE ACQUIRED
PRELIMINARY PHASE

Modified TCLP List for Vitrification		PCT[a] List for Vitrification	
Metals	**Radionuclides**	**Metals**	**Radionuclides**
Arsenic (As) Barium (Ba) Cadmium (Cd) Chromium (Cr) Lead (Pb) Selenium (Se) Silver (Ag)	Uranium by IC[b] Gross alpha Gross beta	Aluminum (Al) Boron (B) Iron (Fe) Potassium (K) Sodium (Na)	Uranium by IC[b] Gross alpha Gross beta
		General chemistry Chloride Nitrate Sulfate	
Physical parameters Bulking factor Temperature of oven Time of sample heating			

TABLE 3-1. (continued)

ADVANCED PHASE

TCLP Organic List[c]	Five-Day Static Leach Test, PCT, and TCLP Inorganic List			
	Metals		Radionuclides	General Chemistry
TCL[d] Volatiles TCL Semivolatiles TCL Pesticides/PCBs	Aluminum (Al) Antimony (Sb) Arsenic (As) Barium (Ba) Beryllium (Be) Boron (B) Calcium (Ca) Cadmium (Cd) Chromium (Cr) Cobalt (Co) Copper (Cu) Cyanide (CN) Lead (Pb)	Magnesium (Mg) Manganese (Mn) Mercury (Hg) Molybdenum (Mo) Potassium (K) Nickel (Ni) Selenium (Se) Silicon (Si) Silver (Ag) Sodium (Na) Thallium (Tl) Vanadium (V) Zinc (Zn)	Cs-137 Np-237 Pb-210 Pu-238 Pu-239/240 Ra-226 Ra-228 Sr-90 Tc-99 Th-total U-total Radon	alkalinity chloride reactivity fluoride ammonia nitrate pH phosphorus sulfate
Physical Parameters : Bulking factor Temperature of oven Time of sample heating				

[a]Product Consistency Test (see Appendix C for SOP).
[b]Ion chromatography.
[c]TCLP organics will not be analyzed if the compounds are not found in the characterization study portion of the work plan.
[d]Target Compound List (TCL).

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The raw waste was analyzed on a dry basis for the content of total aluminum as alumina, silicon as silica, and sodium as sodium oxide. Using the chemical analyses of the raw waste, fly ash, and soil as guides, a series of range-finding experiments was performed. Various amounts of sodium hydroxide was added to mixtures of waste, fly ash, and soil to determine the sodium hydroxide concentration needed to lower the melting point temperature to about 1250°C. After initial concentration ranges were determined, additional testing was performed. The ranges given in Table 3-2 changed after completion of the range-finding experiments and consideration of the chemical analysis of the soil and fly ash.

Sodium hydroxide was added at three levels: 0 percent, 10 percent, and 20 percent of the dry weight of the waste. Site fly ash and soil were added at 50 percent of the dry weight of the waste. Table 3-3 shows the analytical tests performed on the vitrified waste.

Advanced Phase - Stage 1 (Strata Samples)

The one or two most promising vitrification formulations encountered during the Preliminary Phase were applied to the top, middle, and bottom strata of each boring from Pits 1 through 4 and the Burn Pit, to determine the effect of varying waste composition. In addition, the one or two most promising formulations were also applied to composite samples from Pits 5, 6, and the Clearwell. The most promising formulations were those which met the leachability criteria, and minimized both the volume increase of the resultant waste and the cost of reagents.

For this stage, full TCLP, bulking factor, and PCT tests were run. Radon emissions were also determined (See Table 3-3).

Advanced Phase - Stage 2 (Strata Samples)

This phase of testing was not performed because sufficient data was generated during previous stages and in other treatability studies.

TABLE 3-2
VITRIFICATION EXPERIMENT MATRIX
PRELIMINARY PHASE (STAGE 1)

Run Number	Sodium Hydroxide[a] (w/w)%	Active Site Fly Ash[a] (w/w)%	Site Soil[a] (w/w)%
1	0	0	0
2	0	50	0
3	0	0	50
4	10	50	0
5	10	0	50
6	20	50	0
7	20	0	50

[a]Weight of reagent to dry weight of waste.

TABLE 3-3

ANALYTICAL TESTS - VITRIFICATION OF UNTREATED WASTE MATERIAL

	Preliminary Phase	Advanced Phase	
	Stage 1	Stage 1	Stage 2
Fly ash, soil, and waste characterization	X		
Bulking factor	X	X	X
MTCLP - metals	X		
MTCLP - gross alpha - beta	X		
MTCLP - U by IC	X		
TCLP - organic		X	X
TCLP - metals		X	X
TCLP - radionuclide		X	X
TCLP - general chemistry		X	X
PCT - metals	X	X	X
PCT - radionuclide		X	X
PCT - general chemistry		X	X
PCT - gross alpha - beta	X		
PCT - U by IC	X		
Radon emanation		X	X

Procedures

The appendices and detailed procedures used can be found in the Treatability Study Work Plan for Operable Unit 1, dated October 10, 1991 by IT Corp.. The following represents a listing of the procedures found in that work plan:

Appendix B Procedures

- Laboratory Notebook Recording Procedure
- Analytical Logbook Recording Procedure
- Standard Laboratory Sieves: Specification, Calibration, and Maintenance
- Bulking Factor Measurement for Pourable Sludge
- Calibration of Thermometers
- Unconfined Compressive Strength

Appendix C Procedures

- Nuclear Waste Glass Product Consistency Test - Version 3.0 (U)
- Bulking Factor Procedure for Nonsludge Type Waste
- 5-Day Static Leach Test Procedure
- Modified TCLP Leach Test Procedure
- Waste and Reagent Mixing Procedure
- Stabilization Waste Form Temperature Rise Generic Procedure
- Permeability
- Generic pH and Eh Procedure
- Proposed Radon Emissions from Stabilized Solids
- Shear Strength
- Vitrification of Waste
- Generic Uranium by Ion Chromatography with Post-Column Reactions and Phosphorescence or Fluorescence Detection

Data Required

The following data was recorded during the vitrification screening:

- MTCLP (for preliminary phase), or TCLP and PCT (for strata sample experiments) leach procedure
- Weights of reagents and waste in the final waste form
- Temperature of oven
- Time heating sample
- Bulking factor
- General description of the waste before and after melting
- Physical characteristic: percent moisture, bulk density
- Metal characterization (SiO_2, Al_2O_3, Na_2O) of the site soil, site fly ash, and successfully vitrified samples
- Radon emissions

3.1.1.3 Sampling and Analysis

Waste Stream

Two sampling and analysis programs for Operable Unit 1 were conducted to collect waste samples for RI/FS characterization and to provide material for treatability studies. The first sampling program consisted of borehole sampling of Pits 1 through 4 and the Burn Pit. The second consisted of composite samples from Pits 5, 6, and the Clearwell. Actual field sampling for Waste Pits 1 through 4 and the Burn Pit began in June 1991. Sampling for Waste Pits 5, 6, and the Clearwell took place in December 1991.

A total of 13 borings were taken from Waste Pits 1 through 4 and the Burn Pit under the first sampling program. The borings were sectioned into top, middle, and bottom zones which consisted

of three tubes collected at 1/3, 1/2, and 2/3 of the estimated depth of each pit (from which 39 strata samples were taken). These demarcations were used on the following estimated depths:

- Pit 1 - 20 feet
- Pit 2 - 22 feet
- Pit 3 - 27 feet
- Pit 4 - 24 feet
- Burn Pit - 13 feet

If a greater number of strata were observed, more samples were taken from the boring. A total of five composite samples were prepared, one each from Waste Pits 1 through 4 and the Burn Pit. The composites were collected based on details as described in the Sampling and Analysis Plan. These samples consisted of waste material from each identified stratum in the boring such that a representative sample was prepared. In the second sampling program (handled by WEMCO), composite samples were collected from Pits 5, 6, and the Clearwell. Composite samples were collected because of the consistency of the Pits 5, 6, and Clearwell material.

Treatment Process

Table 3-3 lists the analytical tests performed in each stage and phase of the treatability study. Table 3-1 lists the chemical and radiological data obtained.

3.1.1.4 Deviations

The following details the deviations from the work plan which occurred while conducting this treatability study.

DQO Levels

TCLP extraction data was not reported in a CLP format; therefore, it will not support an analytical level relative to DQOs of Level IV. Also, the full TCLP as defined in the work plan provides for full radiological analyses of the TCLP extract in addition to normal TCLP analyses. Therefore, it is a nonstandard method requiring a Level V designation. Spike recovery values used for vitrified waste were calculated based on data from site characterization as indicated in Sections 7.2 and 7.3 of the

work plan, respectively. This is a modification of the standard TCLP method requiring a Level V designation.

Spike Recovery

The work plan specified TCLP results be corrected for spike recovery. This had been a requirement of SW-846. The spike recovery correction requirement was retracted by the EPA in the November 24, 1992 Federal Register. Spikes and determination of percent recovery were performed; however, the results were not corrected for spike recovery.

Dilution Adjustment of Analytical Results

The work plan specified results be adjusted for dilution by reagents. The dilution adjustment factor is defined as the ratio of the mass of the treated material (including reagents) to the mass of the untreated material. For material treated by vitrification, this ratio is sometimes less than one, due to the loss of mass such as moisture and other volatiles. In cases where the dilution adjustment factor was less than one, no dilution adjustment was made to the results.

Formulations

Table 4-2 of the work plan lists seven formulations to be tested during the preliminary phase of vitrification. Two formulations without sodium were deleted because range-finding experiments showed sodium was needed to form a glass product.

3.1.2 Vitrification Remedy Design - Laboratory Scale

Vitrification remedy design laboratory scale treatability studies were performed by GTS Duratek and Catholic University of America (CUA) Vitreous State Lab (VSL) according to the Treatability Study Work Plan For Operable Unit 1 - Remedy Design Laboratory Studies - Vitrification, dated November, 1992, by GTS Duratek/Catholic University of America.

3.1.2.1 Test Objectives and Rationale

The scope of this treatability study was the laboratory scale remedy design and process development for the waste in Waste Pits 1 through 6, the Burn Pit, and the Clearwell. Specifically, this treatability work consisted of laboratory scale process studies for vitrification of Waste Pit 5. Waste pit 6 and Clearwell sludges were also analyzed for vitrification characteristics, but no process studies were performed. Characterization and process studies on the other waste pits will be performed subsequently and will be based on the results of this study. The work was performed in accordance with EPA's "Guide for Conducting Treatability Studies Under CERCLA" (EPA 1988) and the Fernald RI/FS Sitewide CERCLA Quality Assurance Project Plan (SCQ).

The data generated from the remedy screening and remedy selection studies (Section 3.1.1) was the basis for the remedy design vitrification work. Preliminary formulations and compositional ranges developed in these studies comprised the starting point for the test matrix in this program. These preliminary formulations were refined and a data base of process information was developed to support remedial design during the bench- and pilot-scale studies.

The objective of the remedy design tier of the treatability studies is to generate detailed scale-up, design, performance, and cost data to implement and optimize the selected remedy. They require moderate levels of QA and are vendor-specific. This study focused on optimizing process parameters which were not developed as a part of the remedy screening and remedy selection performed under the Treatability Study Work Plan for Operable Unit 1, October 1991, by IT Corp..

The data generated for this study by GTS Duratek/CUA VSL was of the following types:

- Physical and Chemical Characterization Data;
- Process Measurements (Rates, physical parameters such as temperatures);
- Product Characterization Data (such as viscosity, conductivity, leachate analysis).

The acquired data was intended to assess whether the immobilization of the hazardous/radioactive components in the vitrified waste form had been achieved and if the product was leach resistant while

remaining a good processable material. Both specialized (nonstandard), and nonspecialized procedures were followed.

3.1.2.2 Experimental Design and Procedures

The objective of this study was to develop process information for vitrification of Operable Unit 1 pit wastes and possibly use soils and fly ash as vitrification process additives. The study was intended to delineate the compositional range which meets the combined requirements of leach resistance and processibility. Samples from Pit 6 and the Clearwell were characterized for vitrification properties only. Vitrification crucible melts and mini-melter testing focused exclusively on Pit 5 sludge. The other pit wastes will be addressed in future work dependent on the outcome of this study. Flyash and FEMP site soils were investigated as sources of silica to permit vitrification of the pit sludges and thereby study the possibility of integrating the site waste streams synergistically to reduce the overall volume after treatment and reduce the amount of chemical additives required.

Activities in this task were directed toward the development of optimum compositions for vitrification of FEMP pit sludges by making full use of FEMP flyash and soils in the process to reduce the amounts of chemical additives needed and thereby the process costs. The characterization data obtained for the waste samples was used to select the blends used in the vitrification composition variability study. Chemical additives investigated included (as oxides) Na_2O, B_2O_3, and CaO.

A series of testing using crucible melts and minimelter runs were performed to select design and operating parameters. A flow-diagram illustrating the sequential steps in glass preparation and glass characterization is given in Figure 3-4.

Crucible Melts

The composition study was based on a minimum of 20 crucible melts of about 400 g each. Raw-mix recipe calculations for the feed were based on previous experience and glass composition-property correlations developed at VSL. The initial test matrix used is detailed in Table 3-4. The remaining melt formulations were determined after results of the initial 10 melts were analyzed. A further essential component was feed-back data from the glass characterization studies which was used to

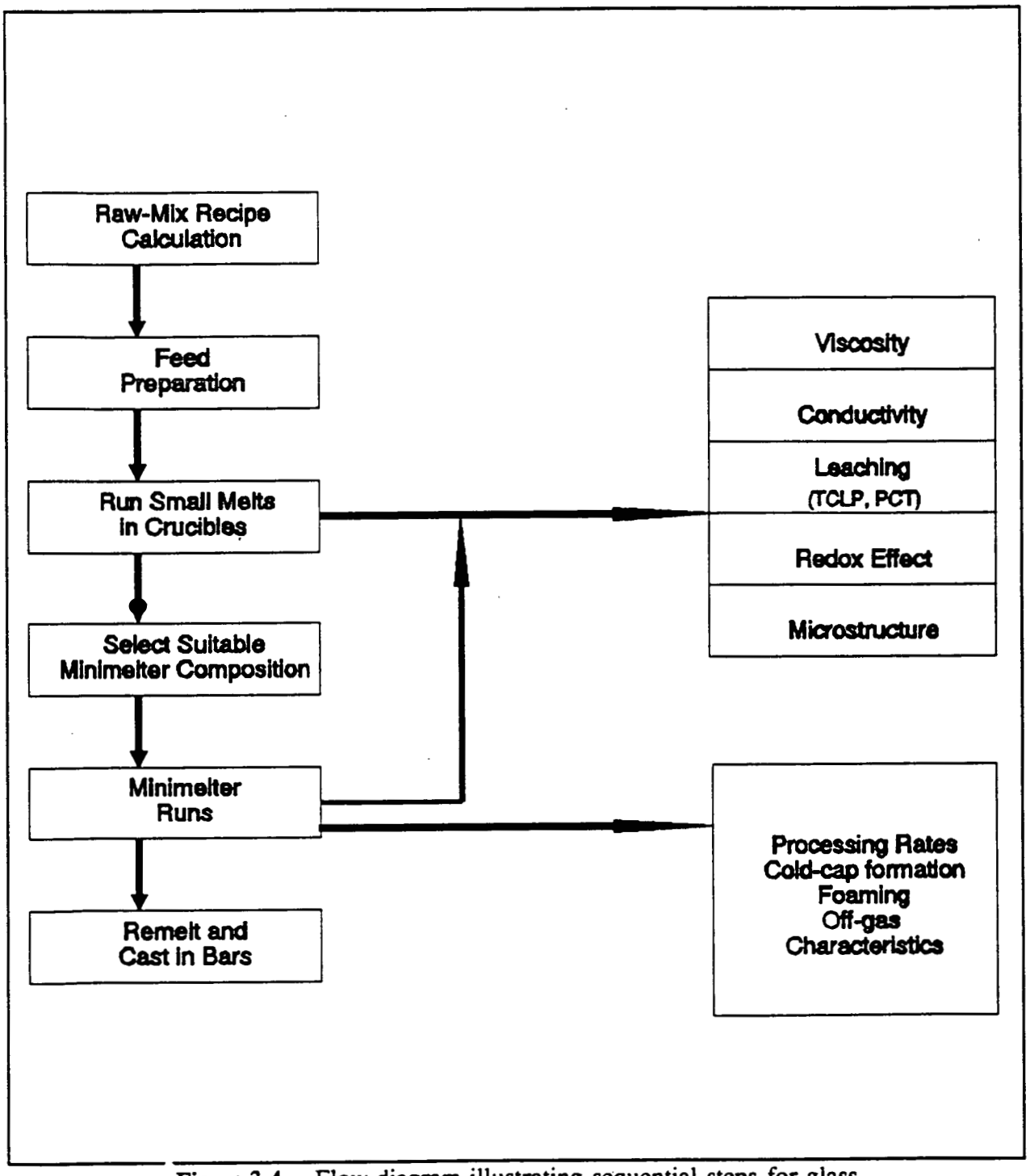


Figure 3-4 Flow diagram illustrating sequential steps for glass preparation and characterization.

TABLE 3-4
VITRIFICATION EXPERIMENT MATRIX PRELIMINARY FORMULATIONS

Melt Number	Pit 5 (W/W)%	Site Soil (W/W)%	Site Fly Ash (W/W)%	Na_2O* (W/W)%	B_2O_3** (W/W)%
1	40	40	0	10	10
2	50	40	0	5	5
3	60	40	0	0	0
4	70	30	0	0	0
5	80	20	0	0	0
6	40	30	10	10	10
7	40	20	20	10	10
8	50	20	20	10	0
9	50	40	0	10	0
10	60	30	0	10	0

Notes:

(1) All entries are dry weight percent of total batch.

(2) Na_2O and B_2O_3 will be added as the stoichiometrically equivalent quantities of Na_2CO_3 and either B_2O_3 or $Na_2B_4O_5(OH)_4 \times H_2O$ (Borax).

(3) Formulations may be revised as appropriate to reflect data from previous melts and waste characterization studies.

refine the glass composition study. These small melts were prepared in clay, platinum/gold, and Inconel crucibles at temperatures of between 1,100-1,250°C (typically around 1,150°C) depending on the observed melt behavior. The objectives of this study were twofold: (1) to provide a data base on the composition dependence of key process and product parameters to permit selection of the optimum feed composition under a variety of alternative assumptions, and (2) to permit an assessment of the tolerance of these parameters to variations in feed stream composition. The key process parameters included sludge loading, melt viscosity, electrical conductivity, development of secondary phases, and processing temperatures.

Some of the crucible melts were produced under reducing conditions to determine the effect of redox state on the glass materials as indicated. The redox state was determined by wet chemical analysis or Mossbauer spectroscopy using standard techniques used in the high-level waste vitrification program.

Minimelter

Two compositions were selected based on the collected process and leach data, waste loading, and additive requirements from the crucible melts and used for process demonstrations in a small-scale continuous joule-heated ceramic melter. Approximately 20 kg of glass were to be produced in each of these runs at temperatures of around 1150°C. These runs were used to collect data on processing parameters which could not be obtained from crucible melts alone. These runs provided data on processing rates, cold-cap formation, foaming, and off-gas characteristics. Processing rates were determined in terms of both kg/hr of feed material fed to the melter and kg/hr of glass produced. Cold-cap formation is the accumulation of unmelted feed on top of the glass pool which occurs at high feed rates and ultimately limits the maximum throughput achievable. Process parameter measurements taken included temperature readings, current and voltage readings, and feed rates and concentrations of significant species in the off-gas stream. Species in the off-gas included oxides of nitrogen (NOX), hydrofluoric acid (HF), oxides of sulfur (SOX), and volatile metals determined from the sample characterization data.

From the data collected, a range of optimal compositions was identified, and the requirements for additives such as glass formers or fluxing agents were determined. However, the composition

development program made full use of any suitable FEMP waste materials which would result in cost savings for the vitrification process. Throughout these efforts, maximum loading of the raffinate pit sludge per glass volume was considered a critical parameter.

3.1.2.3 Sampling and Analysis

Sampling

Two sampling and analysis programs for Operable Unit 1 were conducted to collect waste samples for RI/FS characterization and to provide material for treatability studies. The first sampling program consisted of borehole sampling of Pits 1 through 4 and the Burn Pit. The second consisted of composite samples from Pits 5, 6, and the Clearwell. Actual field sampling for Waste Pits 1 through 4 and the Burn Pit began in June 1991. Sampling for Waste Pits 5, 6, and the Clearwell took place in December 1991.

A total of 13 borings were taken from Waste Pits 1 through 4 and the Burn Pit under the first sampling program. The borings were sectioned into top, middle, and bottom zones which consisted of three tubes collected at 1/3, 1/2, and 2/3 of the estimated depth of each pit (from which 39 strata samples were taken). These demarcations were used on the following estimated depths:

- Pit 1 - 20 feet
- Pit 2 - 22 feet
- Pit 3 - 27 feet
- Pit 4 - 24 feet
- Burn Pit - 13 feet

If a greater number of strata were observed, more samples were taken from the boring. A total of five composite samples were prepared, one each from Waste Pits 1 through 4 and the Burn Pit. The composites were collected based on details as described in the Sampling and Analysis Plan. These samples consisted of waste material from each identified stratum in the boring such that a representative sample was prepared. In the second sampling program (handled by WEMCO), composite samples were collected from Pits 5, 6, and the Clearwell. Composite samples were collected because of the consistency of the Pits 5, 6, and Clearwell material.

Waste Stream

Both physical and chemical characterization of Pit 5 samples were performed in this study. These characterization studies provided the information necessary to develop the vitrification composition experimental matrix. Approximately 50 kg of each of 5 samples (Pit 5, Pit 6, Clearwell, site soil and site flyash) was delivered to GTS Duratek-VSL/CUA by FEMP. Table 3-5 lists characterization methods for raw waste from Pits 5, 6, and the Clearwell. Sample characterization included the following:

1. Density
   Sludge, soil, and flyash densities were determined by weighing a known volume of the sample and determining the weight/volume ratio following the ASTM D854 procedure. Tests were carried out on wet (as received) samples and oven-dried (110 $\pm$ 5°C for at least 12 hrs) samples following ASTM D854.

2. Particle Size Analysis
   The particle size distribution of each sample was determined by sieving the sludges, soils, and flyash according to ASTM procedure. The weight of each fraction was measured, and a maximum of 11 fractions were collected. Uranium contaminant distributions as a function of particle size were investigated for the major fractions.

3. Chemical Analysis
   The chemical composition of each sample was determined by a variety of techniques (Table 3-6). Each solid sample was first dissolved in a nitric acid/hydrofluoric acid solution using a microwave dissolution technique. Samples of the solution were then subjected to the following analyses:

   - Cations
     Major inorganic cations such as Na, K, Ca, Mg, Al, Si, and Fe were determined by DC plasma spectroscopy, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

   - Anions
     Major inorganic anions such as F^-, SO_4^-, and NO_3^- were determined by Dionex ion chromatography.

   - Radionuclides
     The isotopic radionuclide composition of the samples were measured using ICP-MS for long lived isotopes in combination with γ-counting spectroscopy.

TABLE 3-5 CHARACTERIZATION OF WASTE SAMPLES

Number of Samples	Matrix	Study/Method	Procedure	Objective/ Intended Use	ASL
5	Sludge; solid	Density (wet/as-received)	ASTM D854	Feed system development	B
5	Sludge; solid	Density (Dry)	ASTM D854	Feed system development	B
5	Sludge; solid	Particle Size Distribution	ASTM D4211 and D422	Feed system development	B
> 5	Solution	Chemical Composition (Inorganics)/DC-Plasma	VSL-SOP	To quantify components affecting glass/melt properties	E
> 5	Solution	Anions/Ion Chromatography	VSL-SOP	To quantify components affecting glass/melt properties	E
> 5	Solution	Radionuclides ICP-MS	VSL-SOP	To determine radionuclide constituents	E
> 5	Sludge; solid	Radionuclides/γ-Spectroscopy	VSL-SOP	To determine radionuclide constituents	E
> 5	Solution	Total Organic Content/ TOC-Analyzer	VSL-SOP	Impact of organics on glass redox	E
5	Sludge; solid	Thermogravimetric Analysis	VSL-SOP	To determine weight loss vs. temperature	E

Table 3-6
Requirements for Chemical Analysis of OU1 Wastes

Analysis	Level*	Method	Required Precision
CATIONS			
Major (Ca, Mg, Na, Si, etc)	≥ 0.5 wt%	DCP/ICP-MS	± 10%
Minor	0.01-0.5 wt% (100-5000 ppm)	DCP/ICP-MS	± 20%
ANIONS			
Major	≥ 0.5 wt%	IC	± 10%
Minor	0.01-0.5 wt% (100-5000 ppm)	IC	± 20%
RADIONUCLIDES			
	≥ 1 ppb	ICP-MS γ-Spectroscopy	± 20%
TOTAL ORGANICS			
	≥ 100 ppm	TOC analysis	± 20%

* Calculated on a dry basis

- Organics
  The presence of organics in the samples were checked by carrying out a total organic carbon (TOC) measurement on each sample using a total organic carbon analyzer.

Treatment Process

Treatment process parameters and waste form effectiveness were evaluated. Process parameters included sludge loading, processing rate, melt viscosity, electrical conductivity, development of secondary phases, and processing temperatures. Key product parameters included durability, in terms of both EPA Toxicity Characteristic Leaching Procedure (TCLP) and Product Consistency Test (PCT), modified Materials Characterization Center Test (MCC-3 Test), microstructure, and overall volume reduction. Results of the PCT and TCLP leach tests were used to evaluate the long-term effectiveness of each waste form. Table 3-7 details

methods used to analyze glass from crucible melts and mini-melter runs using Pit 5 sludge. Table 3-8 details process measurements made during crucible melts and mini-melter runs. Leachate analysis was carried out for glass chemical durability testing as outlined in Table 3-9.

1. EPA TCLP Test
   The TCLP was performed on glasses produced which indicated good process characteristics. This is a one-day procedure at room temperature (22$\pm$ 3^{0}C) and a relatively small ratio of glass surface area to leachate volume.

2. PCT
   The Savannah River Product Consistency Test (PCT) is the present standard test for high-level waste glasses. This test is significantly more aggressive than TCLP and is run for a nominal duration of 7 days. PCT tests on FEMP glasses were performed at room temperature (22$\pm$ 3^{0}C) and were sampled at 7, 28, 56, and 180 days to acquire data on the long-term durability of these glasses.

   At least two of the most promising glasses were also subjected to PCT testing at 90°C to make full contact with the substantial data base on high-level waste glass performance. Experience with Weldon Spring glasses has shown they compare very favorably with high-level waste glasses, even under these severe conditions.

TABLE 3-7 CHARACTERIZATION OF VITRIFIED PRODUCTS

Number of Samples	Matrix	Study/Method	Procedure	Objective/ Intended Use	ASL
> 5	Solution (dissolve d glass)	Chemical composition/ DCP, ICPMS, IC	VSL-SOP	To confirm chemical composition	E
≥ 20	Glass	Temperature/ thermocouples	VSL-SOP	To obtain measure of leachability	E
≥ 20	Glass	Leach resistance/TC LP	EPA-TCLP	To obtain measure of leachability	B
≥ 20	Glass	Crystal content SEM-EDX	VSL-SOP	To determine extent and type of devitrificat ion	E
≥ 20	Glass melt	Viscosity/rot ating spindle	VSL-SOP	To determine melt viscosity vs. temperature	E
≥ 20	Glass melt	Electrical conductivity/ AC bridge	VSL-SOP	To determine melt conductivity vs. temperature	E
≥ 3	Glass	Redox state/ Mossbauer spectroscopy	VSL-SOP	Effect of Redox State on glass properties	E

TABLE 3-8 LAB-SCALE PROCESS MEASUREMENTS

Number of Samples	Matrix	Study/Method	Procedure	Objective/ Intended Use	ASL
> 5	Feed slurry	Flow rate/metering pump	VSL-SOP	To determine feed rate to melter	B
≥ 20	Glass melt	Temperature/ thermocouples	VSL-SOP	To determine melt pool temperature in various locations	B
≥ 20	Glass melt	Current & voltage/ ammeters, voltmeters	VSL-SOP	To determine power input to glass melt	B
≥ 20	Glass	Glass output/balance	VSL-SOP	To determine glass production rates	B
≥ 5	Off-gas	Off-gas composition/ specific absorption tubes, sampling train-ICPMS; DCP	VSL-SOP	To determine concentratio ns of selected components in off-gas stream	E
≥ 5	Off-gas	Off-gas flow rate/flow meter; thermocouple	VSL-SOP	To determine flow rate for calculation of emission rates	B

Table 3-9 Leachate Analyses for Glass Chemical Durability Testing

Test	Analyte	Method	Required Detection Limits	Required Precision
TCLP	Ag, As, Ba, Cd, Cr, Hg, Pb, Se	DCP/ICP-MS	Per EPA-TCLP	± 10%
PCT (Standard)	B, Si, Na, Al, Ca, Cr, Fe, K, Li, Mg, Mn, Ni, P, Sr, Ti, U, Zr	DCP	1 ppm	± 10%
	Ph	Glass Electrode	0.5	± 0.1
PCT (Selected Samples)	^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, ^{226}Ra, ^{99}Tc	ICP-MS	1 ppb	± 20%
	Ag, As, Ba, Cd, Cr, Hg, Pb, Se	DCP/ICP-MS	1 ppm	± 10%

3. Melt Viscosity and Electrical Conductivity
These are both key processing parameters and were determined as functions of temperature up to 1300°C. Melt viscosity was measured using a Brookfield rotating spindle viscometer, and electrical conductivity was be measured as a function of frequency using a Hewlett Packard Signal Analyzer to permit extrapolation to zero frequency.

4. Microstructure
The homogeneity of the glasses was determined by microstructural analysis using Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDX) techniques. At least two of the most promising glasses were subjected to heat treatments before microstructural analysis to detect any secondary phases that might form over likely melter residence times and temperatures which might adversely affect processibility.

3.1.2.4 Deviations

The following details the deviations form the work plan which occurred while conducting this treatability study.

- This work plan was modified to include characterization, crucible melt studies on Pit 3 and 4 wastes. Work is currently under way and is scheduled for completion in February 1994. The same work plan and procedures are being used as for the Pit 5 studies.
- In some crucible melts for Pit 5, concentrated residues from the MAWS site soil washing project were substituted for site soils.
- Additional and alternate analytical methods were used for analysis of fluorides in the waste due to the inability to recover fluoride for analysis by standard methods.

3.1.3 Vitrification Remedy Design Bench Scale (MAWS)

This study was originated as an Operable Unit 1 treatability project and is currently ongoing. Responsibility for this project has been reassigned to OU4 to consolidate vitrification development for the FEMP. Only preliminary results and observations are included in section 4 in this report. A separate report on this project will be issued by OU4 at a later date.

Vitrification remedy design bench scale treatability studies are being performed per the Operable Unit 1 Minimum Additive Waste Stabilization (MAWS) Remedial Design Bench-Scale Treatability Study

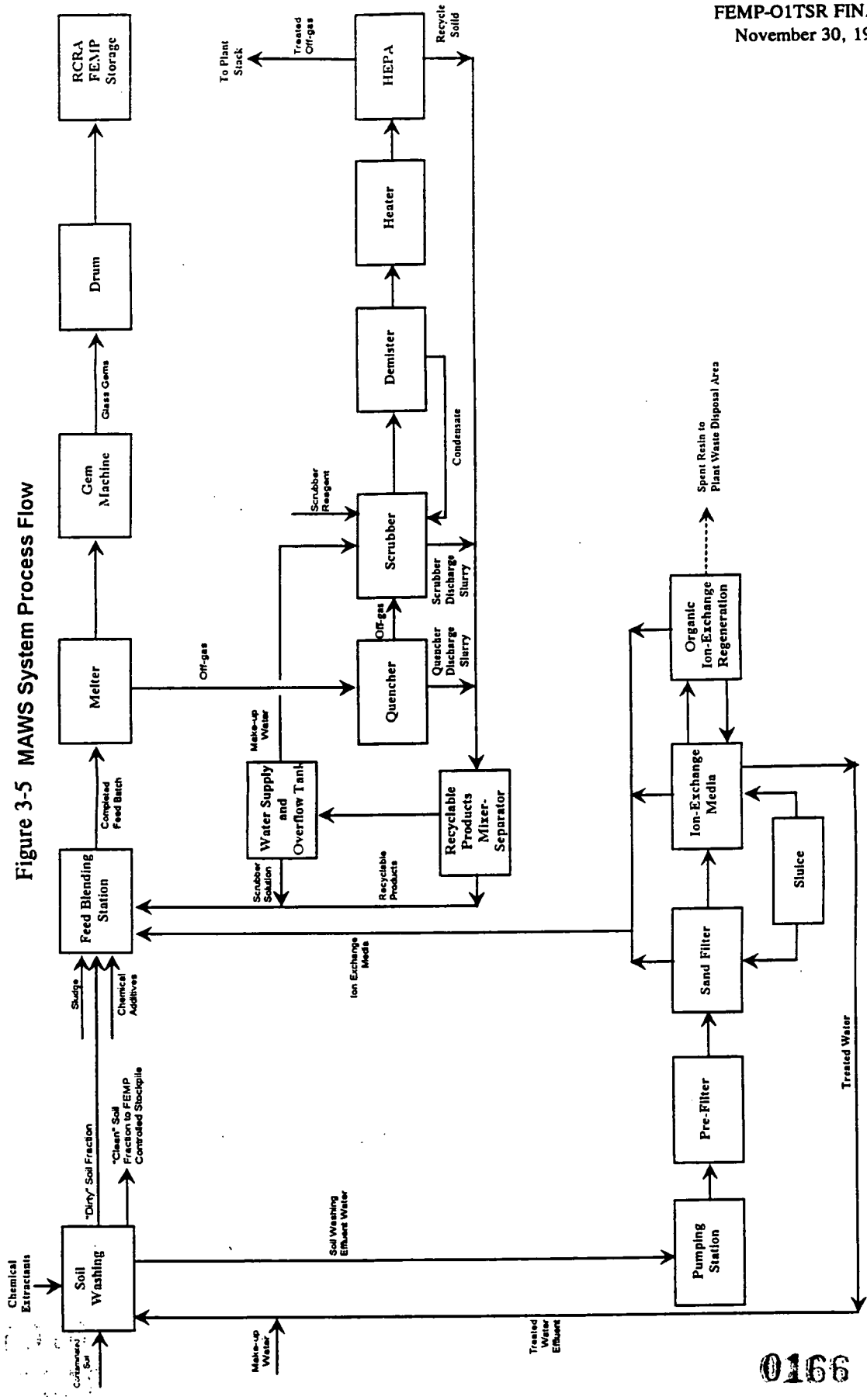
Work Plan (Volume I and II), dated March, 1993, by R. M. Parsons. The bench-scale treatability studies are being administered by Argonne National Laboratory through the DOE. GTS Duratek is the contractor responsible for vitrification, water treatment, and soil washing. Catholic University of America (CUA) Vitreous State Lab (VSL) and Lockheed Environmental Systems (Lockheed Analytical Laboratory [LAL]) are subcontractors to GTS Duratek.

Remedial design studies are being initiated prior to the Record of Decision (ROD) to ensure the remedial design may proceed without delay after issuance of the ROD should vitrification be chosen as the remedial alternative.

The MAWS is an extension of the Operable Unit 1 remedy design laboratory study and will determine if glass can be produced on a remedial scale. The MAWS technology demonstration program is an integrated waste treatment system where vitrification is the core technology used for stabilization of waste sludges and other contaminated material. The process includes the integration of multiple technologies required to blend multiple waste streams to minimize the need for chemical additives. Integrating multiple waste streams with the optimal mix of process technologies will: 1) Maximize volume reduction, 2) Minimize the requirements for additives otherwise necessary for vitrification, and 3) Greatly enhance overall waste treatment economics.

Figure 3-5 shows the process flow of the integrated MAWS system. The MAWS system utilizes soil washing to reduce the contaminated soil volume by producing a large fraction of treated "clean" soil. The treated "clean" soil will be returned to the site for disposition and the concentrated contaminated (e.g., "dirty") soil fraction will be one of the major components of the glass feed. Contaminated wastewater from the soil washing process is treated using ion exchange techniques and recycled to the soil washing system. Spent ion exchange media may be regenerated or used as a feed material to the vitrifier. The planned MAWS vitrification feed consists of the "dirty" soil fraction, contaminated raffinate sludge, and a minimum of other additives. The vitrification process produces a stabilized glass waste form, such as gems or marbles, which can be easily stored, and has a high waste loading and packing density. Particulate matter and liquids exhausted from the vitrifier are collected in an off-gas treatment system and recycled into the vitrification feed.

Figure 3-5 MAWS System Process Flow



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From a vitrification perspective, waste streams can be broadly classified on a spectrum of silica-rich to flux-rich, these extremes having opposite effects on melt temperature and viscosity. The total mix is expected to be dominated by the silica-rich components due mainly to the very large volume of uranium-contaminated soils at the FEMP. A simple but volume-enlarging correction is to buy soda ash or some other suitable flux and introduce it as an additive. A potentially more cost-effective solution is the integration of multiple technologies and the blending of waste streams demonstrated in the MAWS program.

The bench-scale treatability unit was installed in Plant 9 at the FEMP and will be operated to obtain test information. The bench-scale unit consists of a 0.25 cubic yard per hour (cy/hr) soil washing unit, a 300 kilogram per day (kg/day) vitrification unit, and a 100 gallon per minute (gpm) wastewater treatment system. Air emissions and wastewater generated from the MAWS operations are treated to comply with environmental discharge requirements.

MAWS will be based on support studies ongoing at LAL, Las Vegas, Nevada, and the VSL at CUA in Washington, D.C. Off-site studies at LAL include physical and chemical soil washing tests to provide operating parameters for the bench-scale study. Support studies at VSL include 500 gram crucible melts and 100 kg/day melts. Studies at VSL will determine critical large-scale process control and operational data for the 300 kg/day bench-scale vitrification unit at the FEMP.

3.1.3.1 Vitrification Development Support Studies

Vitrification development support studies were performed at the Catholic University of America Vitreous State Laboratory (CUA VSL). Soil wash concentrates (i.e., the "dirty" fraction) from the LAL support studies were shipped to VSL for use in vitrification laboratory studies and involved blending them with Pit 5 wastes. The vitrification study was conducted in overlapping layers of increasingly large glass production rates. Data from ongoing OU-1 vitrification treatability studies will be used along with other relevant information to direct a composition variability study using crucible melts (about 500 g each). Suitable compositions were tested on a 10 kg/day vitrification system and then progressed to a 100 kg/day system testing. Data from these tests was used to finalize

the design of the 300 kg/day system to be installed at the FEMP. Major composition changes or other operating parameter changes will first be tested through the three laboratory scales before passing to on-site testing. This step approach is more efficient both in testing time and costs since both of these factors increase with the scale of the test.

The following sections provide a summary of the vitrification support studies.

Chemical Characterization of Soil Fines

Soil was separated into three fractions -- coarse, middle, and fine. Soil from the middle fraction was fed to the melter by gravimetric means. Coarse and fine fractions was leached, and the leachate will be sent to the water treatment.

Vitrification Crucible Tests

A glass composition variability study was designed for combinations of soil-wash concentrates, Operable Unit 1 sludges, and media from the water treatment system loaded with concentrated radioactive waste, with and without addition of chemical additives. At least twenty crucible melts, of about 500 grams each, were prepared on this basis, and all of the glasses were characterized. Approximately ten glasses were made from combinations of soil-wash fines and Operable Unit 1 sludges, four from spent ion exchange media and Operable Unit 1 sludges, five from all three waste streams, and one with OU-1 sludge and purchased sand. The Operable Unit 1 sludge and sand mix were used as a basis to judge the other glass mixes.

Joule-Heated Melter Tests - 10 kg/day

Based on the results of the glass composition variability study using crucible melts, a series of feed compositions was selected for the 10 kg/day joule-heated melter tests. Six such tests were conducted in order to acquire detailed process data including throughput rates, cold cap formation, foaming events, and off-gas characterization. At least one test was carried out with a surrogate, non-radioactive feed.

Joule-Heated Melter Tests - 100 kg/day

A melter capable of producing approximately 100 kg/day of vitrified waste was installed at VSL. A total of four runs were performed on the 100 kg/day melter. The first two runs used non-radioactive, surrogate feeds for initial system tests. The second two runs will involve actual FEMP waste materials. These runs provided critical large-scale process data necessary in the development of process controls and operating protocols for the 300 kg/day unit installed at the FEMP. Process data included throughput rates, cold cap formation, and foaming events, as well as off-gas system performance evaluation. These data, collected on a series of units, will provide the basis for scale up to the larger pilot-scale and full-scale units if this approach proves to be optimal for the FEMP.

Laboratory vitrification activities were directed toward the development of optimum compositions for vitrification of sludge/soil concentrate blends and definition of the operational process parameters. The characterization data obtained for the waste samples was used to select blends and calculate raw-mix formulations. Previous experience and glass composition-property correlations developed were utilized while preparing these formulations. A further essential components is feed-back data from the glass characterization studies which was used to refine the glass composition studies.

A flow diagram illustrating the sequential steps in glass preparation and glass characterization is shown in Figure 3-6. As described previously, the MAWS program involves a stepwise scale up of melter systems culminating in the 300 kg/day on-site unit. However, the general approach is as illustrated in Figure 3-6.

3.1.3.2 Vitrification Data

The composition range studied will be selected on the basis of maximizing the Waste Pit 5 sludge loading while using soil washing concentrates and other additives, as necessary. The data will be analyzed using semi-empirical correlation schemes employed previously for vitrification process development. These correlations will utilize multi-variate linear and non-linear least squares fitting techniques and statistical propagation of error methods. Waste form leachability data from PCT and TCLP tests will be similarly correlated to glass composition. Together, these correlations will define a multidimensional composition space or operating region which satisfies a given set of constraints.

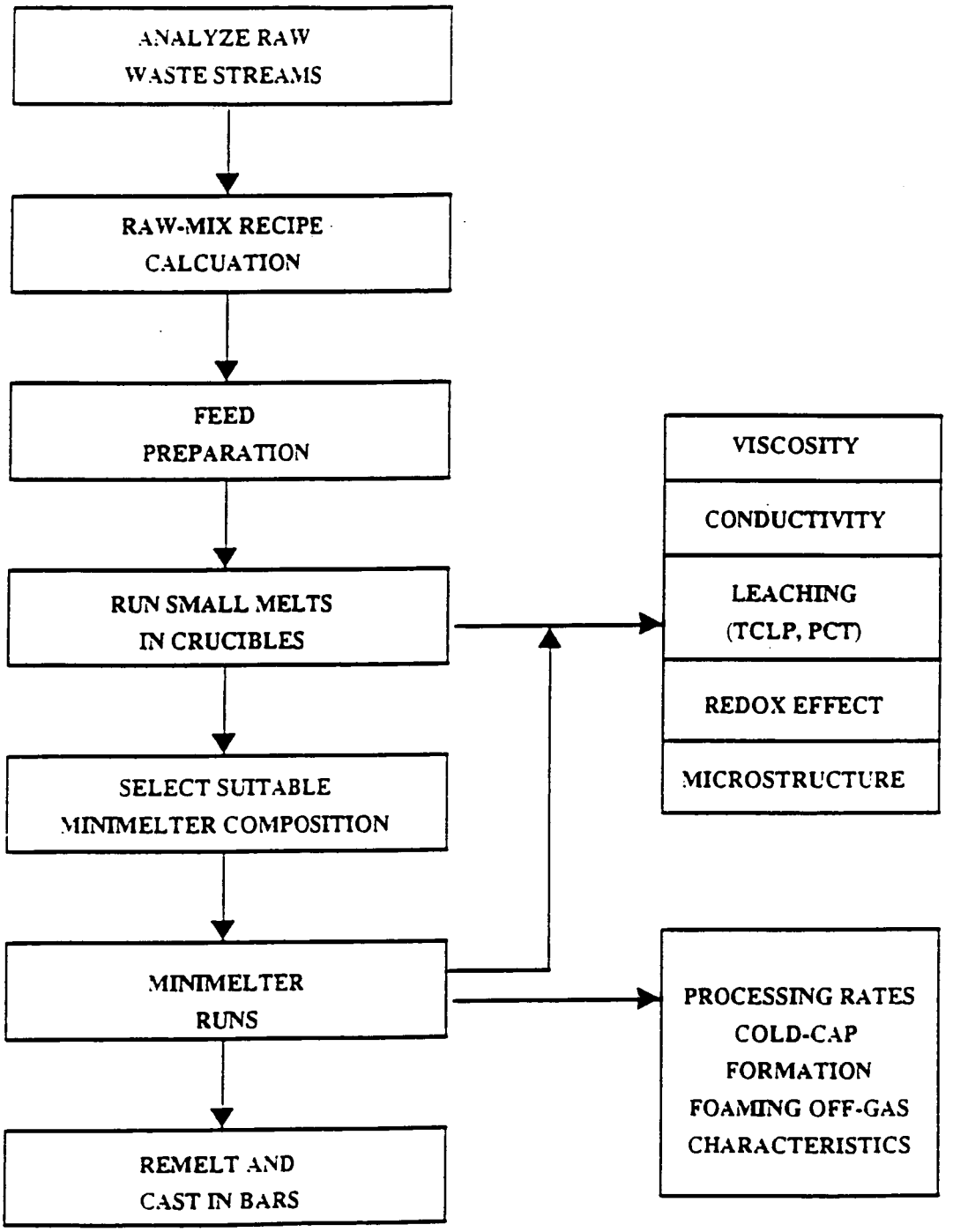

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Figure 3-6 Glass Preparation and Characterization Steps

A typical set of constraints might be:

- Pass TCLP
- Pass PCT requirements for high-level waste glasses
- Melt viscosity between 10 and 50 Poise at 1150 degrees C
- Electrical conductivity between 0.05 and 0.5 S/cm at 1150 degrees C
- Liquidous temperature below 1000 degrees C
- Sludge loading above 30 percent weight on a dry basis

Many of these constraints are imposed by the process, and until extensive process testing has been conducted (at increasingly realistic scales), these constraints are at best only estimates. There are frequently trade-offs between these constraints which may have significant impacts on treatment costs. For example, if process testing shows a viscosity as low as 5 Poise is acceptable, this may mean a higher sludge loading can be achieved, which translates into increased volume reduction and reduced treatment costs since Waste Pit 5 sludge tends to reduce the melt viscosity.

A major objective of data collection, analysis, and interpretation is to understand the critical interaction between the constraints imposed by the glass chemistry on the relationship between glass properties and glass composition, and the constraints imposed by the process itself. The composition region over which these sets of constraints are mutually satisfied is the optimal operating region sought in this study. In addition, the results of the PCT and TCLP leach tests will be used to evaluate the potential long-term effectiveness of waste form samples produced.

Process feasibility evaluations will be performed on each technology individually, as well as on the integrated system. A key objective of the MAWS Treatability Study is to determine the most appropriate set of system parameters to optimize the performance of the integrated system. This objective will be accomplished by evaluating the capability and performance of each individual technology. Optimum performance of a system involving multiple and interactive steps is generally not obtained by optimizing each step individually. Furthermore, performance is composed of a

variety of factors including final waste form leach resistance, overall volume reduction, operational range, system throughput rates, and life-cycle cost.

Technical feasibility evaluations will be made to determine the most appropriate set of system parameters for each technology in the integrated process. An assessment will be made to determine if a leaching step is required to achieve the required soil volume reduction and to ensure the optimum contribution of the soil washing process to the integrated system. Vitrification will be tested with respect to glass composition, processability, and durability. The optimum composition for the vitrification feed will be determined by incorporating experimental data from this project into earlier models of glass composition. This composition will be designed to achieve the use of minimum feed additives with maximum waste material, while still providing the required properties of processability and durability. The technical feasibility of regenerating the ion exchange resin in the wastewater treatment system will also be determined in these studies. In addition, the process will be designed to match the wastewater treatment process to the water requirements for the soil washing system.

3.2 CEMENT SOLIDIFICATION/STABILIZATION (CSS)

Two treatability studies were performed for CSS and cover remedy screening/remedy selection (Section 3.2.1) and long-term durability of S/S Hazardous Waste Forms (Section 3.2.2).

3.2.1 CSS Remedy Screening/Remedy Selection Studies

CSS and Vitrification (Section 3.1.1) remedy screening/remedy selection treatability studies were performed by International Technologies (IT) Corporation per the Treatability Study Work Plan for Operable Unit 1 dated October 10, 1991, by IT Corp..

3.2.1.1 Test Objectives and Rationale

Reagent formulations for cement stabilization of the waste material were determined by varying the ratios of waste to binder in order to minimize the amounts of binder required to produce an acceptable stabilized waste form. The objectives of the treatability study were to identify formulations which have a UCS of approximately 500 psi, decrease leachability of metals and radionuclides as measured with toxicity characteristic leaching procedure (TCLP) and modified TCLP (MTCLP) near

the TCLP standards, and a relatively low bulking factor. The third criteria was a secondary requirement. Binding agents considered uncluded portland cement, fly ash, and sodium silicate. Clay (attapulgite and clinoptilolite) was added to reduce the leachability of metals in the waste.

The cement stabilization treatability study consists of the following:

- Preliminary Phase - Stages 1 and 2 for remedy screening
- Advanced Phase - Stages 1, 2, and Optional for detailed analysis of alternatives and remedy selection

The preliminary phase corresponds to remedy screening. The advanced phase or strata sample experiments, which correspond to the remedy selection testing, provided sufficient data to support the detailed analysis of alternatives. This treatability study does not provide enough data for remedy design.

The Preliminary Phase - Stage 1 for cement stabilization was designed to take advantage of samples collected in 1989-1991. These tests were designed to range-find the reagent levels necessary to meet the UCS requirement of approximately 500 psi. The MTCLP test was added to this stage to augment the UCS results, thus providing additional information on the fixation as well as the solidification of the waste matrices. Composite samples were used in the remedy screening phase to minimize the total number of experiments, and minimize costs and the generation of laboratory waste. The most promising formulations from this stage had metal concentrations in the MTCLP near or less than the TCLP standards, a relatively low bulking factor, and UCS values of approximately 500 psi or greater. The 500 psi value is a recommended value for low-level waste set forth by NRC in "Technical Position on Waste Form" (Revision 1), Low-Level Waste Management Branch Division of Low-Level Waste Management and Decommissioning,(January 1991). Where possible, these experiments were based on a statistically designed matrix to maximize the information gained in the fewest experiments.

The Preliminary Phase - Stage 2 screening was utilized to test additional reagent mixtures in the event the Preliminary Phase - Stage 1 mixtures were unsuccessful, or to refine the formulation of those successful mixtures. This stage was designed to achieve a greater level of confidence in the data.

The most promising formulations from this stage had UCS values of approximately 500 psi, metal concentrations in the MTCLP at or below the TCLP standards, and a relatively low bulking factor.

The Advanced Phase applied the best formulations discovered in the previous stages to strata samples. It is important to test the individual layers of the waste pits because much of the material was added in batch to the pits (i.e., truck loads) over an extended period of time, producing a heterogeneous mixture. The effect of waste material variability was tested in this stage.

The composite and strata samples were treated with varying combinations of cement, sodium silicate, clay, zeolite, and fly ash from the active fly ash pile to determine the viability of the cement stabilization option. Portland Type I and II cements, PQ Corporation Type N sodium silicates, and Type F and site fly ash, attapulgite, clinoptilolite, and water were used in various combinations to determine the optimum overall mix. Blast furnace slag was added as an additional reagent for testing during the Preliminary Stage II experiments. Site fly ash from the active fly ash pile in Operable Unit 2 was used as an additional pozzolanic agent in the screening in an effort to determine its effectiveness in achieving an adequate stabilized waste form. This allows the stabilization of contaminated materials from two operable units in the same treatment system.

An iterative process was used in planning this evaluation, where the results from matrices of experiments were used to determine the course of the next set of experiments.

Specific test objectives were established so the performance of the various stabilization mixtures could be evaluated. These performance objectives were used to determine if a particular reagent mixture produces an acceptable waste form. The specific objectives of the treatability study were:

- To develop a database of stabilization reagents and corresponding hazardous and radioactive materials leachability for stabilized waste forms
- To determine the cement stabilization reagents and relative quantities required to minimize leachable concentrations of radionuclides and HSL constituents from the final waste form
- To determine the cement stabilization reagents and relative quantities required so that the final waste form achieves a UCS of approximately 500 psi

- To minimize the final volume of treated waste
- To estimate the volumes of treated waste that will be generated by each process
- To provide leaching characteristics for use in fate and transport modeling
- To develop preliminary reagent mixtures for future treatability studies
- To develop process parameters for use in future treatability studies - shear strength, waste form temperature rise with reagent addition, general description of waste before and after reagent addition, permeability of stabilized waste percent of water in the waste, pH of the leachate solutions, and evolution of gas during mixing or during the curing process
- To provide the chemical and radiological data as shown in Table 3-10
- To establish the proof of process and applicability of the selected stabilization technology
- To screen a large number of parameters and identify those that will be critical for future bench-scale studies
- To provide data for evaluation of alternatives:

  - 4 -> Waste removal, treatment, and on-property disposal
  - 5 -> Waste removal, treatment, and off-site disposal
  - 6 -> Waste removal, treatment, on-property disposal, and cap
  - 7 -> Waste removal, treatment, on-property disposal, soil treatment, and cap

A list of tests and associated DQOs for cement stabilization are listed in Table 3-11. In addition, the appendices containing descriptions of the procedures are listed. (The referenced appendices appear in the Treatability Study Work Plan for Operable Unit 1, dated October 10, 1991 by IT Corporation.) Standard Operating Procedures (SOPs) and nonstandard test methods are described in Appendices B and C, respectively. In Table 3-11, two appendices are listed for bulking factor. If the untreated waste is a slurry, the bulking factor was determined according to the SOP in Appendix B. If the untreated waste is a solid, the bulking factor was calculated using densities in accordance with Appendix C.

3.2.1.2 Experimental Design and Procedures

There are many unknown variables regarding the behavior and activity of the waste and the performance of the stabilizing reagents with the waste. From the available analytical data and process

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TABLE 3-10

CHEMICAL AND RADIOLOGICAL INFORMATION TO BE ACQUIRED PRELIMINARY PHASE

Modified TCLP List for Cement Stabilization	
Metals	**Radionuclides**
Arsenic (As) Barium (Ba) Cadmium (Cd) Chromium (Cr) Lead (Pb) Selenium (Se) Silver (Ag)	Uranium by IC[b] Gross alpha Gross beta
Physical parameters Bulking factor Temperature rise Unconfined compressive strength Shear strength	

Table 3-10 continued

ADVANCED PHASE

TCLP Organic List[c]	Five-Day Static Leach Test, PCT, and TCLP Inorganic List			
	Metals		Radionuclides	General Chemistry
TCL[d] Volatiles	Aluminum (Al)	Magnesium (Mg)	Cs-137	alkalinity
TCL Semivolatiles	Antimony (Sb)	Manganese (Mn)	Np-237	chloride
TCL Pesticides/PCBs	Arsenic (As)	Mercury (Hg)	Pb-210	reactivity
	Barium (Ba)	Molybdenum (Mo)	Pu-238	fluoride
	Beryllium (Be)	Potassium (K)	Pu-239/240	ammonia
	Boron (B)	Nickel (Ni)	Ra-226	nitrate
	Calcium (Ca)	Selenium (Se)	Ra-228	pH
	Cadmium (Cd)	Silicon (Si)	Sr-90	phosphorus
	Chromium (Cr)	Silver (Ag)	Tc-99	sulfate
	Cobalt (Co)	Sodium (Na)	Th-total	
	Copper (Cu)	Thallium (Tl)	U-total	
	Cyanide (CN)	Vanadium (V)	Radon	
	Lead (Pb)	Zinc (Zn)		
Physical Parameters :				
Bulking factor				
Temperature rise				
Shear Strength				
UCS				
Permeability				

[a]Product Consistency Test (see Appendix C for SOP).
[b]Ion chromatography.
[c]TCLP organics will not be analyzed if the compounds are not found in the characterization study portion of the work plan (Section 6.0).
[d]Target Compound List (TCL).

TABLE 3-11 SOLIDIFICATION DQO LEVELS

PRELIMINARY (REMEDY SCREENING)			
TEST	**APPENDIX**	**DQO/COMMENT**	**DQO LEVEL**
Bulking Factor	B or C	Minimize waste volume increase. To estimate the volume of waste that will be generated.	V
Modified Toxicity Characteristic Leaching Procedure (MTCLP)	C	During the screening phases, to determine the relative leachability of hazardous and radiological constituents associated with the various stabilization reagent formulations.	V
Waste Form Temperature Rise	C	Preliminary process parameters	I
Shear Strength	C	Preliminary process parameters	I
Unconfined Compressive Strength (UCS)	B	To determine the unconfined compressive strength associated with each of the reagent formulations	II
pH, Eh	C	Preliminary process parameter	I

Table 3-11 (Continued)

ADVANCED (REMEDY SELECTION)			
TEST	APPENDIX	DQO/COMMENT	DQO LEVEL
Bulking Factor	B or C	Minimize waste volume increase. To estimate the volume of waste that will be generated.	V
Unconfined Compressive Strength	B	To determine the unconfined compressive strength associated with each of the stabilization reagent formulations.	III
Full TCLP	See QAPP	To determine leachability of each of the stabilization reagent formulations. To provide data for the FS risk assessment calculations.	V
5-Day Static Leach Test	C	To provide data for the FS risk assessment calculations	V
Permeability	C	To provide data for the FS risk assessment calculations	III
Waste Form Temperature Rise	C	To provide preliminary process parameters	I
Shear Strength	C	To provide preliminary process parameters	I
Radon Emanation	C	To determine effect of stabilization on radon emanation	V
pH, Eh	C	Preliminary process parameter	I

history of the waste, the organic compound concentrations should be low. Inorganic inhibitors (e.g., Magnesium Fluoride$_2$ and inorganic or organic phosphate compounds) were expected to cause more problems than organic contaminants. Due to the anticipated problems resulting from the inorganic inhibitors and the potential organic constituents, a wide range of cement and fly ash concentrations was investigated.

This treatability study will consist of three distinct stages. The Preliminary Phase - Stage 1 was divided into two sets of experiments: the first will involved a statistically designed mixture experiment (Group I experiments in Table 3-12); the second involved five single variable experiments (Groups II through V experiments in Table 3-12). The statistically designed matrix was developed through a statistical analysis of the variable parameters and the practical ranges of these parameters. The stabilization matrix was based on the extreme vertices design for mixtures which have constraints on the values of each factor (McLean and Anderson 1966; Diamond 1981). Because was is a screening study, and to decrease the number of experiments, only the matrix vertices and center point of the complete matrix values was used. The single variable matrices, Group II, III, IV, and V experiments, are similar in structure to the Group I experiments but differ in that a single variable is changed for each experiment group. All of these experiments were conducted on composite samples. Up to 160 experiments (8 composite samples x 20 experiments/sample) were planned in the preliminary studies on the composite samples.

Mathematical models relating results from UCS, MTCLP, and bulking factor to reagent loading were generated from the data gathered during the Group I experiments of the Preliminary Phase. These models aided in the interpretation of data and in the formulation of reagent combinations for the additional testing phase of the screening. Stage 2 of the Preliminary Phase was planned to consist of 0 to 5 experiments depending on the success of the Preliminary Phase - Stage 1. This stage used new combinations of reagents if the preliminary phase was unsuccessful in producing adequate waste forms or if those successful experimental mixtures run in the Preliminary Phase - Stage 1 needed further refinement. The Preliminary Phase experiments were run on composite samples.

TABLE 3-12 CEMENT STABILIZATION EXPERIMENT MATRICES (STAGE 1)

GROUP I EXPERIMENTS-STATISTICALLY-BASED MATRIX						
Run Number	Waste (g)	Portland Cement Type II (g)	Fly Ash Type F (g)	Sodium Silicate Type N (g)	Attapulgite and Clinoptilolite Each (g)	Potential Range of Water Needed (g)
1	100	64	64	0	6	9 - 65
2	100	68	68	7	6	11 - 71
3	100	51	31	0	6	0 - 35
4	100	54	33	7	6	0 - 38
5	100	31	51	0	6	0 - 35
6	100	33	54	7	6	0 - 38
7	100	26	26	0	6	0 - 15
8	100	27	20	7	6	0 - 16
9	100	43	43	4	6	0 - 37
GROUP II EXPERIMENTS-SINGLE VARIABLE MATRIX, EFFECT OF SITE FLY ASH						
Run Number	Waste (g)	Portland Cement Type II (g)	Site Fly Ash (active) (g)	Sodium Silicate Type N (g)	Attapulgite and Clinoptilolite Each (g)	Potential Range of Water Needed
10	100	43	43	0	6	0 - 37
11	100	43	43	4	6	0 - 37
GROUP III EXPERIMENTS-SINGLE VARIABLE MATRIX, EFFECT OF ADSORBENT						
Run Number	Waste (g)	Portland Cement Type II (g)	Fly Ash Type F (g)	Sodium Silicate Type N (g)	Attapulgite or Clinoptilolite (g)	Potential Range of Water Needed (g)
12	100	43	43	4	12A	0 - 37
13	100	43	43	4	12C	0 - 37
14	100	26	26	0	0	11 - 71
15	100	64	64	0	0	11 - 71

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TABLE 3-12 (Continued)

GROUP IV EXPERIMENTS-SINGLE VARIABLE MATRIX, EFFECT OF CEMENT TYPE						
Run Number	Waste (g)	Portland Cement Type I (g)	Fly Ash Type F (g)	Sodium Silicate Type N (g)	Attapulgite and Clinoptilolite Each (g)	Potential Range of Water needed (g)
16	100	43	43	4	6	0 - 37
17	100	43	43	0	6	0 - 37
18	100	43	43	0	0	0 - 37
GROUP V EXPERIMENTS-CEMENT ONLY						
Run Number	Waste (g)	Portland Cement Type II (g)	Fly Ash Type F (g)	Sodium Silicate Type N (g)	Attapulgite and Clinoptilolite Each (g)	Potential Range of Water needed (g)
19	100	60	0	0	0	11 - 71
20	100	80	0	0	0	11 - 71

*12A and 12C: Add 12 grams of attapulgite and clinoptilolite, respectively.
Total number of experiments is 160. (160 experiments = 8 composite samples x 20 runs/sample.)

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The Advanced Phase applied the two most promising mixtures developed in the Preliminary Phase - Stages 1 and 2 to each of the 15 strata composite samples from Pits 1 through 4 and the Burn Pit, and 3 composite samples from Pits 5 and 6 and the Clearwell. This determined if the successful mixtures from the preliminary phase would work on the strata samples. See Figure 3-7 for the logic of the cement stabilization screening and Table 3-13 for the estimated number of experiments per phase and stage.

Preliminary Phase - Stage 1 (Composite Samples)

The Group I experiments treated each composite sample with a combination of portland Type-II cement, PQ Corporation Type N sodium silicate, Type F fly ash, clay and zeolite (attapulgite and/or clinoptilolite), and water according to the matrix shown in Table 3-12.

The Groups II, III, IV, and V experiments changed a single variable in the reagent mixture. The Group II experiments substituted site fly ash from the active fly ash pile (Operable Unit 2) for the commercial Type F fly ash. This allowed contaminated material from two operable units to be stabilized in the same treatment system. The Group III experiments modified the type and level of adsorbents which may affect the leachability of the heavy metals and radionuclides in the treated waste. In the Group IV experiments, portland Type I cement was substituted for Type II cement. This was done due to the cost difference between the two types of cement. In Group V experiments, portland Type II cement with water was the only additive.

For each of the test runs, the waste form temperature rise, bulking factor, shear strength, and general appearance was recorded. The waste form temperature rise and shear strength was measured within 10 minutes of when reagents and waste were mixed. These temperature measurements were relative values only because they were performed in an open, plastic container. The shear strength was measured with a Soiltest Torvane. The UCS, MTCLP, and bulking factor were measured on day 28. Twenty to thirty percent of the samples were expected to meet the UCS and leaching requirements. In addition, the following observations, measurements, or tests were performed: general description

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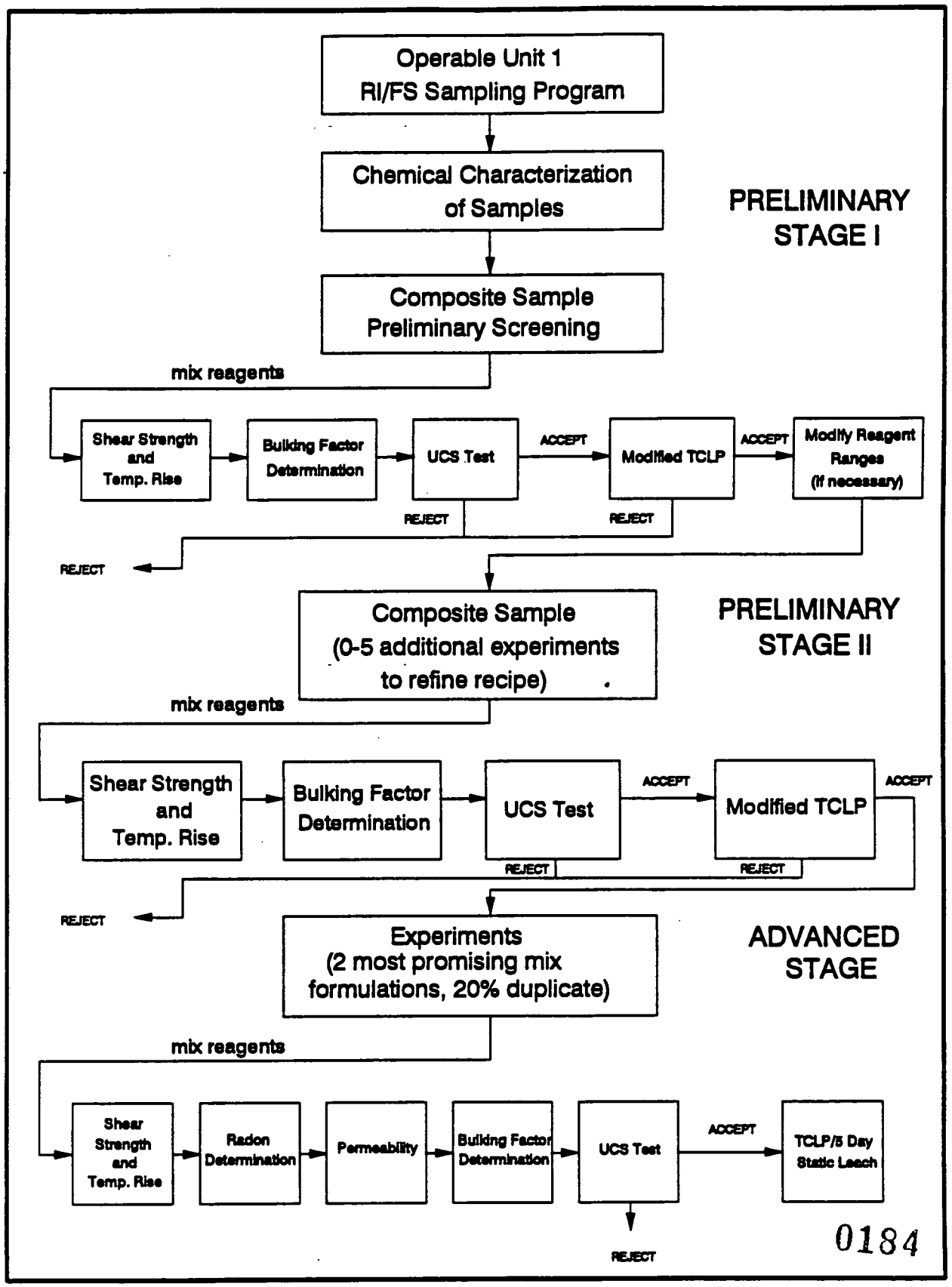

FL/FERMCO/OU1-TR ST/9-93/FIG 3-3

FIGURE 3-7 CEMENT STABILIZATION LABORATORY SCREENING FLOWCHART

TABLE 3-13 ESTIMATED NUMBER OF EXPERIMENTS BY PHASE
CEMENT STABILIZATION

	Remedy Screening (Preliminary Phase)		Remedy Selection (Advanced Phase)		
Waste Pit Number	Stage 1	Stage 2[a]	Stage 1	Stage 2[a]	Optional[b]
1	20	0 to 5	6	6 to 8	
2	20	0 to 5	6	6 to 8	
3	20	0 to 5	6	6 to 8	
4	20	0 to 5	6	6 to 8	
5	20	0 to 5	2	2 to 3	
6	20	0 to 5	2	2 to 3	
Burn Pit	20	0 to 5	6	6 to 8	
Clearwell	20	0 to 5	2	2 to 3	
Subtotal	160	0 to 40	36	36 to 49	
Duplicate	0	0	7	0 to 10	
Total	160	0 to 40	43	36 to 59	

[a]The total number of experiments in Stage 2 will depend on the results from the previous stage.

[b]The scope of the optional stage will be based on the results from the remedy selection Stages 1 and 2.

of the waste before and after reagent addition, percent water in waste, pH of stabilized waste analytical leachate solutions, and an indication if there is gas evolution during the mixing or curing process.

Preliminary Phase - Stage 2 (Composite Samples)

The Preliminary Phase - Stage 1 may not always yield a successful mixture or it may indicate a promising reagent combination requiring more data for adequate evaluation. Additionally, analysis of the Preliminary Phase - Stage 1 data may indicate lesser quantities of reagents will yield adequate results. If any of these were the case, an additional experimental matrix was designed to gather this data. The mathematical models developed from the Group I experiment data was used to aid in the development of this additional experiment matrix. This additional testing could consist of 0 to 5 additional experiments.

The same data was required for these experiments as was required for the Preliminary Phase - Stage 1 experiments.

Advanced Phase - Stage 1 (Strata Samples)

The two most promising stabilization formulations encountered during the Preliminary Phase were applied to the top, middle, and bottom strata of strata composites from the borings to determine the effect of varying waste composition. The two most promising formulations were also applied to the composite samples from Pits 5, 6, and the Clearwell. The most promising formulations are those with a high UCS, low leachability of hazardous and radioactive contaminants, minimum volume increase of the resultant waste form, and lowest cost of reagents. Based on two formulations per strata per pit and per composite sample from Pits 5, 6, and the Clearwell, with 20 percent of testing in duplicate, a maximum of 43 experiments were possible. The mathematical models developed from the Group I experiment data were also used to aid in the development of these experiments.

For this phase, a full TCLP, a bulking factor, permeability test, shear strength, temperature rise, and a five-day static leachability test were run in addition to a UCS test. Radon emissions from the final waste form were also determined. In addition, the following observations, measurements, or tests

were performed: general description of waste before and after reagent addition, percent water in waste, pH of stabilized waste analytical leachate solutions, and indication of gas evolution during mixing or during the curing process.

Procedures

The appendices and detailed procedures used are taken from the Treatability Study Work Plan for Operable Unit 1, dated October 10, 1991 by IT, Corp. The following is a listing of the procedures found in that work plan:

Appendix B Procedures

- Laboratory Notebook Recording Procedure
- Analytical Logbook Recording Procedure
- Standard Laboratory Sieves: Specification, Calibration, and Maintenance
- Bulking Factor Measurement for Pourable Sludge
- Calibration of Thermometers
- Unconfined Compressive Strength

Appendix C Procedures

- Nuclear Waste Glass Product Consistency Test - Version 3.0 (U)
- Bulking Factor Procedure for Nonsludge Type Waste
- 5-Day Static Leach Test Procedure
- Modified TCLP Leach Test Procedure
- Waste and Reagent Mixing Procedure
- Stabilization Waste Form Temperature Rise Generic Procedure
- Permeability
- Generic pH and Eh Procedure
- Proposed Radon Emissions from Stabilized Solids
- Shear Strength
- Vitrification of Waste
- Generic Uranium by Ion Chromatography with Post-Column Reactions and Phosphorescence or Fluorescence Detection

Data Required

The following data will be recorded during cement stabilization Preliminary and Advanced Phases:

- UCS measured by a soiltest U-590 or U-610 instruments (SOP No. TCL 1109, Appendix B)
- Permeability (for Advanced Phase)
- MTCLP (for Preliminary Phase), or TCLP and 5-day static leach test (for Advanced Phase) on those mixtures with a compressive strength of approximately 500 psi
- Bulking factor
- Waste form temperature rise after waste and reagents are mixed, and the time between mixing and temperature measurements
- Approximate shear strength measured within 10 minutes of when waste and reagents are mixed
- Physical characteristics: percent moisture, bulk density
- Amount of water added to each waste form
- The maximum particle size treated; weight and percentage of material sieved from the raw waste before treatment
- General description of the waste form before and after reagents are mixed. This includes a description of any grinding of the sample to meet particle size requirements for UCS
- Description of vapor released during mixing and during curing of mixture
- Physical appearance of mold after 90-day soak in deionized water in Optional Stage
- pH and Eh of the reagent waste mixture before adding mixture to molds
- pH of MTCLP and TCLP extraction fluids, pH of TCLP extraction fluid determination test
- pH of 5-day static leach solution and 90-day leach solution (if required)
- pH and Eh of slightly wet water waste mixture
- Radon emissions from each waste form

- TCLP metals results for reagents combined with clean sand or quartz

Durability Testing

During comment resolution with OEPA and EPA on the IT Treatability Study Work Plan, an agreement was reached that a durability assessment would be performed for cement stabilized waste samples according to the requirements of ASTM D 4842-90, Standard Test for Determining the resistance of Solid wastes to Freezing and Thawing, and ASTM D 4843-88, Standard Test method for Wetting and Drying of Solid Waste. This assessment was to be performed on successful cement formulations developed from the IT Treatability Work.

The durability testing was performed by the University of Cincinnati using two different formulations which satisfied preliminary test requirements in the Advanced Stage I testing. Specimens were produced by IT using the two different formulations for each of seven different waste pits, namely Pit 1, Pit 2, Pit 3, Pit 5, Pit 6, Clearwell, and the Burn Pit. In addition, a duplicate set of specimens was produced for one of the formulations for Pit 3 and Pit 6. Samples from Pit 4 were not tested for durability. A technical determination was made that cement stabilization was not proving to be an effective treatment method for Pit 4 waste due to the high uranium concentration. Difficulty in handling and licensing requirements for Pit 4 samples was also a major consideration in the decision to omit Pit 4 from the durability testing.

Both of the durability test procedures require seven specimens for each different mix formulation. This includes one specimen for moisture content determination, three control specimens, and three specimens for the cyclical environment testing. Both durability tests for each mix formulation were performed concurrently, therefore one set of three specimens for control and one specimen for moisture content served both tests simultaneously. It follows then that only ten specimens, instead of fourteen specimens, were required for each of the 16 sample mix formulations. Tables 3.14 and 3.15 list the two mix designs for each of the seven waste pits listed above, plus the mix design for both of the duplicate sets. Note that typically for each pit waste, one of the mix designs contains fly ash, while the other mix design contains both fly ash and blast furnace slag.

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Table 3-14 Mix Designs*

Pit - Mix	1-BFS	1-FA	2-BFS	2-FA	3-BFS	3-FA	5-1	5-2
Test Series	06	08	10	12	14	16	18	20
Cement (g)	613.22	621.32	564.82	578.62	554.66	589.87	549.87	500.51
Waste (g)	1225.57	1217.54	1063.95	1135.87	1086.32	1155.51	1030.42	754.63
Fly Ash (g)	184.96	377.12	160.88	351.78	162.51	357.29	161.67	294.25
Clay (g)	0	0	0	0	0	0	0	0
BFS (g)	306.38	0	266.77	0	271.39	0	269.91	245.61
Added Water (g)	421.82	399.5	429.42	407.36	237.59	213.18	0	0
Total (g)	2751.95	2615.48	2485.84	2473.63	2312.47	2315.85	2011.87	1795.00

Pit - Mix	1-BFS	1-FA	2-BFS	2-FA	3-BFS	3-FA	5-1	5-2
Test Series	06	08	10	12	14	16	18	20
Cement (g)	613.22	621.32	564.82	578.62	554.66	589.87	549.87	500.51
Solid Waste (g)	983.34	977.03	768.00	819.94	562.88	598.67	190.46	139.48
Fly Ash (g)	184.96	377.12	160.88	351.78	162.51	357.29	161.679	294.25
Clay (g)	0	0	0	0	0	0	0	0
BFS (g)	306.38	0	266.77	0	271.39	0	269.91	245.61
Total Water (g)	664.05	640.01	725.37	723.29	761.03	770.02	839.96	615.15
Total (g)	2751.95	2615.48	2485.84	2473.63	2312.47	2315.85	2011.88	1795.00

Pit - Mix	1-BFS	1-FA	2-BFS	2-FA	3-BFS	3-FA	5-1	5-2
Test Series	06	08	10	12	14	16	18	20
%Cement	22.28%	23.76%	22.72%	23.39%	23.99%	25.47%	27.33%	27.88%
%Waste	44.53%	46.55%	42.80%	45.92%	46.98%	49.90%	51.22%	42.04%
%Fly Ash	6.72%	14.42%	6.47%	14.22%	7.03%	15.43%	8.04%	16.39%
%Clay	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
%BFS	11.13%	0.00%	10.73%	0.00%	11.74%	0.00%	13.42%	13.68%
%Added Water	15.33%	15.27%	17.27%	16.47%	10.27%	9.21%	0.00%	0.00%

Pit - Mix	1-BFS	1-FA	2-BFS	2-FA	3-BFS	3-FA	5-1	5-2
Test Series	06	08	10	12	14	16	18	20
%Cement	22.28%	23.76%	22.72%	23.39%	23.99%	25.47%	27.33%	27.88%
%Solid Waste	35.73%	37.36%	30.90%	33.15%	24.34%	25.85%	9.47%	7.77%
%Fly Ash	6.72%	14.42%	6.47%	14.22%	7.03%	15.43%	8.04%	16.39%
%Clay	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
%BFS	11.13%	0.00%	10.73%	0.00%	11.74%	0.00%	13.42%	13.68%
%Total Water	24.13%	24.47%	29.18%	29.24%	32.91%	33.25%	41.75%	34.27%

* - Added water is the water used during the mixing of the specimens and total water is the added water plus the moisture contained in the waste.

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Table 3-15 Mix Designs*

Pit - Mix	6-BFS	6-FA	CW-1	CW-BFS	BP-BFS	BP-FA	3-BFS(D)	6-BFS(D)
Test Series	22	24	26	28	30	32	42	44
Cement (g)	587.52	499.54	411.67	231.58	486.56	526.72	554.37	587.71
Waste (g)	1108.10	1160.63	1580.84	1539.23	954.28	973.11	1086.61	1108.01
Fly Ash (g)	166.84	499.66	0	0	143.81	321.63	162.10	166.18
Clay (g)	0	0	0	0	0	38.69	0	0
BFS (g)	277.68	0	0	231.68	295.44	0	271.46	277.36
Added Water (g)	49.09	34.39	299.21	288.59	502.72	474.54	237.34	49.20
Total (g)	2189.23	2194.22	2291.72	2291.08	2382.81	2334.69	2311.88	2188.46

Pit - Mix	6-BFS	6-FA	CW-1	CW-BFS	BP-BFS	BP-FA	3-BFS(D)	6-BFS(D)
Test Series	22	24	26	28	30	32	42	44
Cement (g)	587.52	499.54	411.67	231.58	486.56	526.72	554.37	587.71
Solid Waste (g)	450.29	471.59	1157.24	1126.98	735.72	750.28	562.88	450.34
Fly Ash (g)	166.84	499.66	0	0	143.81	321.63	162.10	166.18
Clay (g)	0	0	0	0	0	38.69	0	0
BFS (g)	277.68	0	0	231.68	295.44	0	271.46	277.36
Total Water (g)	706.90	723.43	722.81	700.84	721.28	697.37	761.07	706.87
Total (g)	2189.23	2194.22	2291.72	2291.08	2382.81	2334.69	2311.88	2188.46

Pit - Mix	6-BFS	6-FA	CW-1	CW-BFS	BP-BFS	BP-FA	3-BFS(D)	6-BFS(D)
Test Series	22	24	26	28	30	32	42	44
%Cement	26.84%	22.77%	17.96%	10.11%	20.42%	22.56%	23.98%	26.85%
%Waste	50.62%	52.89%	68.98%	67.18%	40.05%	41.68%	47.00%	50.63%
%Fly Ash	7.62%	22.77%	0.00%	0.00%	6.04%	13.78%	7.01%	7.59%
%Clay	0.00%	0.00%	0.00%	0.00%	0.00%	1.66%	0.00%	0.00%
%BFS	12.68%	0.00%	0.00%	10.11%	12.40%	0.00%	11.74%	12.67%
%Added Water	2.24%	1.57%	13.06%	12.60%	21.10%	20.33%	10.27%	2.25%

Pit - Mix	6-BFS	6-FA	CW-1	CW-BFS	BP-BFS	BP-FA	3-BFS(D)	6-BFS(D)
Test Series	22	24	26	28	30	32	42	44
%Cement	26.84%	22.77%	17.96%	10.11%	20.42%	22.56%	23.98%	26.85%
%Solid Waste	20.57%	21.49%	50.50%	49.19%	30.88%	32.14%	24.35%	20.58%
%Fly Ash	7.62%	22.77%	0.00%	0.00%	6.04%	13.78%	7.01%	7.59%
%Clay	0.00%	0.00%	0.00%	0.00%	0.00%	1.66%	0.00%	0.00%
%BFS	12.68%	0.00%	0.00%	10.11%	12.40%	0.00%	11.74%	12.67%
%Total Water	32.29%	32.97%	31.54%	30.59%	30.27%	29.87%	32.92%	32.30%

* - Added water is the water used during the mixing of the specimens and total water is the added water plus the moisture contained in the waste.

Upon receipt of the samples from IT, the specimens were stored in a curing cabinet at constant temperature (20°C) and humidity (95 percent) for 7 days in order that each specimens would have time to reach an equilibrium state under the same environmental conditions. All specimens were at least twenty eight days old from the date of casting when initially received. The test procedures for both the wet/dry and freeze/thaw tests require the test specimens to be subjected to 12 cycles of alternating environmental conditions. Each two-day testing cycle consists of two 24-hour periods of different temperature and humidity conditions. The following presents conditions that a specimen is subjected to alternately for each of these 24-hour periods.

Freeze/Thaw	Wet/Dry	Control
Freezer [-20°]	N_2 purged oven [60°]	Moisture chamber [20°C]
Submerge H_2O [20°C]	Submerge H_2O [20°C]	Submerge H_2O [20°C]

After each cycle, the weight loss from each specimen was determined by the weight of the residue remaining in the beaker that had contained the specimen during that testing cycle. The weight loss of each test specimen is adjusted later to reflect the weight loss in the control specimens. The ASTM procedures for both durability tests specify that when the specimen weight loss exceeds 30 percent, the test is to be terminated.

The following modifications were made to the test procedure:

1. All of the specimens were at least 28 days old at the beginning of the durability test program. The requirement for a 28-day age at the beginning of the durability testing could not be satisfied when their age was in excess of this upon receipt. The additional week required in the humidity cabinet attenuated the influence of the different age of the specimens.

2. In the procedure for the determination of the weight loss from the specimen, the residue remaining in the beaker following the evaporation of the water from the submerged phase of the test cycle was allowed to accumulate for each succeeding test cycle. This weight was then a cumulative value for all preceding test cycles. From this data, the loss for each cycle was readily calculated.

3. When the limited amount of pit waste material resulted in a reduced size specimen or the lack of a specimen, this shortage was assigned to and accounted for in either the moisture content test or the control specimens, not the freeze/thaw or wet/dry specimens.

3.2.1.3 Sampling and Analysis

Treatment Process

Table 3-16 lists the analytical tests to be performed in each stage and phase of the treatability studies. Table 3-10 lists the chemical and radiological data to be obtained.

3.2.1.4 Deviations

The following details the deviation from the work plan which occurred while conducting this treatability study.

TCLP extraction data was not reported in a CLP format; therefore, this data will not support an analytical level relative to DQOs of Level IV. Also, the full TCLP as defined in this work plan provides for full radiological analyses on the TCLP extract in addition to normal TCLP analyses. Therefore, it is a nonstandard method that requires a Level V designation. Spike recovery values used for cement stabilized waste were calculated based on data from site characterization as indicated in Sections 7.2 and 7.3 of the work plan, respectively. This is a modification of the standard TCLP method requiring a Level V designation.

Spike Recovery

The work plan specifies TCLP results will be corrected for spike recovery. This had been a requirement of SW-846. The spike recovery correction requirement was retracted by the EPA in the November 24, 1992 Federal Register. Spikes and determination of percent recovery were performed; however, the results were not corrected for spike recovery.

Waste Description

The work plan specifies a description of the waste be recorded before and after mixing with stabilization reagents. This was not done on some samples where the descriptions were redundant.

TABLE 3-16 ANALYTICAL TESTS - CEMENT STABILIZATION OF UNTREATED WASTE MATERIAL

	Preliminary Phase		Advanced Phase	
	Stage 1	Stage 2	Stage 1	Stage 2
Bulking factor	X	X	X	X
UCS	X	X	X	X
Temperature rise	X	X	X	X
Shear strength	X	X	X	X
MTCLP - metals	X	X		
MTCLP - gross alpha - beta	X	X		
MTCLP - U by IC	X	X		
TCLP - organic			X	X
TCLP - metals			X	X
TCLP - radionuclide			X	X
TCLP - general chemistry			X	X
5-Day Static - metals[a]			X	X
5-Day Static - radionuclide			X	X
5-Day Static - general chemistry			X	X
Radon emanation			X	X
Permeability			X	X

[a]Optionally, after extraction for 5 days, the samples will be soaked for an additional 85 days. The sample will be inspected for physical degradation.

Sieving of Waste

The work plan specifies raw material be sieved before mixing with reagents. One sample (10729602, Pit 2, Zone 3) was not sieved before mixing due to the small volume of material available.

Temperature Measurement

The work plan specifies the time be recorded between mixing the cement mixture and temperature measurement. Time was not recorded for one preliminary phase sample (10448201).

Uranium Analysis

The work plan indicates uranium in the MTCLP leachate will be analyzed by ion chromatography (IC). Four preliminary samples (10497801 through 10498601) were analyzed by inductively coupled plasma (ICP), which is not as sensitive as the IC.

Percent Moisture

The work plan specifies the percent moisture of the raw waste be measured before treatment. The percent moisture was not measured on three samples (preliminary phase, Pit 4, 1049602 through 10496601).

Zone Composites

Zone composite samples were prepared for treatability testing by combining zone samples from different borings. Some of the Pit 2, Zone 3 material was inadvertently mixed with waste from another pit making the material unsuitable for treatability tests. This resulted in a shortage of Pit 2, Zone 3 material.

Permeability

A permeability test was not performed on Pit 2, Zone 3 treated material. Sufficient material to make a permeability test specimen was not available.

Radon Emanation in Air

Radon emanation measurements were made on permeability samples before permeability testing. The rate of radon emanation on one sample (10729601, Pit 2, Zone 3) was not measured because a permeability test specimen was not made.

Radon Diffusion Rate In Water

The procedure for this test specifies suspension of each sample in water with measurement of the radon concentration in the water after 7 days, and again after 30 days. Neither measurement was made on one cement stabilized sample (10729601, Pit 2, Zone 3). The 7-day measurement was not made on one another sample (10702401, Pit 1, Zone 1), and the 30-day measurement was not made on two other samples (1070601 and 10720801, Burn Pit, Zones 2 and 3).

In addition, some of the measurements were made on samples after only 5 days, and some of the 30-day measurements were made after Thirty plus or minus several days. These differences in soak time do not matter as long as the actual times of soaking are used in calculations of diffusion rates.

3.2.2 LONG-TERM DURABILITY OF S/S HAZARDOUS WASTE FORMS

3.2.2.1 Preliminary Studies

The majority of current Solidification/Stabilization (S/S) research has focused on the effectiveness of the processing or the short-term leaching and physical durability of the final S/S waste form. Current physical test procedures used to determine structural integrity include unconfined compressive strength (UCS), and wet/dry, freeze/thaw cycling. Some standardized chemical tests utilized are the TCLP, the American Nuclear Society (ANS) 16.1 Leaching Test, and the EPT. These tests assist in quantifying the initial durability and leachability, but reveal little knowledge about the longevity of the final waste form.

The UC Accelerated Life Testing and Environmental Research (ALTER) Facility is developing new methods to assess the long-term durability of S/S waste utilizing a combination of standardized tests and accelerated aging. Complete information on the project, including results, is given in the final

report "Long-Term Durability of Solidified/Stabilized Hazardous Waste Forms" dated November, 1992. Section 3.2.2.1 summarizes the work performed on surrogate wastes which forms the basis for the approach used on the actual waste samples used in the Long-Term Durability Study (Section 3.2.2.2 - 3.2.2.3).

Long-Term Durability Test Plan

The overall test and evaluation plan is presented in Figure 3-8. The tests were chosen to provide an extensive evaluation of the chemical and physical nature of the surrogate cement-stabilized specimens. Additionally, an accelerated aging procedure was developed to assess long-term durability in conjunction with standardized tests.

- Specimen Development
  Surrogate cement-solidified specimens were made with Type I portland cement and a synthetic sludge. The synthetic waste sludge was prepared using reagent grades of lead nitrate ($Pb(N)_3)_2$), sodium arsenite ($NaAsO_2$) and cadmium nitrate ($Cd(NO_3)_2$) at 0.02 Molar (M) concentration. Lead, arsenic and cadmium were chosen because they are heavy metals that are commonly treated and have exhibited useful characteristics in past studies as successful tracers for leach tests (Cheng 1991). a 30-gallon volume of sludge was made by adding the following quantities of each reagent in water: lead nitrate- 752.215 grams, sodium arsenite- 295.026 grams, and cadmium nitrate- 536.907 grams. Chosen to simulate cement-stabilized waste containing heavy metals. A sludge/cement weight ratio of 0.70 was used to simulate low density, relatively high permeability, and low strength paste. There was no aggregate added due to the high sludge/cement ratio. The paste was cast into cylindrical specimens (3 in. diameter x 6 in length), and cured according to ASTM C 192-90, Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory. After stripping the molds, some bleed water was removed. The specimens were saw cut to achieve an even top surface, resulting in an average sludge/cement ratio of approximately 0.6 and a size of 3 x 4.75 inches. The specimens were stored in a humidity room and then a humidity cabinet at 23°C and greater than 95 percent relative humidity for curing.

  Specimens were randomly designated for either the control group or test group. The control group was subjected to a matrix of standard physical and chemical tests. The test group was "artificially" aged through a method of accelerated aging and then subjected to the same standard tests as the control group. The control group (unaged specimens) results were compared to the test group (aged specimens) results in evaluation of long-term durability.

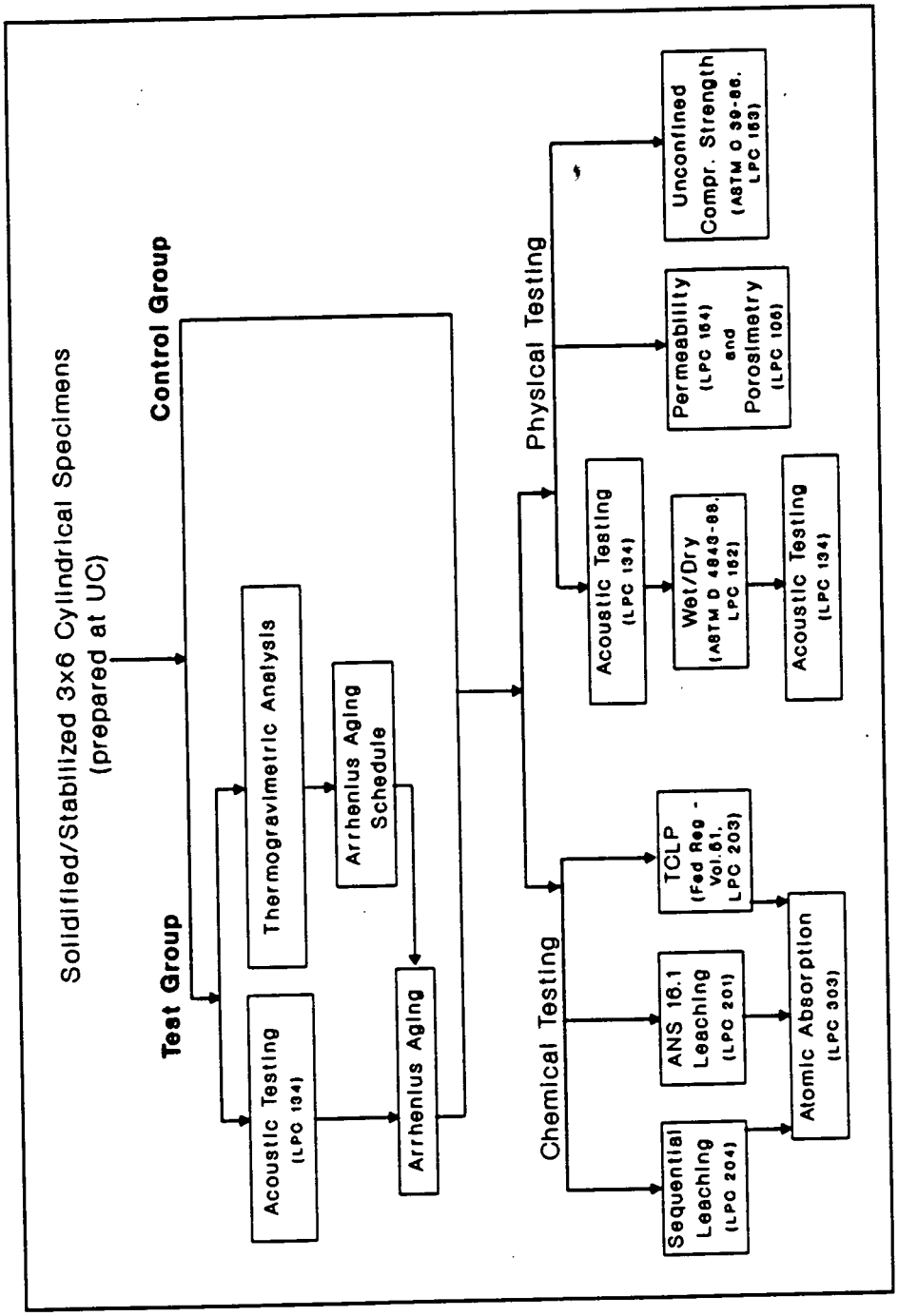

Figure 3-8 Long-Term Durability Testing Flow Chart

Accelerated Testing

In considering a waste treatment technology, the ultimate concern is the long-term endurance in the specific disposal site. There are essentially three different techniques for predicting long-term performance of a material: natural or historic analogues, modeling, and accelerated testing. Accelerated tests set the independent variables of the test to result in increased alteration rates of the test specimens. The important consideration in accelerated testing is that the alteration mechanism under examination must not be changed. Reactions that would not occur in the natural environment cannot be generated in the accelerated testing or the results will not be indicative of actual long-term performance.

- Accelerated Aging

  Accelerated aging is one type of accelerated testing which refers to accelerating the reactions a material will undergo during the natural aging process. The accelerated aging of specimens in this study was based upon ASTM C 684-89, Procedure D (High Temperature and Pressure Method), and the Arrhenius model. ASTM C 684-89 Procedure D uses available moisture, a temperature of 300°F (148°C) and an applied pressure of 1500 ± 25 psi to accelerate curing for early strength testing. The ALTER accelerated aging method uses a saturated steam environment at ≤300°F (148°C). For this study, a temperature of 300°F (148°C) and saturated steam pressure of 57 psi were used. These conditions were selected from initial thermograms which indicated little structural change in the cementitious material at or below this temperature.

  ASTM C 1074-87 uses an equivalent age function based on the Arrhenius equation to predict the degree of hydration. A similar approach was used in calculating the equivalent age of the ALTER specimens. The Arrhenius equation relates the rate of reaction to the activation energy of a material. The form of the Arrhenius equation used is as follows:

$$t_a = t_t \cdot \exp\left[\left(\frac{E_a}{R}\right)\left(\frac{1}{T_s} - \frac{1}{T_t}\right)\right] \qquad \text{Equation 2}$$

where :

t_a	=	"accelerated" age
t_t	=	actual duration of accelerated aging test
E_a	=	activation energy
R	=	Universal Gas Constant
T_s	=	anticipated temperature of service environment
T_t	=	accelerated aging temperature during test

This form of the Arrhenius equation was used to calculate the accelerated ages (t_a) of the test group specimens relative to the actual duration of the test (t_t). The values for the

activation energy, accelerated testing temperature, and anticipated service temperature were calculated to determine an accelerated aging schedule. This schedule was determined for two different groups of specimens, targeted for accelerated ages of 50 and 100 years.

- Aging Schedule

Dynamic thermogravimetry was used to determine the waste specific kinetic parameters for use in the Arrhenius equation. The thermal curves of weight change versus temperature provide chemical composition and thermal stability data about the specimen. From these curves, the activation energy (E_a) of the specimens was determined and found to be in good agreement with published values for portland cement as stated in ASTM C 1074-87.

In addition to the activation energy, a baseline temperature was determined for use the Arrhenius equation. The baseline temperature for this project was the average anticipated temperature of the waste storage environment (T_s). To simulate worst case conditions, the baseline temperature was based on outdoor storage for the Cincinnati, Ohio region.

- Specimen Aging

Accelerated aging of the specimens was performed in temperature and pressure controlled stainless steel pressure vessels. Surrogate specimens were placed in the pressure vessels and subjected to an accelerated temperature and saturated steam pressure of approximately 300°F and 57 psi, respectively. The first group of specimens was placed in a pressure vessel for an accelerated test duration of approximately six months. The second group of specimens were in a pressure vessel for three months. The pressure vessels were intermittently shut down during the accelerated aging to characterize the specimens.

Testing times and temperature data were processed for each temperature range to calculate the actual accelerated age of the specimens. The incremental accelerated ages were tabulated for each temperature range and summed. Specimens targeted for 100 year-aged were actually accelerated to 179 years and specimens targeted for 50 year-aged were accelerated to 98 years. Target ages (100 and 50 years) were based on preliminary estimates of activation energy and test temperature, and discounted temperature ramping times. The 1:2 age ratio between specimen groups of 50/100 (target) was doubled as 98/179 (actual). This age ratio is shown in the results of the physical and chemical tests conducted. Throughout the rest of the text, the two test groups will still be referred to as 50-year and 100-year aged specimens for convenience.

- Thermogravimetric Analysis
  Thermogravimetric (TG) analysis was performed on the samples from the interior of the aged specimens to examine the chemical reactions that may have occurred during the aging process. These analyses show the interior of the aged samples were approximately 31 percent $Ca(OH)_2$, which is high when compared to typical portland cement. Since $Ca(OH)_2$ is a byproduct of hydration reactions, the high value possibly indicates the hydration reaction was successfully accelerated during the aging process.

  TG analysis of the exterior of the aged samples found little or no $Ca(OH)_2$. It did show, however, these samples were approximately 62 percent $CaCO_3$. This is consistent with TG analysis of naturally aged cement samples from local sources. It seems the highly soluble $Ca(OH)_2$ migrated to the exterior and carbonated. It is believed the carbonation did not advance deeper into the specimens because of insufficient CO_2 in the air tight aging chambers. In general, TG analysis supports the assumption that samples experienced accelerated chemical reactions which occur naturally, thereby aging them.

Physical Testing

Physical tests were used to evaluate the relative strength, durability, and permeability of the surrogate cement-stabilized waste specimens. These standardized tests characterize the waste form or analyze the performance of the specimens under adverse conditions.

- Unconfined Compressive Strength
  ASTM C 39-86, Standard Testing Method for Compressive Strength of Cylindrical Concrete Specimens, was used to determine the unconfined compressive strength (UCS) of the unaged and aged surrogate specimens. This destructive test shows the strength loss in the specimens when exposed to accelerated aging. The unaged specimen strength was approximately 4500 psi. The strength decreased dramatically during accelerated aging, resulting in strength values of approximately 2500 psi for the 50-year aged specimens and 900 psi for the 100-year aged specimens (see Figure 3-9).

  During natural aging with adequate hydration conditions and normal weathering, a concrete specimen may not lose strength over long periods of time. The surrogate specimens tested, however, did lose strength after the accelerated aging process. This was probably due to the unique chemical nature of the surrogate specimens in which reactions may vary greatly from normal concrete. The strength test results, though not truly indicative of the strength of a full size waste form, can provide indication of problems in the solidification process.

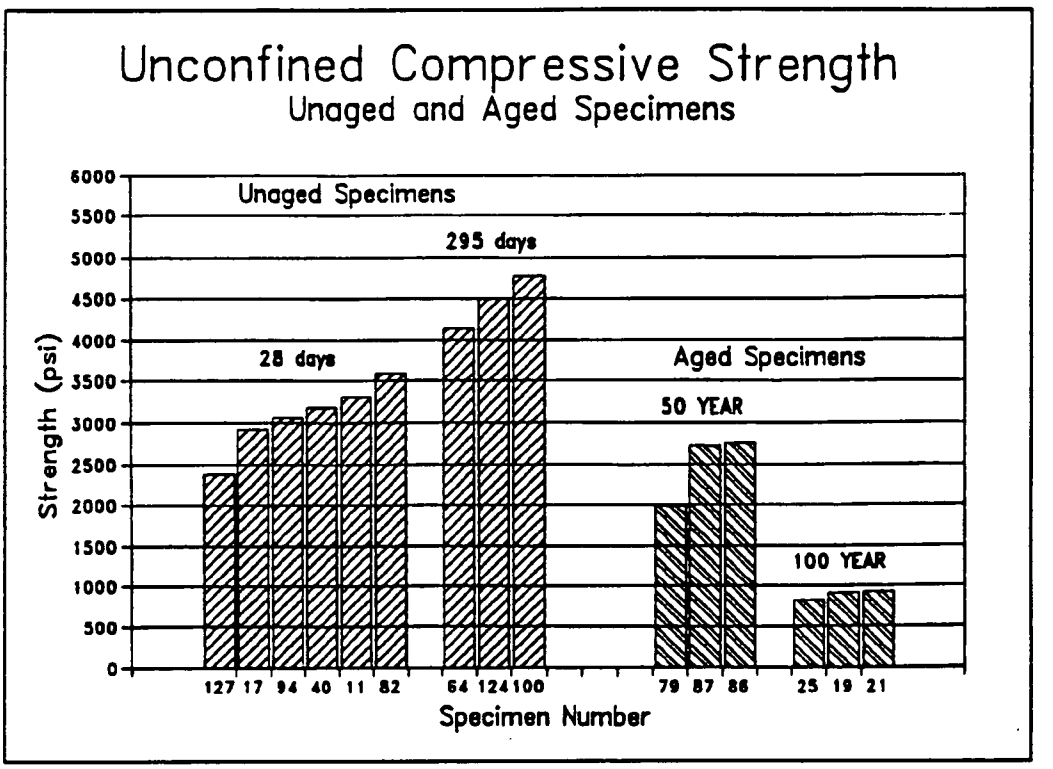

Figure 3-9 ASTM C 39-86 unconfined compression strength of unaged and aged samples.

- Wet/Dry Cycling

Cyclic durability testing was conducted to determine the specimen's resistance to natural weathering conditions. The test was performed in accordance with ASTM D 4843-88, Standard Test Method for Wetting and Drying of Solid Wastes (wet/dry). The test is designed to give a weight lost per cycle of testing and the number of cycles before specimen failure.

Surrogate specimens were extremely durable throughout the wet/dry testing. Non-destructive acoustic test methods (resonant frequency and pulse velocity analysis) were developed at the ALTER Facility to provide a more precise measure of deterioration than the ASTM D 4843-88 wet/dry standard weight loss method. Wet/dry testing showed total weight loss of less than 0.2 percent. Acoustic methods indicated a decrease in dynamic modules of elasticity of 0.5×10^6 psi in the first 3 wet/dry cycles and then a fluctuation around that value for the next 9 cycles. A decrease of 0.5×10^6 psi is 25 percent decrease in the dynamic modules of elasticity. An additional 9 cycles of wet/dry testing were performed at elevated temperatures displaying greater degradation (see Figure 3-10).

- Permeability Testing

Falling-head permeability boards were erected to determine the permeability of the specimens. The specimens were contained in triaxial flexible-wall permeameters with deionized water as the permeant. Unaged specimens required eleven months of saturation before an equilibrium permeability reading could be determined. An increased pressure head was required to induce water flow through the specimens. Unaged specimens had an average permeability with water of 10^{-10} cm/sec which is typical of other permeability studies on concrete. Aged specimens soaked in water for roughly five months before mounting in the permeameters. Saturation was reached almost immediately under a natural gradient or gravity head. These specimens had permeability values between 10^{-7} and 10^{-6} cm/sec (see Figure 3-11).

Dye tests were performed to determine the flow paths in the aged specimens after they had reached equilibrium with the deionized water permeant. Slicing the 50-year dyed specimen revealed the flow was concentrated around the exterior and to localized interior channels. Slicing the 100-year specimen revealed nearly all flow was in the exterior portion of the specimen. These results indicate the permeability values for the aged specimens are representative of the outer ring.

Mercury intrusion porosimetry was performed to determine the porosity of the unaged and the interior and exterior of the aged specimens. Unaged specimen porosity was found to be 41 percent. Aged interior porosity was 50 percent for the 50-year and 43 percent for the 100-year samples. The aged exterior porosity was 61 percent for the 50-year and 66 percent for the 100-year sample (see Figure 3-12). In addition, the pore structure openings followed a logical and expected pattern: the unaged specimens contained the

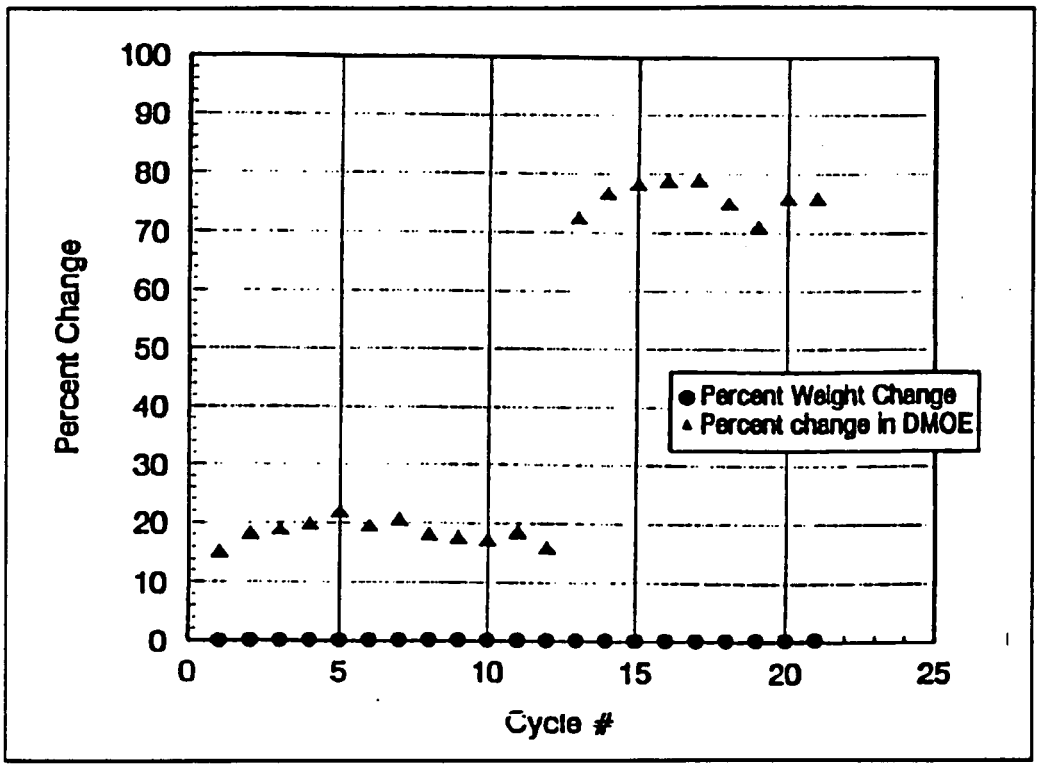

Figure 3-10 Comparison of ASTM D 4843-88 weight loss and change in dynamic modulus of elasticity.

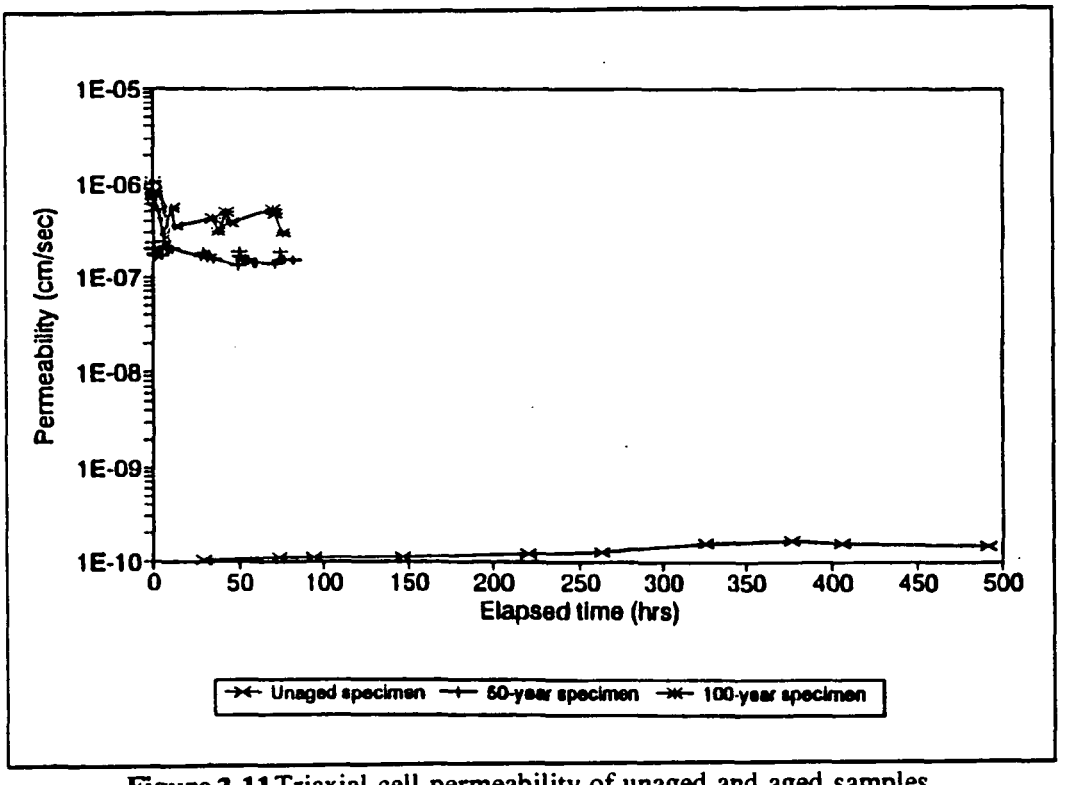

Figure 3-11 Triaxial cell permeability of unaged and aged samples.

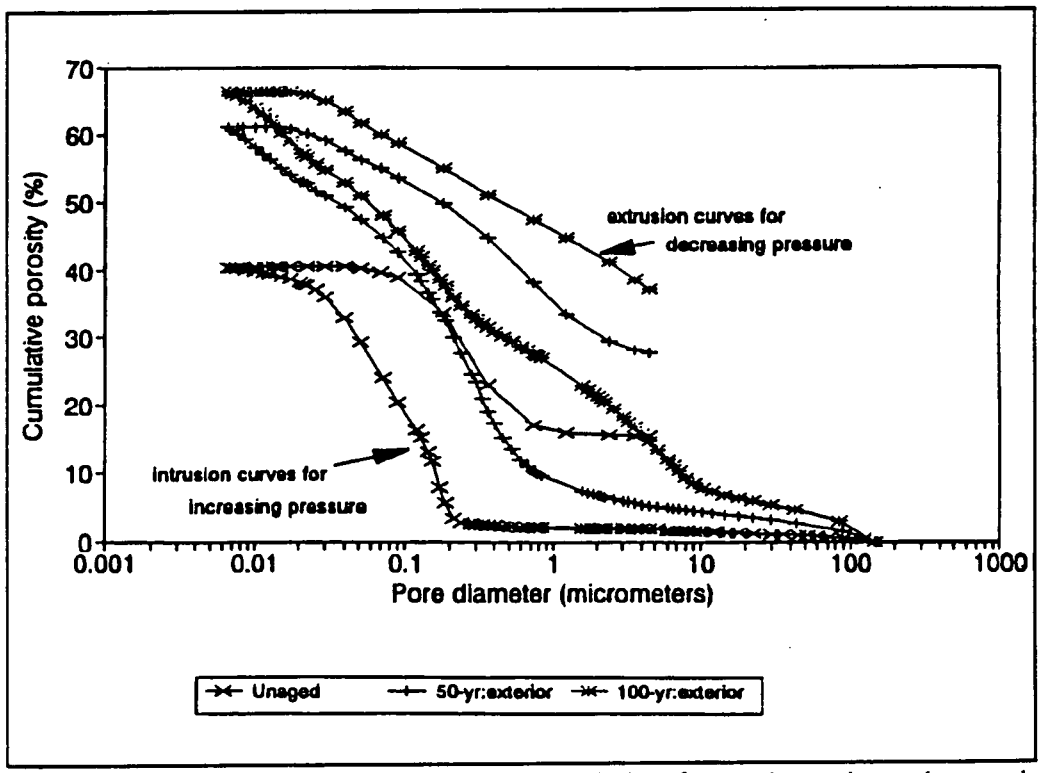

Figure 3-12 Porosity by mercury intrusion porisimitry for aged exterior and unaged samples.

least open pores to the 100-year aged specimens having the most open pores. This porosimetry testing has shown there is more open pore structure near the exterior of the samples, which is in agreement with the permeability and dye testing.

The percent voids in the specimens were also calculated using ASTM C 642-82, Standard Test for Specific Gravity, Absorption, and Voids in Hardened Concrete, yielding nearly identical results. This method only yields final porosity values, whereas mercury porosimetry yields curves showing pore size distribution. For mixed waste testing, ASTM C 642-82 may be used in place of mercury intrusion porosimetry to minimize waste generated in testing.

Chemical Testing

Chemical tests are probably the most common means of evaluating a solidified waste. A specific leaching condition is usually performed to study a specific chemical reaction. The leaching tests used in this project were static and dynamic batch tests.

- American Nuclear Society (ANS 16.1) Leach Test
  The American Nuclear Society (ANS) 16.1 Leach Test was performed on unaged and aged specimens with deionized water and dilute acetic acid as leachants. The acid leachant, not specified in the test method, was used to accelerate leaching for some of the specimens. Analytical measurements conducted on the leachate included pH, acidity, alkalinity, and metals analysis.

  Leachate metals analysis was performed for cadmium, arsenic, and lead tracers using graphite furnace atomic absorption spectrometry. Results of the ANS 16.1 leach test for the unaged, 50-year aged, and the 100-year aged specimens for the three metals are available in the long term durability of S/S Waste Forms Draft Report (UC Alter, November 1992). The concentration of metal leached per hour is plotted vs. the leaching cycles. The data presented are for the leach tests using acetic acid, since these results had fewer outliers. The leaching rates generally had decreasing trends, with disturbances observed at 96 hours (Cycle 6), 120 hours (Cycle 7), and 1128 hours (Cycle 9).

  At the beginning of the tests, easily removed metals were leached from the matrix. The leaching rate slowly decreases as less metal is available for leaching. By the sixth cycle, most of the easily removed metals have been leached. The leaching rate decreases sharply. At the end of the seventh cycle, the decline of the leaching rate becomes much more gradual. The leaching rate actually increases for arsenic. It is speculated this trend is due to calcium hydroxide from the cement matrix dissolving in the leachate. This process would open up more pores in the cement matrix, thereby allowing more metal to be leached. This theory is supported by the pH data for the acid leachate samples. The pH of the leachate rose dramatically after 120 hours, most likely indicating an increased amount of calcium hydroxide in solution. At this same point, the acidity sharply

decreased. At some point after the ninth cycle, the pH of the solution reached equilibrium, and the leaching rate again dropped off.

Metal tracers were removed from the specimen through bleeding of water during curing, leaching during the accelerated aging process, and leaching during the leach tests. The liquid from the first two sources was analyzed, and the results indicate less than 1.33 percent of the total metals were removed in the bleed water during curing. In addition, less than 0.1 percent of the total metals were removed in the aging process. During acid leaching approximately 7 percent of the cadmium was leached and less than 2 percent of the lead and arsenic leached. However, in the standard ANS 16.1 leaching where water was used as the leachant, less than 1 percent of the total metals leached. There were minimal differences between the unaged and aged specimens for metals leached.

- Toxicity Characteristic Leaching Procedure (TCLP)

  The TCLP test was performed on unaged and aged specimens. The specimens were crushed into two size categories: 4.75 mm to 9.52 mm and less than 4.75 mm. Leachate samples from the test were analyzed for arsenic, cadmium, and lead using graphite furnace atomic absorption spectrometry.

  All metal concentrations from the leachate were well under federal regulatory levels. For arsenic, the average leached concentrations were 7 ppb for the unaged samples, 22 ppb for the 50-year samples, and 33 ppb for the 100-year samples. For cadmium, the average leached concentrations were < 1ppb for the unaged samples, 52 ppb for the 50-year samples, and 30 ppb for the 100-year samples. Finally, for lead, the average leached concentrations were 300 ppb for the unaged samples, 780 ppb for the 50-year samples, and 860 ppb for the 100-year samples. There was essentially no difference in the amount of metal leached from the two different sample sizes, and therefore their results were combined in the above average leaching estimates.

Natural Weathering

The only irrefutable measure of long-term durability results from monitoring a stabilized waste over natural time. Therefore, a natural weathering system has been designed to evaluate the accuracy of the accelerated aging predictions. The natural weathering system will contain stabilized waste specimens and expose the specimens to environmental conditions. These natural conditions can include freezing and thawing, wetting and drying, leaching, and radiation exposure, resulting in natural aging. Some of the different storage scenarios may include tumulus storage, direct burial, above ground storage, or warehouse containment. The choice of the natural weathering system depends on the proposed storage conditions the waste will undergo.

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A total of four containment systems were constructed. Three of these are test systems, each containing forty-seven 2-in. X 4-in. specimens packed in sand. The fourth is a control system, containing only packed sand. Leachate from the systems will be collected on a regular basis to determine if any of the waste constituents are being released from the specimens. The leachate collection reservoir inside each containment system holds 18" of leachate. Given the average yearly precipitation in Ohio of 52-in. per year, a bimonthly sampling schedule is planned.

Specimens will be harvested from the systems on a regular schedule to determine the effects of aging. Each natural weathering system is designated for a specific harvesting event. The proposed harvesting schedule is 2, 10, and 15 years from the time the systems are buried. The specimens will be removed from the systems and will undergo the same physical and chemical testing as the "artificially" aged specimens from this project. This comparison will be used to verify the results of this aging study.

The following covers the scope of current treatability study work:

3.2.2.2 Test Objectives and Rationale

Assessment of physical degradation in stabilized waste forms is important and may significantly affect the leaching potential of the waste form. The UC ALTER Facility is currently developing a test protocol for Accelerated Aging of stabilized waste samples to assess their long-term durability in the environment. During preliminary studies, ALTER developed a non-destructive test method using acoustical methods modified from ASTM standards for testing structural concrete. This acoustical technique was applied to surrogate specimens. Results from this testing have been extremely promising with very high rates of repeatability.

The ALTER Long Term Durability Work Plan (January, 1993) covers the continuation of work started in the preliminary studies. The objective of this research is to assess the long-term durability of stabilized hazardous and radioactive waste forms through accelerated aging with various performance and characterization tests. This laboratory scale study will assess the long-term

durability of cement stabilized FEMP Pit 5 waste in place of surrogate specimens. Control samples from the preliminary studies will continue natural weathering for future verification of the model. Data generated by IT Corp. and Catholic University of America (CUA) will be used to determine cementitious mix designs for this durability study.

Data generated at the UC ALTER Facility are of the following types:

- Physical and Chemical Product Characterization Data
- Product Characterization Data (such as leachate analysis)

The acquired data are intended to assess whether the immobilization of the hazardous/radioactive components in the cement stabilized form has been achieved and if the product is leach resistant and durable over time. Both specialized (nonstandard) and nonspecialized procedures are followed. The study will be conducted in accordance with the CERCLA guidance and the FEMP Quality Assurance Project Plan.

3.2.2.3 Experimental Design and Procedures

Cement Solidification/Stabilization of Pit Wastes

Pit 5 samples will be provided from a previous sampling program of Pit 5. Required waste quantities are undetermined at this time. Characterization data from CUA and mix designs from IT Corp. will be utilized when solidifying the pit wastes. The mix design used will be the best candidate for the specific pit waste as determined by IT Corp.

Specimens will be prepared according to ASTM C 192-88, LPC 402 (Ref. ALTER Work Plan; Appendix A: Laboratory Procedures Catalog). The specimens will be cast into 2-in. dia. x 4-in. length cylindrical molds. Specimens will cure for a minimum of 28 days in a humidity cabinet at 23 $\pm$ 1.7°C and $\geq$ 95 percent relative humidity.

Selection of Test Procedures and Parameters

Using the surrogate tests evaluation and data analysis from the preliminary tests, a matrix of tests was developed to be performed on the Waste Pit 5 cement stabilized specimens (see Figure 3.13).

Solidified pit waste specimens will be divided into test (aged) and control groups (unaged). Test group will be artificially aged in two sets and subjected to the baseline chemical and physical testing. These baseline tests are also conducted on the control group (unaged) specimens and the results are analyzed and compared with the test group.

- Accelerated Aging
  Before the accelerated aging is conducted, thermogravimetry (TG) will be used to determine the activation energy of the specimens. In addition, the specimens will be acoustically tested before aging for comparison to data after accelerated aging. Accelerated testing utilizing the Arrhenius equation will be conducted on two groups of Pit 5 stabilized waste specimens (i.e., two different ages). Using the activation energy, accelerated temperature, and natural service temperature, an aging schedule will be determined for the target service times (50 and 100 years). The specified chemical and physical tests will be conducted on the aged specimens and the data compared to the unaged specimen data.

- Chemical Testing
  Chemical tests to be performed include:

  1. American Nuclear Society (ANS) 16.1 Leach Test will be performed on the monolithic specimens in dilute acetic acid (LPC 201, ANS 16.1).

  2. Toxicity Characteristic Leaching Procedure (TCLP)

  3. A Graphite Furnace Atomic Absorption Spectrometer (AA) will be used to analyze the leachate for waste constituents (LPC 303).

  4. The main waste elements of concern for Waste Pit 5 will be barium, chromium, and arsenic. The leachate from the standard tests will be analyzed for these three metals by AA analysis.

  5. Acidity and Alkalinity procedures will also be conducted on the leachate samples (LPC 301 and LPC 302).

- Physical Testing
  Physical testing will include:

  1. UCS - LPC 153, ASTM C 39-86

  2. Permeability testing conducted with falling-head permeameters to calculate the permeability coefficient (LPC 154).

3. Percent voids from water (LPC 102, ASTM C 642-82)

4. Wet/dry testing - LPC 152, ASTM D 4843-88

5. Calculation of the durability factor from weight loss measurements. However, if the waste form is extremely durable, an acoustic measure of deterioration is more reliable.

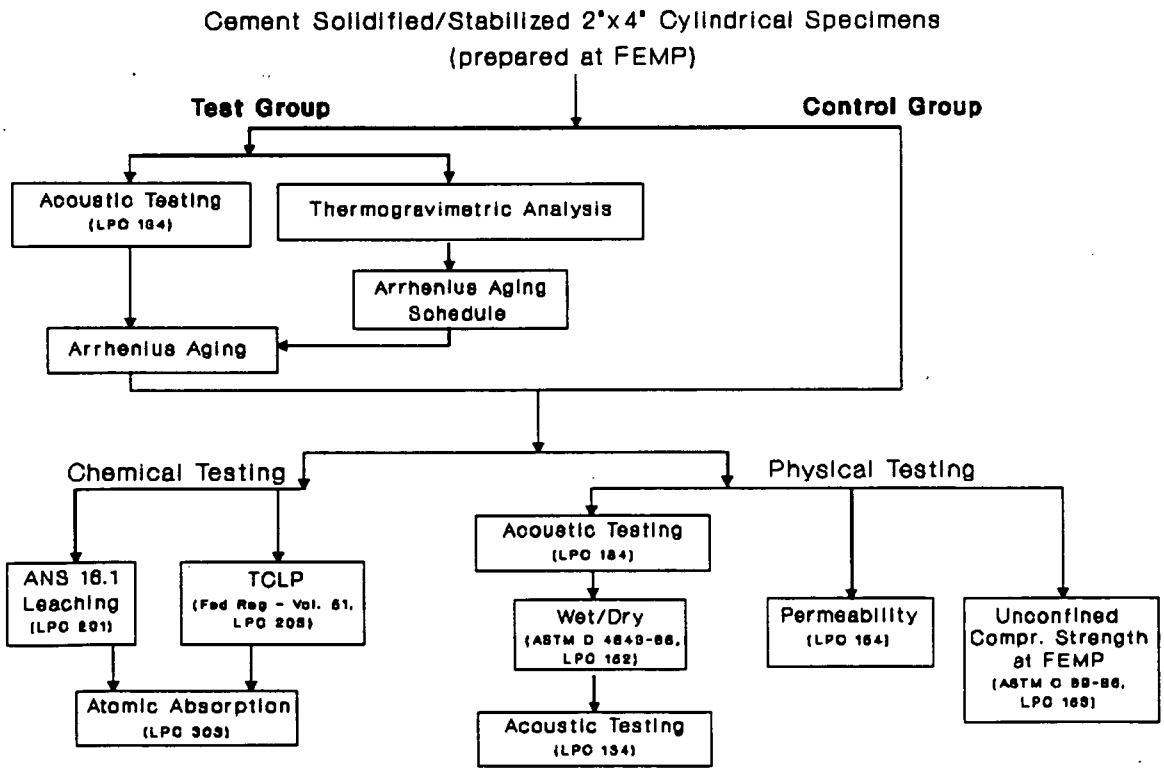
- Acoustic Testing

Acoustic testing procedures are being adapted and upgraded from concrete testing standards for use in waste form durability verification at the ALTER facility (LPC 134). These procedures are used to track stiffness as a measure of deterioration in the stabilized waste specimens during aging or cyclic durability testing. Acoustics testing is currently conducted by two techniques: resonant frequency and pulse velocity. The most useful laboratory technique is resonant frequency. This method consists of computing the resonant frequency of a specimen from vibrations and calculating the dynamic modulus of elasticity. Changes in the modulus of elasticity show the deterioration during wet/dry test cycles or for comparison of unaged and aged specimens.

The other nondestructive technique to be developed is pulse velocity. The pulse velocity method will be used mainly for field testing of solidified waste forms. These nondestructive test techniques as developed by the ALTER Facility provide higher data resolution for deterioration determination than standard methods of weight and strength loss measurements currently used.

- Natural Weathering Plan
  A natural weathering system has been designed in conjunction with the accelerated testing program to monitor the solidified specimens and evaluate the physical and chemical changes over time. This natural time monitoring program will also attempt to verify the results of the accelerated aging program. The natural weathering plan will include procedures for placement of specimens, schedule and procedure for harvesting the specimens, characterization of the specimens, data analysis methods, and a quality assurance plan.

FIGURE 3-13



3.3 THERMAL TREATMENT AND PARTICLE AGGLOMERATION

The ALTER facility is working as part of a team effort in coordination with the FERMCO Treatability Engineering group to perform the Cooperative Remedy Screening Program (CRSP). The remedy screening alternatives to be addressed include dewatering, drying, calcining, clinkering, pelletizing, briquetting, polymer encapsulation, and low strength cement stabilization. These treatment alternatives will be tested at the laboratory scale and evaluated for their effectiveness. This program consists of a screening phase only.

The CRSP Work Plan was prepared in accordance with the EPA's Guide for Conducting Treatability Studies Under CERCLA (EPA 1992) and the Fernald RI/FS Quality Assurance Project Plan (QAPP).

3.3.1 Test Objectives and Rationale

Data resulting from the study will be used to establish or identify the following:

- Technical Applicability of treatment options
- Process data for support of bench and pilot scale design
- Compliance of technology with applicable or relevant and appropriate requirements (ARARs)
- Initial database for use in subsequent bench- and pilot-scale studies used in support of remedial design

Data generated by UC ALTER facility and Operable Unit 1 Treatability Engineering are:

- Physical and Chemical Product Characterization Data
- Product Characterization Data (such as leachate analysis)

The acquired data are intended to provide a qualitative assessment of the technical applicability of the treatment methods and technologies as applied to each Operable Unit 1 waste unit (i.e., Pits 1-6, Burn pit, and Clearwell). Both specialized (nonstandard) and nonspecialized procedures are followed.

3.3.2 Experimental Design and Procedures

The initial waste samples processed will be provided from a previous sampling program. Prior to evaluation of the stabilization methods to be screened by this program, the wastes will be classified using a variety of physical and chemical characterization methods (See Section 3.3.3.1).

A qualitative evaluation of several stabilization methods will be performed. These methods include thermal processing, non-thermal processing (use of waste derived and commercial pozzolan binders), and polymer encapsulation. The following outline identifies the range of screening possibilities within these treatment areas.

1. Thermal Processing
   A. Dewatering
   B. Drying only
   C. Drying --> calcining
   D. Drying --> calcining --> clinkering
   E. Formation of a waste dervied portland cement

2. Non-Thermal Processing
   A. Phase I: Addition of portland cement (PC) or other pozzolan binder to form low strength soil like matrix
      1. Addition of PC or other binder to dried material
      2. Addition of PC or other binder to dried --> calcined material
      3. Addition of PC or other binder to dried --> calcined --> clinkered ground material
   B. Phase II: Addition of waste derived portland cement to form low strength soil like matrix
      1. Add to dried material
      2. Add to dried --> calcined material
      3. Add to dried --> calcined --> clinkered ground material

3. Polyethylene Encapsulation

3.3.2.1 Thermal Processing

Thermal processing is accomplished in several phases dependent upon minimum heating values. Minimum heating values have been determined for each phase in laboratory investigations. Extensive rotary kiln thermodynamics studies have also been performed based upon practical kiln data. Combining these studies, Table 3-17 Phase Formations, was developed. This table provides the temperature range at which phase changes may occur.

While these temperatures will be used to guide the CRSP study, it should be noted that even though the waste to be processed contains cement formers, a variety of constituents/contaminants not found in typical cement feeds are also present. Optimum temperatures for drying, calcining, and clinkering phases of the individual waste units (i.e., Pits 1-6, Clearwell, Burn Pit) will be determined experimentally.

Thermal Analysis

Thermal analyses of the waste will be performed using thermogravimetric analysis or similar thermal analysis method. These thermograms will provide temperature/phase change data as well as compositional information. A maximum of 10 thermograms will be generated on each waste unit using samples randomly selected and dried at 60°C prior to analysis.

Based on the data generated, waste specific processing temperatures for drying, calcining and clinkering will be selected. Based on the analysis presented in Table 3-18, it is anticipated the temperatures required will be close to those presented in Table 3-17 for typical cement kiln feed. Ultimately, the wastes will be thermally treated in a laboratory scale tube furnace or rotary tube kiln. Residence times and feed rates will be estimated from the data generated for determining the processing temperatures.

3.3.2.2 Non-thermal Processing

Two phases of non-thermal processing will be performed. The first phase involves the addition of Portland cement (PC) or other pozzolan binder to material produced by thermal processing (see Section 3.3.2.1). The second phase will utilize a waste derived PC which will be added to each of

Table 3-17

PHASE FORMATIONS

	Thermal work	*Minimum temp.* °C	°F	
1.	Evaporation of free water from the feed	100	212	Required low-grade heat 363 kcal/kg (652 Btu/lb)
2.	Evolution of the chemically combined water in the clay minerals	550	1022	
3.	Evolution of CO_2 from calcium and magnesium carbonate (calcination)	805	1481	Required high-heat grade heat 511 kcal/kg (919 Btu/lb)
4.	Formation of interm phase C_2F	800	1472	
5.	Formation of interim phase CF	900	1652	
6.	Formation of interim phase $C_2S + C_2AS + CF + C_2F$	1000	1832	
7.	Formation of interim phase $C_2S + C_5A_3 + C_5A + C_3S + CF + C_2F$	1100	2012	
8.	Formation of interim phase $C_2S + C_3A + C_5A_3 + C_2F + C_3S$	1200	2192	
9.	Formation of C_3A, C_3S, C_2S, C_2F	1300	2372	
10.	Equilibrium in C_3A, C_3S, $C_2S + C_6A_2F$	1400	2552	

*Taken from Peray, K. E., *The Rotary Cement Kiln*, Second Edition, Chemical Publishing Co., Inc., New York, 1986.

Table 3-18 Cement Kiln Feed Analysis of Pit 5

Key Oxides for Cement Manufacture:		Typical Values for Cement Kiln Feed:
pH 5 Equivalent Oxides		
Al_2O_3	2.42%	S/R = 2.5 - 3.2
CaO	42.63%	A/I = 1.6 (Values lower than this indicate more favorable burning)
Fe_2O_3	3.64%	LSF = 90 - 95
SiO_2	16.03%	

Silica Ratio (S/R):

$$\frac{SiO_2}{[Al_2O_3 + Fe_2O_3]}$$

S/R = 16.03(2.42 + 3.64) = <u>2.64</u>

Alumina-Iron Ratio (A/I):

$$\frac{Al_2O_3}{Fe_2O_3}$$

A/I = 2.42/3.64 = <u>0.66</u>

Lime Saturation Factor (LSF):

$$\frac{100CaO}{[(2.8\ SiO_2) + (1.1\ Al_2O_3) + (0.7\ Fe_2O_3)]}$$

LSF = (100 * 42.63)/[(2.8 * 16.03) + (1.1 * 2.42) + (0.7 * 3.64)] = <u>85.1</u>

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the materials produced by thermal processing. In both phases, the waste material produced will consist of low-strength, soil-like material.

Phase I - Addition of portland cement (PC) or other pozzolan binder

In Phase I, portland cement (or other pozzolan binders) will be added to the waste material produced by thermal processing. Various binder amounts will be added separately to the dewatered, dried, calcined, clinkered, and ground clinkered waste materials. A maximum of three waste/binder ratios, utilizing three binders, will be studied for each waste material produced by thermal processing. Additionally, a maximum of three water/binder ratios will be studied.

Phase II - Addition of a waste derived portland cement

Waste material processed (clinkered) at the upper end of the thermal treatment spectrum (Table 3-17) will be utilized in the Phase II. Clinkered material will be ground to form a low efficiency portland cement. This waste derived PC will be added separately to each waste material produced by thermal processing to form a stable low-strength material. A maximum of three waste/binder and three water/binder ratios will be used. If desired, small quantities of commercial binders may also be utilized in this phase.

3.3.2.3 Polymer Encapsulation

The applicability of Polymer encapsulation technology for Operable Unit 1 wastes will be assessed as a simultaneous activity with the thermal and non-thermal technology assessments. Polyethylene (PE) will initially be used to assess polymer encapsulation.

PE encapsulation involves adding dried wastes and polyethylene feed material into a heated mixing apparatus, then allowing the mixed material to cool, producing a dimensionally stable waste form. An advantage of PE encapsulation is that the encapsulating polyethylene material does not interact chemically with the dried waste. As heated, PE is an extremely viscous material. Particle size, density, and dryness of the waste appear to be the primary factors in successful encapsulation.

The ALTER facility has created a chemically inert surrogate material for use in the PE encapsulation evaluation. The properties are based upon particle size, density, and soil type analyses performed in the initial baseline characterization of the archived Operable Unit 1 wastes.

Several heated mixing units have been tested at off-site vendor facilities using the surrogate waste form and low density polyethylene (LDPE) and other polymers. These mixing runs were performed on dried surrogate wastes. Information regarding waste loading, processing time, and mix efficiency was collected during these test runs. Surrogates are useful as this type of encapsulation is physical in nature rather than chemically interactive.

3.3.3 Sampling and Analysis

Samples for these studies were collected and archived during sampling programs described in section 3.1.1.4. A sampling plan was generated to sample the archived waste inventory by the FERMCO Sampling and Analysis Group. An inventory of the waste available from the earlier pit samplings with the number and volume of samples required for the CRSP project, are provided in Table 3-19. Two 1 gallon samples were taken from each inventoried drum specified. For Pits 3, 5, and 6, an additional 5 gallon sample was taken. These samples are being stored near the testing laboratories. Additional samples may be required and will be taken as necessary.

Individual samples for testing are being taken from the 1-and 5-gallon sample containers. A container to be sampled is thoroughly homogenized by a commercial paint shaker prior to each test sample extraction. The time required to homogenize the waste was determined in the lab prior to testing.

3.3.3.1 Waste Stream

Prior to evaluating stabilization methods screened by this program, characterization testing of the wastes was performed. The first level of characterization testing involved the classification of wastes contained in inventory. Physical characterization was performed on the homogenized contents of each of the available 55 drums of waste. Due to the heterogeneity of the waste in general, baseline chemical characterization consisted of a modified TCLP leach test to screen for waste constituents of

Table 3-19 OU1 Treatability Sample Collection Inventory

Pit Number	Number of Drums	Weight, lbs	Drums to Sample for CRSP	Volume of each CRSP Drum Sample
1	8	132-926	8	2 - 1 gallon cans
2	4	428-694	4	2 - 1 gallon cans
3	7	209-697	7	2 - 1 gallon cans 1 - 5 gallon can
4	21	484-990	6	2 - 1 gallon cans
5	34	Unknown	14	2 - 1 gallon cans 1 - 5 gallon can
6	5	Unknown	5	2 - 1 gallon cans 1 - 5 gallon can
Burn Pit	3	283-569	3	2 - 1 gallon cans
Clearwell	17	Unknown	8	2 - 1 gallon cans

concern in each waste unit. Table 3-20 provides a list of these leachate analyses. Waste stream testing consisted of the following:

- Moisture content: laboratory test, ASTM D2216; microwave oven method, ASTM D4643

  Significance: water content is one of the most significant index properties used in establishing a correlation between soil behavior and its properties. In fine-grained (cohesive) soils, the consistency of a given soil type depends on its water content.

- Grain size analysis (sieve/hydrometer): amount finer than No. 200 sieve, ASTM D1140; correction for oversize particles, ASTM D4718; sieve/hydrometer analysis, ASTM D422

- Atterberg limits (Note the Atterberg limits called for in this instance include the liquid and plastic limits as applicable to the drum contents):

  - Liquid Limit: ASTM D4318

    Significance: the liquid limit, plastic limit, and plasticity index are used as an integral part of several engineering classification systems to characterize fine-grained soil fractions. They are used extensively, either individually or together with other soil properties, to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink-swell, and shear strength. The liquid and plastic limits of a soil can be used with the natural water content of the soil to express its relative consistency or liquidity index.

  - Plastic Limit: ASTM D4318

    Significance: see liquid limit.

- Specific Gravity: by pycnometer, ASTM D854; paraffin-coated specimens, ASTM D1188

  Significance: used in calculating the phase relationships of soils (i.e., the relative volumes of solids to water and air in a given volume of soil).

- pH: for uses other than corrosion testing, ASTM D4972

  Significance: useful variable in determining the solubility of soil minerals, and the mobility of ions in the soil.

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Table 3-20 Remedy Screening Analyses

Analyte	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5	Pit 6	CW	BP	Method	ASL	Matrix
Uranium	X	X	X	X	X	X	X	X	3002	B	Leachate
Thorium	X	X	X	X	X	X	X	X	3059	B	Leachate
Radium	X	X	X	X	X	X	X	X	4002	B	Leachate
Technetium	X	X	X	X	X	X	X	X	4007	B	Leachate
Cesium						X	X		4006	B	Leachate
Aluminum	X	X	X	X	X	X	X	X	9043	B	Leachate
Calcium	X	X	X	X	X	X	X	X	9043	B	Leachate
Iron	X	X	X	X	X	X	X	X	9043	B	Leachate
Silicon	X	X	X	X	X	X	X	X	2563	B	Leachate
Magnesium	X	X	X	X	X	X	X	X	9043	B	Leachate
Barium	X	X	X	X	X	X	X	X	9043	B	Leachate
Arsenic					X	X			9074	B	Leachate
Cadmium					X	X			9043	B	Leachate
Lead				X	X	X			9079	B	Leachate
Vanadium			X	X		X			9043	B	Leachate
Fluoride				X					3039	B	Leachate

An analysis of the grain size distribution, specific gravity, Atterberg limits, and Ph results provides information on the similarity of the contents of the various sampling points from the pits. After this first level of characterization, selected materials will be tested for:

- Soil moisture/density relationships (standard proctor): Standard Proctor test, ASTM 698; modified Proctor test, ASTM D1557

  Significance: soil placed as engineering fill is compacted to a dense state to obtain satisfactory engineering properties such as shear strength, compressibility, or permeability. Compaction tests provide the basis for determining the percent compaction and water content needed to achieve the required engineering properties, and for controlling construction to ensure the required compaction and water content are achieved.

- Unconfined compression (as applicable): cohesive soil, ASTM D2166

  Significance: used to quickly obtain the approximate compressive strength of soils that possess sufficient cohesion to permit testing in the unconfined state.

- Shrinkage limit: wax method, ASTM D4943; mercury method, ASTM D427

  Significance: used to evaluate the shrinkage potential, crack development potential, and swell potential of earthwork involving cohesive soils.

- Direct shear: consolidated drained conditions, ASTM D3080

  Significance: used for relatively rapid determination of consolidated drained strength parameters of cohesion and angle of internal friction.

The complete range of tests will be conducted on at least one drum from each of the pits, contingent upon the availability of waste. All baseline characterization testing will be conducted on decanted and/or dried waste.

Table 3-21 shows the suggested physical testing from a level of difficulty point of view. In general, those tests lower on the table require more sophisticated equipment, require more technical expertise

TABLE 3-21 CHARACTERIZATION OF ARCHIVED WASTES

Test Procedure	Sampling Point	Estimated Number of Tests
moisture content	each drum	55
pH	each drum	55
liquid limit	each drum	55**
plastic limit	each drum	55**
sieve analysis	each drum	55
hydrometer analysis	each drum	55**
specific gravity	each pit	5
standard proctor	each pit	5
unconfined compression	each pit	5**, replicate
maximum index density	each pit	5**
minimum index density	each pit	5**
relative density	each pit	5**
shrinkage limit	each pit	5**, replicate
permeability	each pit	5, replicate
direct shear	each pit	5
triaxial shear	each pit	5

** Note: if the test is applicable to the soil type found in the drum.

in conducting the test and in analyzing the results, and would be of more value once the general treatability screening has been accomplished. Those nearer the bottom of the list may be used in the RSP, but will more likely be recommended once a treatment method has been decided upon (beyond remedy screening) and for testing of as-placed waste in the off-site disposal area. These additional tests include:

- Maximum Index Density: cohesionless soils, via vibratory table, ASTM D4253

  Significance: the maximum index density is the reference dry density/unit weight of a soil in the densest state of compactness that can be attained using a standard laboratory compaction procedure that minimizes particle segregation and breakdown.

- Minimum Index Density: cohesionless soils, ASTM D4254

  Significance: the minimum index density is the reference dry density/unit weight of a soil in the loosest state of compactness at which it can be placed using a standard laboratory procedure that prevents bulking and minimizes particle segregation.

- Relative Density Determination: ASTM D4254

  Significance: relative density/unit weight expresses the degree of compactness of a cohesionless soil with respect to the loosest and densest conditions as defined by standard laboratory procedures. Only when viewed against the possible range of variation in terms of relative density/unit weight, can the dry density/unit weight be related to the compaction effort used to place the soil in a compacted fill or indicate volume change and stress-strain tendencies of soil when subjected to external loading.

- Permeability: granular soils, via constant head test, ASTM D2434; cohesive soils, via falling head tests, ALTER LPC #154 (falling head has not been standardized by ASTM)

  Significance: used to establish representative values of the coefficient of permeability of soils.

- Triaxial Shear Test: consolidated undrained, ASTM D4767

  Significance: used to determine shear strength parameters in terms of total stresses (undrained conditions) or effective stresses (drained conditions) for use in stability analyses of embankments, earth pressure calculations, and foundation design.

Chemical and physical characterization data from previous work by Catholic University of America (CUA) and International Technologies (IT) was reviewed prior to the UC/ALTER characterization of Operable Unit 1 wastes.

3.3.3.2 Treatment Process

Characterization of waste forms created by thermal processing, non-thermal processing, and polymer encapsulation will be performed using standard and non standard testing methods. Table 3-22 shows the proposed test matrix which provides a summary of test methods, Analytical Support Levels (ASL), and the maximum number of tests to be performed for each processing method. A modified TCLP leaching test will be used for screening constituents of concern (see Table 3-20) for each separate Operable Unit 1 waste unit. Complete procedures for all assessment testing are provided in Appendix A of the CRSP Treatability Study Work Plan, ALTER Laboratory Procedures Catalog (LPC).

3.3.4 Deviations

None reported to date.

Table 3-22 Remedy Screening Characterization Test Matrix*

(* All values represent maximum number of tests to be performed)

Study/Method	Procedure	Objective/ Intended Use	ASL Level	Thermal Treatment			Non-thermal Treatment*	Poly-ethylene Encap.*
				Drying*	Calcining*	Clinkering*		
Acoustic Testing	ALTER	Determine physical integrity of samples	E					32
Thermogravi-metric Analysis	Perkin-Elmer Manufacturing	Determine temperatures associated with compositional changes	E	12	2	2		
TCLP	Federal Register Volume 51	Determine the leach potential of hazardous materials	B					16
Acidity	Std. Methods 2310	Determine leaching characteristics	B	10	6	6	10	16
Alkalinity	Std. Methods 2320	Determine leaching characteristics	B	10	6	6	10	16
Permeability	ALTER	Determine permeability	C					6
Unconfined Compressive Strength	ASTM C 39-86	Determine strength and physical integrity	B					15
Moisture Content	ASTM D 2216-80 FM-GTT-0021	Determine in situ moisture content	B	6	6	6	55	16

Table 3-22 Remedy Screening Characterization Test Matrix* (Cont.)

(* All values represent maximum number of tests to be performed)

Study/Method	Procedure	Objective/ Intended Use	ASL Level	Thermal Treatment			Non-thermal Treatment	Poly-ethylene Encap.
				Drying	Calcining	Clinkering		
Specific Gravity, Absorption and Voids	ASTM C 642-82	Determine specific gravity, % absorption, and % voids	B			16	17	16
Total Solids	Std. Methods 2540 B	Determine total solids	B					
Wet/Dry	ASTM D 4843 ALTER LPC 152	Wetting and drying test of solid waste	B					16
Freeze/Thaw	ASTM D 4842 ALTER LPC 151	Determination of resistance of solid wastes to freezing and thawing	B					16
Leaching Test	ANS 16.1 ALTER LPC 201	Determination of leaching characteristics of treated wastes	B					16
Soil Classification	ASTM D 2487 FM-GTT-0011	Laboratory classification of soil	B	3			55	
Soil Classification	ASTM D 2844 FM-GTT-0012	Visual classification of soil	B	3	3	3	55	
Preserving and Transporting Soil Samples	ASTM D 4220 FM-GTT-0013	Transportation of samples	B					
Wet Preparation of Soil Samples	ASTM D 2217 FM-GTT-0014	Preparation of samples for particle size analysis and determination of constants	B				55	

Table 3-22 Remedy Screening Characterization Test Matrix* (Cont.)

(* All values represent maximum number of tests to be performed)

Study/Method	Procedure	Objective/ Intended Use	ASL Level	Thermal Treatment			Non-thermal Treatment	Poly-ethylene Encap.
				Drying	Calcining	Clinkering		
Dry Preparation of Soil Samples	ASTM D 421 FM-GTT-0015	Preparation of samples for particle size analysis and determination of constants	B	16	16	16	10	
Moisture Content	ASTM D 4643 FM-GTT-0022	Determine moisture content by microwave	B	9	3	3	55	
Moisture Correction	ASTM D 4718 FM-GTT-0023	Moisture content correction for oversize samples	B					
Specific Gravity	ASTM D 854 FM-GTT-0024	Determination of specific gravity of soils	B	9	9	9	17	
Volume-Weight Relationships	COEEM 1110-2-1906 FM-GTT-0025	Volume-weight relationships	B	6	3	3		
Grain Size Analysis	ASTM D 422 FM-GTT-0031	Particle size analysis of soils	B	6	6	6	55	
Atterberg Limits	ASTM D 4318 FM-GTT-0032	Determination of liquid limit, plastic limit, and plasticity index of soils	B	6	6	6	55	
Shrinkage Limit	ASTM D 427 FM-GTT-0033	Determination of shrinkage factors of soils	B	6	6	6	10	

Table 3-22 Remedy Screening Characterization Test Matrix* (Cont.)

(* All values represent maximum number of tests to be performed)

Study/Method	Procedure	Objective/ Intended Use	ASL Level	Thermal Treatment			Non-thermal Tratment	Poly-ethylene Encap.
				Drying	Calcining	Clinkering		
Standard Proctor	ASTM D 698 FM-GTT-0041	Determination of moisture-density relations of soils and soil-aggregate mixtures	B	3			10	
Modified Proctor	ASTM D 1557 FM-GTT-0042	Determination of moisture-density relations of soils and soil-aggregate mixtures	B					
Maximum (Relative) Density	ASTM D 4253 FM-GTT-0043	Determination of maximum index density of soils	B	5	3	3	5	
Minimum (Relative) Density	ASTM D 4254 FM-GTT-0044	Determination of minimum index density of soils and calculation of relative density	B	5	3	3	5	
Unconfined Compression	ASTM D 2166 FM-GTT-0061	Determination of unconfined compressive strength of cohesive soil	B	10			10	
Direct Shear (Controlled-Displacement Method)	ASTM D 3080 FM-GTT-0062	Shear test of soils under consolidated drained conditions	B	4	4	8	10	
Triaxial Compression (UU)	ASTM D 2850 FM-GTT-0064	Determination of compressive strength of unconsolidated undrained soils	B					
Triaxial Compression (CU)	ASTM D 4767 FM-GTT-0065	Consolidated-undrained triaxial compression test on cohesive soils	B					

Table 3-22 Remedy Screening Characterization Test Matrix* (Cont.)

(* All values represent maximum number of tests to be performed)

Study/Method	Procedure	Objective/ Intended Use	ASL Level	Thermal Treatment			Non-thermal Treatment	Poly-ethylene Encap.
				Drying	Calcining	Clinkering		
Permeability (Constant Head)	ASTM D 2434 FM-GTT-0071	Determination of permeability of granular soils	B	3				
Permeability (Triaxial)	ASTM D 5087 FM-GTT-0072	Determination of hydraulic conductivity of saturated porous materials	B	10			10	
Organic Content	ASTM D 2974 FM-GTT-0084	Determination of moisture, ash, and organic matter of peat and other organic soils	B					
LA Abrasion	ASTM C 131	Determine particle stability	B				5	
TCLP Modified	ALTER	Leaching potential screening	B	9	3	3		

4.0 RESULTS AND DISCUSSION

The treatment technologies investigated in laboratory studies include vitrification, cement solidification, thermal processing, and particle agglomeration. The results from these studies detailed in Section 3.0 are presented here. This section includes a discussion of the waste stream characteristics for each waste pit and how those characteristics may affect the different treatment processes. This section also includes data analysis and interpretation for each of the studies performed. The data in this section is a summary of the data found in Volume II, Appendices A-M. A discussion of the Quality Assurance/Quality Control (QA/QC) for these studies is provided in Section 4.2.

To facilitate evaluation of the different treatment technologies, Section 4.0 is grouped by technology and is organized as follows:

Vitrification

Vitrification Remedy Screening/Remedy Selection Studies;

Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1.

Vitrification Remedy Design - Laboratory Scale;

Work Plan - GTS Duratek/CUA, Nov. 1992, Remedy Design Laboratory Studies, Part I: Vitrification Waste Pit 5 results and preliminary results of studies with Waste Pit 3 and 4 material. Complete results of the Waste Pit 3 and 4 studies will be included in an addendum to this report to be issued in Spring 1994.

Cement Solidification/Stabilization (CSS)

CSS Remedy Screening/Remedy Selection Studies;

Work Plan - IT Corp., Oct. 1990, Treatability Study Work Plan for Operable Unit 1

Thermal Treatment & Particle Agglomeration

Work Plan - University of Cincinnati, Nov. 1993, CRU1 CRSP Work Plan

Only preliminary results on soil classification of the waste pit materials and surrogate studies of particle agglomeration are included in this report. Data on baseline drying studies will be included in an addendum to this report to be issued in Spring 1994.

A change in technical direction was implemented under the new FERMCO site management in December 1992, and drying was added as a primary treatment alternative. Sufficient site historical experience drying process residues over the 40 years of plant operations and extensive use of the various drying technologies throughout industry shows that this treatment alternative is feasible and implementable for the FEMP pit wastes. An OU1 treatability study was initiated in June of 1993 to develop baseline drying information. This treatability study includes baseline crucible drying studies and investigation of agglomeration techniques for the dried waste. The work plan for this study is summarized in Section 3.0. Only preliminary results from this study are included in this report. Baseline crucible and TCLP tests are complete but results are not available as of the date of this report. An addendum to this report will be issued with the results of these studies in Spring 1994.

4.1 DATA ANALYSIS AND INTERPRETATION

This section discusses the waste stream characteristics with discussion of how these characteristics may impact the different treatability options. Data from the treatability studies is also summarized here. The data is presented by treatment technology and then broken out by Waste Pit. The waste pit contents vary greatly from pit to pit and within each pit. The heterogeonity of the waste streams is a major factor in analyzing the applicability of a treatment technology for all or part of the waste pit material.

4.1.1 Analysis of Waste Stream Characteristics

A description of the types of materials which may be found in each of the waste pits is included in Section 1.0. The wide variety of materials disposed of in the waste pits over time show the material to be extremely heterogeneous. The heterogeneity not only makes the material difficult to characterize adequately but also provides a significant challenge in identifying treatment processes

which will be effective for all or most of the material types. The following is a short description of waste stream characteristics which may affect the treatment processes being investigated: vitrification, cement solidification and thermal processing.

Vitrification:

Waste stream characteristics which may affect the vitrification process include the presence of glass-forming and fluxing agents. The waste pits contain significant quantities of calcium which is a fluxing agent. The quantity of silica, a glass-former, varies greatly from pit to pit but generally quantities are low. Large quantities of magnesium fluoride are present in all of the waste pits. The large quantity of fluoride may pose a significant problem when waste is heated to temperatures required for vitrification. Waste Pit 2 contains the most significant quantities of organics. These are not expected to have any significant impact on the vitrification processing. Metals can cause problems in a vitrification process. If they cannot be successfully incorporated within the glass they may sink to the bottom of the melter which can cause shorting out of the melter if the melter is not properly designed. The formulations developed for vitrification will need to be extremely robust and capable of successfully vitrifying material with a wide variety of chemical compositions. The waste pits also contain a large quantity of debris. This debris will need to be segrated and treated separately or size reduced and incorporated within the melt. The radionuclides present in the waste pits should be incorporated within the vitrified product without significant problems in off-gas or leaching.

Cement Solidification:

Characterization of the waste pits has shown that there are a wide variety of chemcial constituents within the waste pits which may act as set retarders or as set accelerators in a waste and cement mix. The effect of each of these is impossible to predict emperically. The organics present in Waste Pit 2 are in small concentrations but may impact the setting of Waste Pit 2 formulations. Uranium and thorium metals are readily incorporated into cement mixtures and, except at extremely high concentrations, should not present a significant leach problem. Technetium-99 (TC-99) and Cesium (Cs) are present in the waste pits. These radionuclides are extremely mobile. Tc-99 is very water soluble and is difficult to retain in a cement mixture without leaching. Other metals, such as arsenic (As) and mercury (Hg), are also difficult to retain within a cement and waste mixture. As with

vitrification, formulations for cement solidification will need to be very robust and capable of handling a potentially wide variation in waste material. Debris also must be removed or size reduced.

Thermal Processing:

Characteristics of the waste pits which may affect thermal processing may vary considerably depending opon the type of equipment used and the drying temperature. For rotary drying at low temperatures, variations in waste contents will have little effect. The calcium content will likely be a processing factor at higher temperatures. The pH of the final waste material will have a significant impact on the leachability of the metals and radionuclides. The presence of fluoride will also be a factor at higher temperatures and may produce hydrogen fluoride gas, which is extremely corrosive. The organics present in the waste pits should not be a significant factor. At lower temperatures they may remain in the waste material. At higher temperatures they would need to be treated in the off-gas stream. Depending upon the type of thermal processing unit and its feed size requirement, the debris may or may not pose a problem.

4.1.2 Analysis of Treatability Study Data

A summary of all of the treatability study data developed to date is included in this section. More detail on these studies may be found in the respective appendices or in reports referenced for these projects. The remaining data from the completion of the GTS Duratek/CUA vitrification studies on material from Waste Pits 3 and 4, and the results of the thermal processing and particle agglomeration studies will be included in an addendum to this report expected to be issued in Spring 1994.

4.1.2.1 Vitrification

Laboratory testing of vitrification as a treatment alternative was performed under three separate work plans as described in Section 3.0. These include the International Technologies Corp (IT). Treatability Study Work Plan, the GTS Duratek Treatability Study Work Plan, and the Minimum Additive Waste Stabilization (MAWS) Work Plan. The IT Corporation studies included crucible tests of waste from Waste Pits 1-6, the Burn Pit, and the Clearwell. The GTS Duratek studies involved more in-depth crucible studies and small melter runs with Waste Pit 5 material only. Studies are underway with Waste Pit 3 and 4 material, but are not yet complete. Only the preliminary results of

the study for Waste Pits 3 and 4 to date are included here. Results from the MAWS program are not included as part of this report, but will be issued as a separate report.

Vitrification Testing - IT Corporation

The overall objective of this treatability testing program was to develop data to assess the applicability of vitrification as a treatment alternative for Operable Unit 1 wastes. The variables considered for evaluation of vitrification were leachability, bulking factor, and physical characteristics (e.g., melt viscosity, "glass-like" final product, crystallinity, porosity, opacity, and texture). These variables were used to determine if a particular reagent mixture could produce an acceptable waste form based on the performance objectives.

The vitrification program consisted of Remedy Screening (preliminary phase), and Remedy Selection (advanced phase) tests of waste from Waste Pits 1 through 6, the Burn Pit, and the Clearwell.

The Remedy Screening study used composite samples. In the Remedy Selection phase, zone (top, middle, and bottom) samples were used for Waste Pits 1 through 4 and Burn Pit, and composite samples for Waste Pits 5, 6 and Clearwell.

In the preliminary vitrification testing, tests were conducted in three stages:

- Characterization of pit waste mineral/metal composition
- Range-finding tests
- Remedy Screening tests

The metals composition of boring composite material from each pit, site soil, and flyash was determined and this information was used to design the initial waste/additive mixtures for the range-finding tests. Initial glass formulations were based on the sodium silicate model with the objectives of greater than 35 percent glass former content with a former to flux ratio of at least 0.5 in each melt.

Formulations were further guided by an attempt to maximize waste loading and minimize the sodium/flux addition while maintaining a viscosity of 20 to 100 poise at a melt temperature of 1250°C.

Thirty-four range-finding tests were performed initially to determine the minimum soil and flyash additions necessary to produce a glass-like product as judged visually. This testing also determined the need for additional sodium/flux to allow vitrification at 1250°C or less.

After evaluation of the range-finding test results, formulations were, if necessary, adjusted for the Remedy Screening stage of the program. Fifty-eight samples were generated during the Remedy Screening testing. During the Remedy Screening tests, each waste/soil and waste/flyash mixture chosen was processed at two different sodium/flux levels to vary viscosity, provide observations on glass processability, and determine the effect of flux concentration on metal leachability during the modified Product Consistency Test (MPCT) and modified Toxicity Characteristic Leaching Procedure (MTCLP) evaluations. Remedy Screening waste/soil and waste/flyash formulations developed in the advanced phase testing were chosen on the following basis:

- Best glass-like appearance
- Acceptable melt viscosity
- Lowest leaching of radionuclides and anions during MPCT and MTCLP leach testing. Figures 4-1 and 4-2 are flowsheets that depict the sequence of activities for the treatability study

An initial complication of this testing program was the detrimental interaction of some waste constituents with the platinum/gold alloy crucibles. Incompletely oxidized organics and base metals in the site flyash produced reductive melts during the vitrification process. This reaction resulted in the formation of platinum/base metal (e.g., iron) alloys with melting points well below the process temperature of 1100 to 1250°C and the consequential destruction of the crucibles. Testing was continued using firebrick crucibles, which allowed the study to continue but introduced the problem of crucible components (e.g., aluminum and silica) being incorporated in glass melts. Some formulations completely fluxed the firebrick, causing crucible etching and meltdown. The greater

Figure 4-1

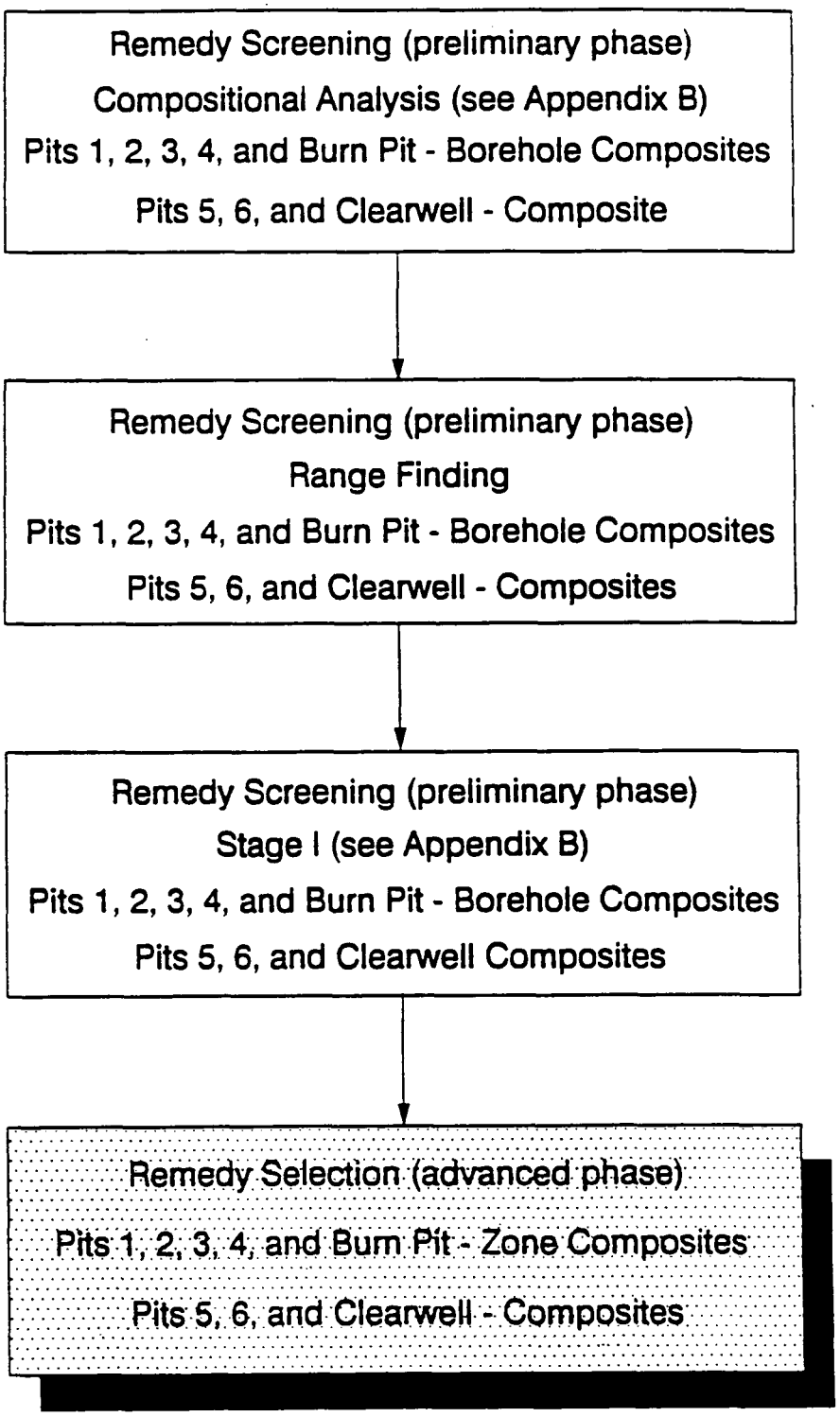
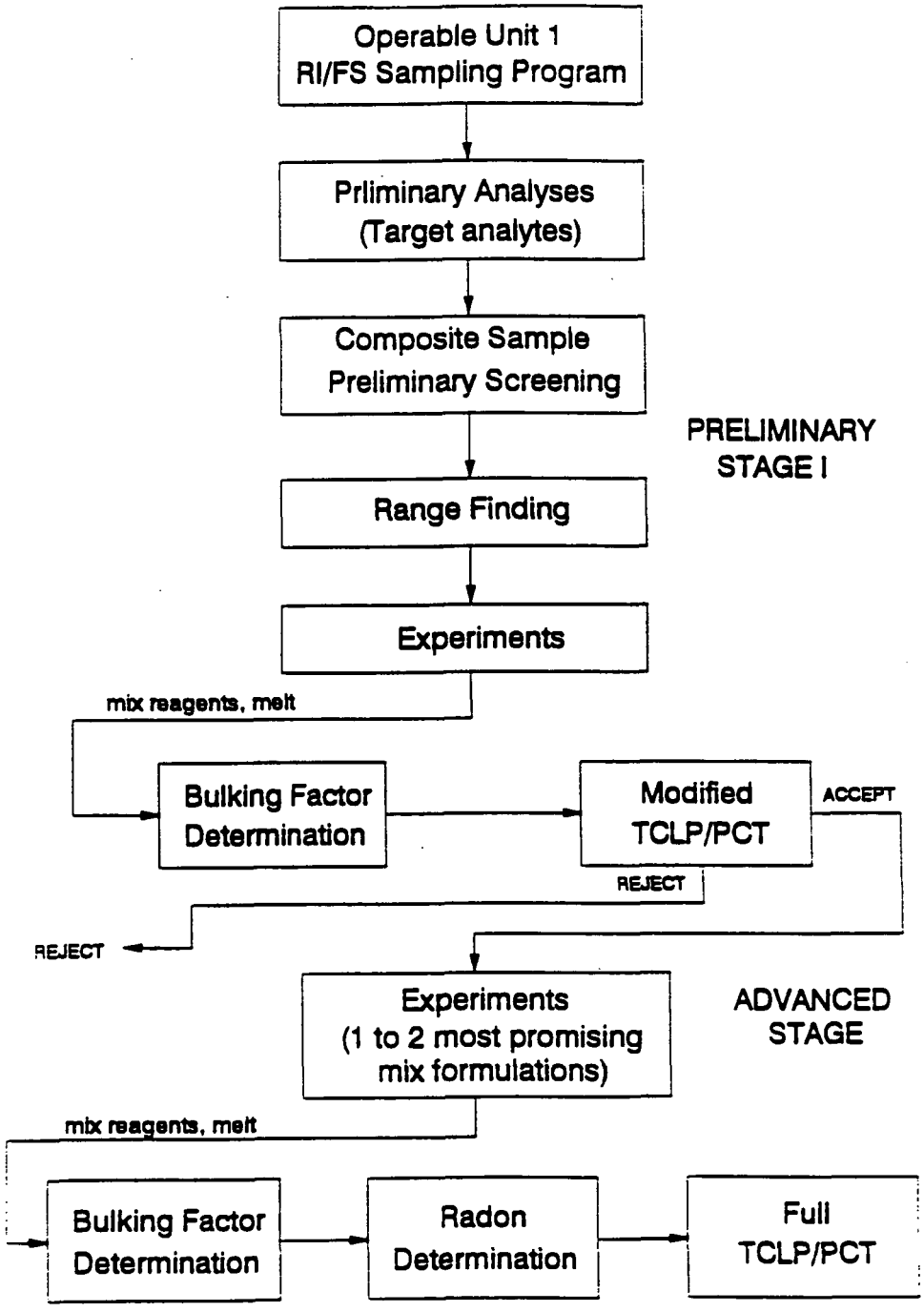

Remedy Screening (preliminary phase)
Compositional Analysis (see Appendix B)
Pits 1, 2, 3, 4, and Burn Pit - Borehole Composites
Pits 5, 6, and Clearwell - Composite
Remedy Screening (preliminary phase)
Range Finding
Pits 1, 2, 3, 4, and Burn Pit - Borehole Composites
Pits 5, 6, and Clearwell - Composites
Remedy Screening (preliminary phase)
Stage I (see Appendix B)
Pits 1, 2, 3, 4, and Burn Pit - Borehole Composites
Pits 5, 6, and Clearwell Composites
Remedy Selection (advanced phase)
Pits 1, 2, 3, 4, and Burn Pit - Zone Composites
Pits 5, 6, and Clearwell - Composites

Figure 4-2


Operable Unit 1
RI/FS Sampling Program
Prliminary Analyses
(Target analytes)
Composite Sample
Preliminary Screening
PRELIMINARY
STAGE I
Range Finding
Experiments
mix reagents, melt
Bulking Factor
Determination
Modified
TCLP/PCT
ACCEPT
REJECT
REJECT
Experiments
(1 to 2 most promising
mix formulations)
ADVANCED
STAGE
mix reagents, melt
Bulking Factor
Determination
Radon
Determination
Full
TCLP/PCT

concentration of glass formers in the resulting melts increased the viscosity, making the molten glass nonpourable. Also, the firebrick crucibles did not free-release the product glasses. In these cases, the sodium/flux additions were increased as necessary to achieve the desired 20 to 100 poise viscosity range, which allowed the molten glasses to be poured into graphite crucibles where the glass would free-release.

Molten viscosities were estimated visually and molten products ranged from very thin pouring liquids to nonpourable monoliths. A scale of five intervals was established as follows:

- V-1: nonpourable at melt temperature; melt remains uniform monolith within crucible when removed from furnace and inverted; estimated as > 100 poise
- V-2: near-pourable at melt temperature; melt deforms when removed from furnace and inverted; may be induced to pour by raising temperature; estimated as approximately 100 poise
- V-3: ideal viscosity; pours freely from crucible at melt temperature; estimated as approximately 70 poise
- V-4: low viscosity; very thin liquid; etches crucible surfaces; estimated as around 20 poise
- V-5: very low viscosity; corrosivity causes crucible damage, dissolution, or meltdown

The color of vitrified samples, while not a direct indicator of the quality of a vitrified product, was also noted. The color of vitrified samples and color changes after their remelting typically highlighted phase separations or incompleteness of vitrification. The range of colors observed were bright yellow, light beige, amber, green, greenish-brown, brown, and black.

Compositional Analyses

The major glass components of the waste, local soil, and local flyash were determined to assist in the formulation development of the various pit wastes and are shown in Table 4-1. In the analysis, all of the metals were assumed to be oxides in their normal highest oxidation state. The normalized

TABLE 4-1

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COMPOSITION of PIT WASTES, SITE SOIL, AND SITE FLYASH

NORMALIZED % METAL OXIDES

CONSTITUENT	PIT 1	PIT 2	PIT 3	PIT 4	PIT 5	PIT 6	BURN PIT	CLEARWELL	SITE FLYASH	SITE SOIL
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.79	13.72	14.74	1.76	3.32	3.32	12.95	6.66	33.01	7.62
As	0.00	0.00	0.00	0.00	0.64	0.00	0.00	0.00	0.00	0.00
Ba	0.03	0.06	0.19	0.08	3.25	0.01	0.07	0.28	0.00	0.00
Be	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	3.67	18.27	16.39	2.46	49.62	24.75	10.79	27.24	1.77	23.01
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.02	0.03	0.03	0.01	0.04	0.02	0.03	0.03	0.00	0.00
Cu	0.00	0.03	0.13	0.01	0.19	0.00	0.01	0.10	0.00	0.00
Fe	0.27	4.55	4.79	0.47	4.65	1.24	5.51	3.01	8.31	3.67
K	0.18	2.93	2.02	0.29	0.86	1.38	3.10	2.56	0.00	0.00
Mg	88.06	9.01	12.95	69.34	18.66	51.96	5.04	5.78	0.96	6.23
Mn	0.16	0.16	1.57	0.28	0.13	0.03	0.13	0.29	0.00	0.00
Mo	0.00	0.00	0.02	0.00	0.40	0.00	0.00	0.00	0.00	0.00
Na	0.18	1.05	1.08	0.20	5.79	0.21	0.97	0.64	0.39	1.43
Ni	0.01	0.03	0.02	0.00	0.02	0.00	0.01	0.01	0.00	0.00
Pb	0.00	0.00	0.05	0.00	0.04	0.00	0.00	0.00	0.00	0.00
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	5.85	49.78	45.33	8.47	9.12	9.89	61.17	53.19	55.55	58.04
Th	0.05	0.06	0.11	0.09	0.08	0.30	0.00	0.00	0.00	0.00
Tl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
U	0.70	0.20	0.34	16.51	0.27	6.76	0.11	0.11	0.00	0.00
V	0.01	0.03	0.14	0.02	2.79	0.08	0.02	0.03	0.00	0.00
Zn	0.00	0.02	0.03	0.01	0.04	0.01	0.02	0.02	0.00	0.00
B	0.01	0.03	0.05	0.01	0.07	0.03	0.05	0.04	0.00	0.00
Li	0.00	0.02	0.02	0.00	0.01	0.02	0.02	0.01	0.00	0.00

METALS AND ANIONS

(Mg/Kg)

CONSTITUENT	PIT 1	PIT 2	PIT 3	PIT 4	PIT 5	PIT 6	BURN PIT	CLEARWELL	SITE FLYASH	SITE SOIL
Al	5549	56820	66030	12020	14810	13470	54760	27840	146000	33600
Ca	34910	102200	99110	22780	298600	135700	61580	153700	10600	137000
Fe	2483	24920	28370	4243	27380	6649	30780	16640	48600	21400
Mg	706500	42510	66110	540900	94750	240400	24270	27540	4836	31300
Na	1732	6073	6753	1924	36150	1187	5767	3729	2430	8830
Si	36360	182100	179300	51230	35900	35460	228400	196300	217000	226000
U	7746	1271	2377	177700	1926	43150	733	740	0	0
OTHER METALS	5167	22010	27869	7957	53440	11915	22745	21753	0	0
Fluoride	187480	7986	17370	185235	6177	155713	4573	6064	2097	5227
Chloride	2838	5378	401	2550	5810	3703	3076	11461	5471	6857
Sulfate	0	0	5852	0	5337	0	0	3501	16467	13566
Phosphate	630	17365	11783	1991	3898	0	6683	3279	3455	10591
Bromide	0	0	0	0	0	0	0	0	0	0
Nitrate	1757	0	0	8045	13617	15050	13546	0	1660	1982
Carbonate	42690	93930	40900	57010	19860	30440	144410	99310	NA	NA

compositional analyses did not take into account the known presence of anions such as fluoride and sulfate. The dry blend formulations of waste and additives were selected for the initial range-finding experiments based on the compositional analyses. Each dry blend formulation was selected so that enough soil or flyash was added to the waste to form a melt with 30 to 60 percent glass formers. The initial range-finding experiments were melts of pit wastes with no additives. These experiments were conducted in platinum/gold alloy crucibles. If the solidified product did not look like a glass, or had obvious crystal in it, or if the crucible became damaged or destroyed during the melt, additional soil or flyash was added to the next range-finding experiment. If the mixture did not melt at 1250°C or if the melt was very viscous, more sodium/flux (e.g., sodium hydroxide or sodium carbonate) was added to the waste.

Compositional analysis was done on the site soil and flyash, as well as the pit wastes. As a vitrification additive, the flyash at 94.98 mole percent glass formers and 5.02 mole percent fluxes is superior to the site soil. While the glass former content of the site soil is significant at 64.20 mole percent, the accompanying 35.80 mole percent fluxes seriously detracts from its usefulness as a vitrification additive. These differences should be kept in mind when reviewing preliminary and advanced phase waste/soil and waste/flyash formulations.

Feed and Reagent Preparation

The pit wastes and additives were dried at 105°C to remove excess water, ground to a powder, and placed in firebrick crucibles. If sodium hydroxide was to be added to the mixture, a solution of the hydroxide was well mixed with the dried waste. The waste and additives were calcined at typically 200, 400, and 750°C to drive off volatile organic compounds (VOC), oxidize remaining organic compounds, and drive off carbonates, nitrate, and water while transforming the waste and additives to oxides. The 200 and 400°C calcination steps were performed for about 2 hours each. The 750°C calcination step normally requires 8 to 12 hours to oxidize the high organic content in the local flyash and in several of the pits. It was critical to destroy (fully oxidize) the organics in the feed to ensure that the melt was not under reducing conditions. Any carbon or other organic remaining in the waste would deplete the melt of oxygen and then start to reduce the iron and other oxides to elemental metals. If metals are reduced in the melt, they may form a lower temperature melting point alloy

with the platinum/gold crucible that would destroy the crucible. Also, reduced metals pool at the bottom of the crucible forming a nonhomogeneous product. This latter situation may lower the chemical and physical durability of the vitrified product.

The calcined wastes and additives were mixed together in the assigned proportions, then ground again to ensure good mixing because minimal stirring would occur during each melt. This well-blended mixture was then added to the platinum/gold crucibles.

Crucibles

Three types of crucibles were used during the Remedy Screening studies: platinum/gold, firebrick (alumino-silicate), and stainless steel crucibles. The platinum/gold were used in the initial range-finding experiments and were planned for use later to prepare samples that would undergo leaching tests. These crucibles are nonwetting to silicate glasses, allowing all of the solidified product to be removed from the crucible and no intrusion of crucible material into the vitrified product. Firebrick crucibles were used to minimize the potential for damage in using the very expensive platinum/gold crucibles. These crucibles, when used at melt temperatures, contributed significant amounts of glass formers (e.g., silica and aluminum) into the processed melts. Such intrusions of glass formers produced a more durable glass product and a higher viscosity melt than the equivalent formulation would have in a platinum/gold crucible. The stainless steel crucibles were used after the degradation of the platinum/gold crucibles was observed in the presence of local flyash.

Performing Melts

The melts were performed on the calcined feeds in a preheated Lindberg Model 51333 box furnace at 1250°C for 4 hours. The melts were stirred with an Inconel wire after 2 to 3 hours in the oven. Mixing the viscous liquid was critical to ensure that a homogeneous product was produced. After 4 hours in the furnace, the molten samples were removed from the ovens and allowed to cool rapidly. To minimize the potential for crystal growth in the product, the temperature of the melt was ramped down from 1250 to about 600°C in 20 minutes while the crucibles remained in the furnace.
The glass product was ground in a Tekmar mill or a Brinkman centrifugal grinder for size reduction for the MPCT and MTCLP leaching tests. The 10 to 200 mesh (75 to 150 microns) size fraction was

used for the modified PCT while the less than 75 micron size fraction was used for the modified TCLP. Using this very fine size fraction, with its very high surface area, for the MTCLP testing provided a much more aggressive evaluation of weak acid leachability than the standard <9.5 millimeter (mm) TCLP size criterion. This procedure provided a more sensitive screening of the leachability of the glass formulations.

As the first step in the remedy screening testing, thirty-four range-finding experiments were carried out to evaluate: (1) the ability of waste material from each pit to vitrify on its own, (2) the need for additional flux (e.g., sodium hydroxide) to produce melts at 1250°C or less, and (3) to show the possible loadings and resulting product character for mixtures of pit waste plus site soil or flyash (Operable Unit 2). Based on the formulations developed in the initial range finding experiments, an additional 58 samples were generated during the Remedy Screening testing. These samples were evaluated visually and then subjected to modified PCT and TCLP to determine the metal, radiological, and anion leachability performance of each formulation. The visual (physical characteristics) parameters that determined if the formulation produced an acceptable waste form were: melt viscosity (pourable), "glass-like" final product, nonporous, color, reactivity with the crucible, and homogeneity of the melt (single phase).

More detailed results of the Remedy Screening tests are presented in Appendix B. Generally, addition of flyash or soil, as compared with vitrification of the waste without additives, decreased the leachability of uranium. There is an apparent trend to adding flyash to achieve lower leachability of uranium as compared to adding soil. Increasing the sodium added with the flyash generally increases the leaching of uranium. However, with samples made with soil from Waste Pits 1, 4, and 6, the leachability of uranium decreased for formulations using the higher loadings of sodium. None of the other metals, except barium, leached in sufficient quantities to present a problem. Barium leached in sufficient quantities to provide trends. Barium leaching in Waste Pits 1 through 6 supported the previously stated trend that increased sodium loadings increased leaching in uranium. This trend was true with both flyash and soil additions. In the Burn Pit and Clearwell, no barium leaching trends could be established as a function of formulation.

The best preliminary phase formulations were carried forward into the Remedy Selection phase testing. The formulations were tested on samples taken from the top, middle, and bottom zones of Waste Pits 1 through 4 and Burn Pit, and from composite samples from Waste Pits 5, 6 and the Clearwell. The formulations used for the Remedy Selection phase are presented in Table 4-2. The 43 samples generated during the advanced phase were subjected to full-scale TCLP, PCT, and radon analysis. The data from these analyses are presented in this section.

Leach Testing

TCLP - Full TCLP analysis was performed for the remedy selection phase. Results are included for metals and radionuclides. No organics were detected in any of the TCLP leachates. Results are presented in dilution adjusted concentrations. Results were multiplied by a dilution factor, defined as the weight of a treated sample divided by the weight of the raw waste that went into the treated sample. For some vitrification samples, the dilution factor was less than 1. In these cases, a dilution factor of 1 was used.

PCT - The Savannah River Product Consistency Test was performed. The PCT is a static 7 day leach test for waste glass which compares the normalized leach rate for glass components to a standard reference glass. The leachate data for the metals of interest to vitrification (aluminum [Al], boron [B], lithium [Li], potassium [K], magnesium [Mg], sodium [Na], silicon [Si] and uranium [U]) were used to calculate a normalized leach rate and are expressed as a percentage of the Savannah River High Level Waste Criteria (SRHLWC). The waste/soil glasses underwent compositional analysis that allowed the Normalized Leach Rate (NLR) to be calculated for each zone. The waste/flyash glass compositions were derived by calculation and their NLRs are presented as averages for the three pit zones.

Radon Emissions - The radon leach testing and radon emenation testing were performed on the vitrified samples. The radon results were multiplied by the reagent dilution factor so the results were expressed relative to the actual amount of pit waste in the vitrified sample. The results in these figures were based on the average result of measurements made on a test specimen from each zone of the pit. It was not possible to draw any conclusions regarding the effectiveness of one vitrification

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VITRIFICATION
ADVANCED PHASE FORMULATIONS
FOR FERNALD OPERABLE UNIT 1

Pit	Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	1	100	150	-	13
1	2	100	-	199	8
2	1	100	50	-	4
2	2	100	-	100	18
3	1	100	100	-	5
3	2	100	-	100	16
4	1	100	150	-	13
4	2	100	-	200	18
5	1	100	299	-	35
5	2	100	-	299	100
6	1	100	175	-	14
6	2	100	-	200	20
Burn	1	100	50	-	4
Burn	2	100	-	-	8
Clearwell	1	100	50	-	16
Clearwell	2	100	-	100	20

Note: All quantities are normalized to express quantities of reagents in grams per 100 grams of waste. Waste weights are after drying to remove moisture.

formulation versus the other because irregular pieces of glass were used for the radon emission tests, and the amount of radon released was a function of the surface area of the glass. With smaller pieces, a higher rate per unit weight would result. This factor also explains why the leach rates were lower than the emanation rates. Larger pieces were used in the emanation experiment, and so higher rates resulted. Rates for both leaching and emenation in air were lower than the calculated rates and the rates measured from the raw waste.

Physical Characterization - In the descriptions of the vitrified pit products that follow, a consistent vocabulary has been used to describe their individual physical texture. The purpose of such descriptions is to locate each product along the scales of increasingly glass-like character and processable viscosity. The terms "charred/charcoal-like," "crystalline," "granite-like," "porcelain," and "glass/vitreous" are descriptors used for describing physical texture. Further definitions are given as follows:

- Charred/charcoal-like: appears charred with cracks, holes, or fissures; spongy texture with no significant volume reduction; very porous
- Crystalline: exhibits minute crystals or flakes; friable into powder; rounded edges on fragments; porous
- Granite-like: surface rough to touch; breaks into powder; appears fairly porous
- Porcelain: exhibits smooth surface; fragments into chunks but does not powder; nonporous; may exhibit slag-like features and entrapped gas bubbles
- Glass/Vitreous: exhibits high glossy, smooth surface; fragments into slivers/shards with sharp edges; very nonporous; translucent

Vitrification Testing - GTS Duratek/Catholic University of America

Additional vitrification laboratory testing was performed by GTS Duratek/CUA to develop a better database to assess vitrification as a treatment process. Work was performed using material from Waste Pit 5. This work as described in Section 3.0 included additional crucible melts, analysis of process variables, and small 10 kg melter runs. Work is currently underway to develop the same information database on materials from Waste Pits 3 and 4. The final results of the laboratory studies

on Waste Pit 5 material are included in the Waste Pit 5 section of this report. The results available to date on work with Waste Pit 3 and 4 material is presented in the Waste Pit 4 section of this report.

WASTE PIT 1

Compositional Analysis

As vitrification feed material, Waste Pit 1 contains only 6.76 mole percent glass formers and 93.24 mole percent flux. The former/flux ratio is only 0.073, significantly less than the desired 0.5 or greater. Additionally, compositional data reveal the presence of Resource Conservation and Recovery Act (RCRA) metals, uranium, and thorium at levels that might result in significant leaching in poor glass formulations.

Range-Finding Tests

Initial testing generated five samples that evaluated the performance of Waste Pit 1 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-3.

The as-is formulation (P1-1) melt resulted in a highly viscous (V-1), multi-phasic, granite-like material with trapped gas bubbles near the top. Addition of sodium/flux was thus recommended in the Remedy Screening formulations to reduce the viscosity and allow more homogeneous processing.

The two waste/soil formulations (P1-2 and P1-3) exhibited good melt viscosities (V-3/V-4) and different products at their lower and higher soil loadings. The lower soil formulation (P1-2) resulted in a granite-like product while P1-3, the higher soil formulation, produced an excellent glass. The Remedy Screening waste/soil formulations would reduce the sodium/flux loading to determine its effect on producing a homogeneous, vitreous product.

The two waste/flyash formulations (P1-4 and P1-5) differed in their flyash and sodium/flux loadings and produced significantly different products. The P1-4 melt had a high viscosity (V-3) and cooled to a slag-like material with streaked inner layers. The P1-5 melt had a lower viscosity (V-3/V-4), was pourable, and cooled to a low gloss glass. The latter formulation was superior because of its

PIT 1
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P1-1 10500301	100	0	0	0	V-1	Multi-phase, granite-like with entrapped gas bubbles
(Soil) P1-2 10501301	100	100	0	5.0	V-3/V-4	Granite-like product
(Soil) P1-3 10501501	100	150	0	5.0	V-3/V-4	Homogeneous, vitreous product
(Flyash) P1-4 10501901	100	0	150	5.0	V-3/V-4	Slag-like material with streaked inner layers
(Flyash) P1-5 10502501	100	0	200	0	V-3/V-4	Low gloss, vitreous product

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

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PIT 1
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P1-6 10503001	100	0	0	5.2	V-5 (melt down)	Non-vitreous, porous	NA[d]
(As-Is) P1-7 10502901	100	0	0	8.5	V-5 (melt down)	Vitreous	NA
(As-Is) P1-8 10503201	100	0	0	2.1	V-5 (melt down)	Non-vitreous, tan, porous	NA
(As-Is) P1-9 10503207	100	0	0	0	V-5 (melt down)	Non-vitreous, tan, porous	NA
(Soil) P1-10 10502601	100	150	0	5.0	V-3	Non-porous, dual phase	122 F, 148 Na (PCT)
(Soil) P1-11 10502701	100	150	0	2.6	V-3	Non-porous, near-vitreous	51 F, 25 Si (PCT)
(Flyash) P1-12 10502801	100	0	150	3.2	V-3/V-4	Black glass with yellow inclusions	1.0 U (MTCLP)
(Flyash) P1-13 10503002	100	0	200	5.0	V-3/V-4	Non-porous, granular/crystalline	1.5 U (MTCLP)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d]Not Analyzed.

increased contribution of glass formers with the flyash and probably because the flyash used was preroasted, allowing for a more oxidative melt. Apparently the sodium/flux loading in P1-4 was not able to overcome the adverse effects of the uncalcined flyash. The flyash formulations in the Remedy Screening retested these flyash loadings with higher and lower sodium/flux loadings.

Remedy Screening Tests

This second round of testing of pit wastes generated eight samples that further refined the evaluation of soil, flyash and sodium/flux additives. Table 4-3 presents these formulations.

Four experiments with the waste-only formulation were performed using increasing loadings of sodium/flux to reduce the high melt viscosity. Products ranging from porous to completely vitreous resulted, all with very low viscosities and all resulting in crucible meltdown. These results reflect the inherent low glass former, high flux content, and the corrosivity such a composition becomes under molten conditions. The melting points of a significant portion of the waste's constituents (e.g.,(MgF_2), (MgO), and (CaO) all exceed 1250°C and may not have vitrified even with additional sodium flux. No leach tests were performed on these products.

Two waste/soil formulations also were tested (P1-10 and P1-11), repeating P1-5 formulation in one and in the other reducing the sodium/flux addition by half. The original formulation produced a better appearing glass, single phase, and less brittle. Neither formulation leached uranium nor gross alpha/beta in the MPCT and MTCLP tests, but the better appearing glass leached higher sodium and fluorine in the MPCT (122 parts per million [ppm] fluorine; 148 ppm sodium). P1-10 was deemed an overall better glass and the formulation was developed in the advanced phase testing.

Two waste/flyash formulations (P1-12 and P1-13) further evaluated the range-finding formulations. The P1-12 formulation produced a pourable melt (V-3/V-4), which cooled to a good quality black glass with some yellow phase separated inclusions. The P1-13 formulation produced a slightly more viscous melt that cooled to a vitreous, near-crystalline glass with granulated streaks running through it. Both formulations performed well in the leach tests, neither leaching significant radionuclides or RCRA metals. P1-12 leached 1.5 ppm uranium in the MTCLP while P1-13 leached 1.0 ppm

uranium in the MTCLP. The lower sodium/flux formulation P1-12 was chosen for testing in the advanced phase. The sodium level was lowered for the advanced phase testing, in the belief that it might further reduce leaching of uranium.

Remedy Selection Tests

The formulations used on each zone in the advanced phase experiments are given in Tables 4-4. Table 4-5 summarizes the bulking factors. The melts had high viscosities that trapped bubbles in them when cooled. The products ranged from granite-like to semi-crystalline, and ranged in color from black to tan. The bulking factors ranged from -2.6 to 84 percent.

Results for the Waste Pit 1 vitrification TCLP radionuclides for the two formulations are shown in Table 4-6. The metals in the TCLP leachates from untreated characterization samples and the waste treated with the two vitrification formulations, and the TC criteria for metals are shown in Figure 4-7. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds.

The results of the PCT are presented in Table 4-8 and show that generally the flyash formulation was less leachable than the soil formulation. The soil formulation exceeded the SRHLWC for boron. The majority of metals leached at less than 6 percent. Uniformly the worst performers were sodium and potassium at 14 to 73 percent and 0.2 to 20 percent of the SRHLWC, respectively. The Zone 3 duplicate sample performed at the 73 percent level. The waste/flyash product had the lowest overall NLR for the Pit 1 waste.

Waste Pit 1 Vitrification - Radon Emissions

Results of radon emissions testing is given in Figures 4-3 and 4-4. These figures show that vitrification was effective in reducing the radon emissions.

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TABLE 4-4

VITRIFICATION--PIT 1
ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	150	0	13
2	100	0	199	8

Note: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste weights are after drying to remove moisture.

TABLE 4-5

VITRIFICATION--PIT 1-ADVANCED PHASE
BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
1	1	72	49
1	1	22	
2	1	60	
2	1	-2.6	
3	1	64	
3	1	3	
1	2	51	
1	2	82	
2	2	50	
2	2	84	
3	2	50	
3	2	53	

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TABLE 4-6

WASTE PIT 1 VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION +

	Raw Waste Characterization* (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	ND	27.874	ND
Radium-226	83.500	4.366	5.614
Radium-228	27.300	24.450	ND
Strontium-90	7.290	14.039	ND
Technetium-99	35.350	33.120	ND
Thorium-228	ND	1.610	4.435
Thorium-230	ND	22.312	36.495
Thorium-232	ND	0.567	0.662
Uranium-234	3990.000	707.903	12.659
Uranium-235/236	247.000	43.494	1.766
Uranium-238	4910.000	903.992	20.288
	Raw Waste Characterization (mg/l)	**Formula 1 (mg/l)**	**Formula 2 (mg/l)**
Thorium (Total)	ND	0.006	0.025
Uranium (Total)	7.381	2.710	0.060

\+ Dilution Adjusted Concentration -
The results for treatability samples were multiplied by a dilution factor, defined as the weight of a treated sample divided by the weight of the raw waste that went into the treated sample. For some vitrification samples, the dilution factor was less than 1. In these cases, a dilution factor of 1 was used.

* TCLP results on similar raw waste samples provided for relative comparison purposes only. Results are from samples taken form the same borehole and same zone as treatability samples but are not identical.

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TABLE 4-7

WASTE PIT 1 VITRIFICATION TCLP METALS
DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.055	0.007	ND	
Arsenic	0.003	0.048	0.005	5.000
Barium	1.562	0.271	0.320	100.000
Beryllium	0.007	0.009	ND	
Boron	ND	0.799	0.257	
Cadmium	0.008	ND	ND	1.000
Chromium	0.100	0.090	ND	5.000
Cobalt	0.022	0.085	ND	
Copper	0.048	0.158	0.034	
Cyanide	ND	ND	ND	
Lead	0.005	0.006	0.011	5.000
Manganese	0.213	3.448	0.050	
Mercury	ND	ND	ND	0.200
Molybdenum	0.027	0.348	ND	
Nickel	0.121	0.026	ND	
Selenium	0.002	ND	ND	1.000
Silver	0.080	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.048	0.142	ND	
Zinc	0.086	0.399	9.194	

TABLE 4-8

PIT 1 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	1	0.4	0.001	37	2.2	0.04	Not Calc'd	6	253
1	2	0.4	0.009	28	2.2	0.07	Not Calc'd	0.5	Not Calc'd
1	3	0.1	0.2	14	0.6	0.09	Not Calc'd	0.2	Not Calc'd
1	3	1.4	0.001	73	3.9	1	Not Calc'd	20.0	>500
2	Average	0.25	0.13	21	0.6	Not Calc'd	Not Calc'd	18	40

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

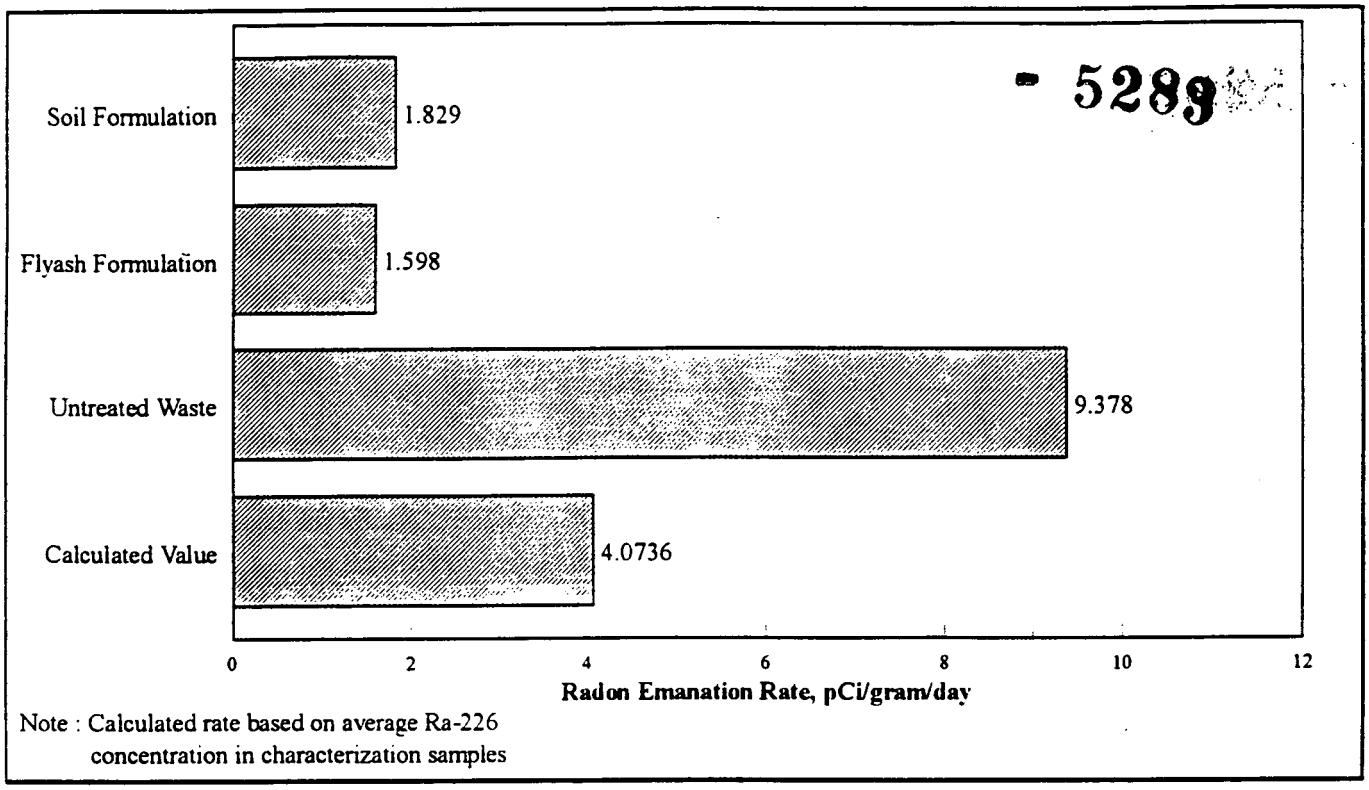

FIGURE 4-3 - PIT 1 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

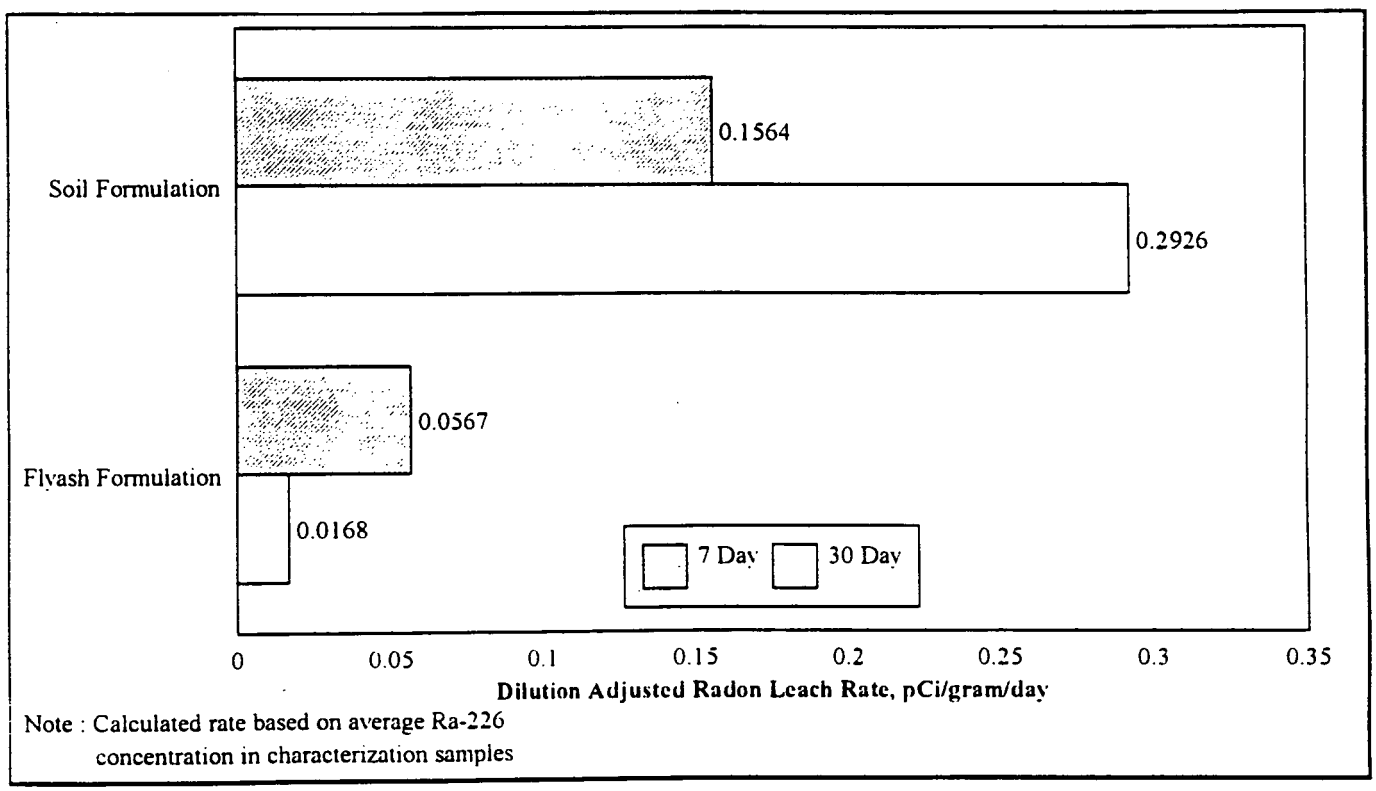

FIGURE 4-4 PIT 1 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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WASTE PIT 2

Compositional Analysis

As vitrification feed material, Waste Pit 2 contains 65.67 mole percent glass formers and 34.33 mole percent flux. The former/flux ratio is 1.913 and satisfies the desired 0.5 or greater target. Additionally, compositional data reveal the presence of chromium (Cr), uranium (U), and thorium (Th) at levels that might result in significant leaching in poor glass formulations.

Range-Finding Tests

Initial testing generated five samples that evaluated the performance of Waste Pit 2 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-9.

The as-is Waste Pit 2 waste (P2-2) melt resulted in a pourable melt (V-3/V-4) that was heterogeneous in character, with vitreous, slag, and porcelain phases. Addition of sodium/flux in the Remedy Screening formulations was recommended to reduce the viscosity and allow more homogeneous processing.

The two waste/soil formulations (P2-2 and P2-3) both produced pourable melts that cooled into excellent glasses. There was only a slight difference in viscosity for P2-3, the lower soil loading. Remedy Screening tests of waste/soil formulations would investigate reduced soil and flux loadings.

The two waste/flyash formulations (P2-4 and P2-5) produced high viscosity melts that cooled into near-vitreous, to slag-like products. P2-5 appeared to be the better glass, homogeneous and glossy, but nonpourable. Remedy Screening tests investigated the potential improvement in viscosity of several different levels of sodium/flux addition.

Remedy Screening Tests

This second round of testing generated seven samples that further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-9 presents these formulations.

PIT 2
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P2-1 10501201	100	0	0	0	V-3/V-4	Vitreous, slag and porcelain
(Soil) P2-2 10501302	100	100	0	5.0	V-3	Good glass product
(Soil) P2-3 10501502	100	50	0	5.0	V-3	Good glass product
(Flyash) P2-4 10501902	100	0	50	5.0	V-2	Near-vitreous, slag-like
(Flyash) P2-5 10502502	100	0	100	0	V-1	Vitreous but non-pourable

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

PIT 2
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P2-6 10502902	100	0	0	7.7	V-3	Single phase glass	NA[d]
(Soil) P2-7 10502602	100	50	0	5.2	V-3/V-4	Single phase glass	9.3 U (MTCLP)
(Soil) P2-8 10502702	100	50	0	2.6	V-3/V-4	Single phase glass	1.2 U (MTCLP)
(Flyash) P2-9 10502802	100	0	100	5.2	V-1	Near-vitreous, slag-like	NA
(Flyash) P2-10 10503003	100	0	100	7.0	V-1	Glossy, vitreous	NA
(Flysah) P2-11 10503004	100	0	100	8.3	V-2/V-3	Good vitreous product	0.3 U (MTCLP)
(Flyash) P2-12 10503202	100	0	100	7.7	V-2/V-3	Good vitreous product	4.0 U (MTCLP)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d] Not analyzed.

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Refinement of the as-is formulation required one additional test (P2-6) to produce a low viscosity melt and good quality glass. A 7.7 percent addition of sodium oxide helped to transform the previously observed multi-phasic (vitreous/slag/porcelain) P2-1 product into a single-phase, homogeneous glass.

Two waste/soil formulations were tested (P2-7 and P2-8), repeating the P2-3 formulation in P2-7, and in P2-8, reducing the sodium/flux addition by half. Both formulations produced single-phase, vitreous products of low to medium viscosity. The leach test performances of these formulations differed only in leachable uranium, 9.3 ppm for P2-7 and 1.2 ppm for P2-8. Leachable gross alpha/beta, metals, and anions were all at low ppm to nondetectable levels. The low flux formulation (P2-8) was chosen for use in the advanced phase testing due to its reduced leachable uranium performance.

Four experiments were performed with waste/flyash mixtures to refine the P2-5 range-finding formulation. Sodium/flux additions at 5.2 percent, 7 percent, 7.7 percent, and 8.3 percent were tested. At 5.2 percent and 7 percent additions, very high viscosity (V-1) melts were produced that cooled into either a near-vitreous, slag-like material (P2-9) or a glossy, nonporous, single-phase monolith. At 7.7 percent and 8.3 percent flux addition, melt viscosity reduced to pourable (V-2/V-3) and achieved a glossy black vitreous character. The two glass samples taken through leach testing (P2-11 and P2-12) both leached small amounts of uranium (0.3 to 0.4 ppm) in the MTCLP but only low to nondetectable gross alpha/beta, metals, and anions. Due to its processable viscosity and satisfactory character as a glass, the 8.3 percent sodium/flux addition formulation (P2-11) was chosen for use in the advanced phase waste/flyash testing.

Remedy Selection Tests

The advanced phase Waste Pit 2 zone samples used the formulations listed in Table 4-10. The soil formulation, Formulation 1, produced a black, nonporous glass of pourable melt viscosity with the Zone 1 material but was less effective on waste from the other zones. With Zones 2 and 3, a high viscosity melt was produced that cooled to a multi-phase, nonporous material, which upon remelting became a more homogenous, better quality glass. Apparently, the heterogeneity of zone composition

requires a longer processing period to produce the kind of glass observed in the remedy screening tests using this soil formulation. The bulking factor of these glasses was uniformly negative, from -47 to -66 percent, indicating substantial volume reduction after processing. Refer to Table 4-11.

The flyash formulation, Formulation 2, produced low to high viscosity melts across the three zones, resulting in products of nonporous, semivitreous character. The Zone 3 glass exhibited a slag-like cap with entrapped gas bubbles as was observed during remedy screening tests (e.g., Sample No. 10501902). Resolution of this slag problem might require a higher sodium/flux loading for the Zone 3 material. The bulking factors for these waste/flyash products was uniformly negative, from -20 to -48 percent, which shows less volume reduction than with the waste/soil glasses.

Results for Waste Pit 2 TCLP radionuclides for the two formulations are shown in Table 4-12. The metals in the TCLP leachates for the waste treated with the two formulations and the TC criteria for metals are shown in Table 4-13. Both formulations pass the TC regulatory criteria. Formula 1 performs slightly better than Formula 2 for inorganic compounds. The leachability of radionuclides varied greatly. Formula 1 had better results for uranium (except for U-235/236)and Th-total. Formula 2 had better results than Formula 1 for Ra-226, Ra-228, Th-228, and Th-230.

The results of the PCT analysis in Table 4-14 show that the soil formulations prepared for each zone performed very well. Their NLRs were all below 1 percent of the SRHLWC except for sodium (Na), which did not exceed 2 percent of the SRHLWC. The waste/flyash glass average NLRs were all below 1 percent except for Na and B at 34 and 29 percent, respectively, of the SRHLWC. The waste/soil product had the lowest overall NLR for the Pit 2 waste. These very low values for the NLRs lend confidence to the durability of all the Pit 2 vitrified products.

Waste Pit 2 Vitrification - Radon Emissions

Figures 4-5 and 4-6 both show that vitrification was very effective in lowering the radon leach and emanation rates. Even though Formulation 1 appeared to be slightly more effective, the highest measured treated rate was approximately 1 percent of the untreated waste.

TABLE 4-10

VITRIFICATION--PIT 2
ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	50	0	4
2	100	0	100	18

TABLE 4-11

VITRIFICATION--PIT 2
ADVANCED PHASE
BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
1	1	-47	-48
2	1	-66	
3	1	-65	
1	2	-20	
2	2	-41	
2	2	-47	
3	2	-48	

TABLE 4-12

WASTE PIT 2 VITRIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	ND	ND	ND
Plutonium-238	ND	0.990	0.510
Plutonium-239/240	ND	1.290	0.990
Radium-226	13.180	171.370	33.620
Radium-228	3.510	35.450	ND
Ruthenium-106	ND	ND	ND
Strontium-90	ND	ND	ND
Technetium-99	67.600	ND	ND
Thorium-228	1.690	3.840	2.390
Thorium-230	1.780	95.840	31.940
Thorium-232	ND	2.750	1.430
Uranium-234	61.710	41.380	42.950
Uranium-235/236	13.500	2.390	1.700
Uranium-238	112.170	45.430	55.250
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	0.010	0.030	0.010
Uranium (Total)	0.050	0.140	0.170

TABLE 4-13

WASTE PIT 2 VITRIFICATION TCLP METALS
DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.156	ND	0.005	
Arsenic	0.600	0.014	0.024	5.000
Barium	0.048	0.256	0.233	100.000
Beryllium	0.004	ND	0.003	
Boron	0.569	0.184	0.185	
Cadmium	0.028	ND	ND	
Chromium	0.077	0.058	0.016	5.000
Cobalt	1.913	0.043	0.054	
Copper	0.244	0.042	0.041	
Cyanide	ND	ND	ND	
Lead	0.006	0.014	0.008	5.000
Manganese	5.215	0.154	0.309	
Mercury	ND	ND	ND	0.200
Molybdenum	0.235	0.026	0.018	
Nickel	2.181	0.110	0.114	
Selenium	0.025	ND	0.003	1.000
Silicon	29.650	8.099	84.293	
Silver	0.052	ND	ND	5.000
Thallium	0.008	ND	ND	
Vanadium	0.429	0.029	0.028	
Zinc	0.134	0.122	0.148	

TABLE 4-14

PIT 2 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	1	0.2	0.004	2	0.8	0.05	0	0.8	13
1	2	0.2	0.01	2	0.9	0.2	Not Calc'd	0.6	Not Calc'd
1	3	0.3	0.003	1	0.8	0	Not Calc'd	0.4	Not Calc'd
2	Average	0.5	0.01	34	0.6	Not Calc'd	Not Calc'd	1	29

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

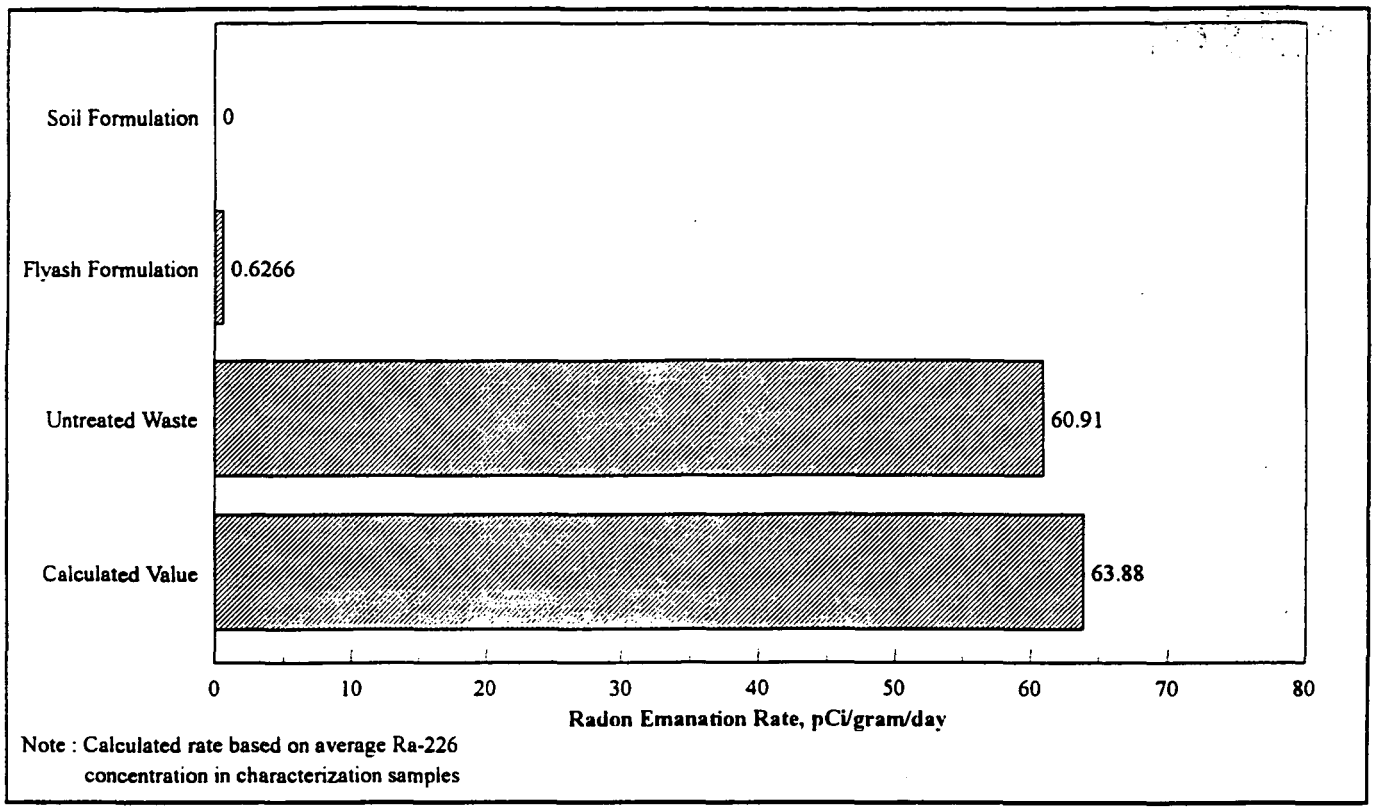

FIGURE 4-5 - PIT 2 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

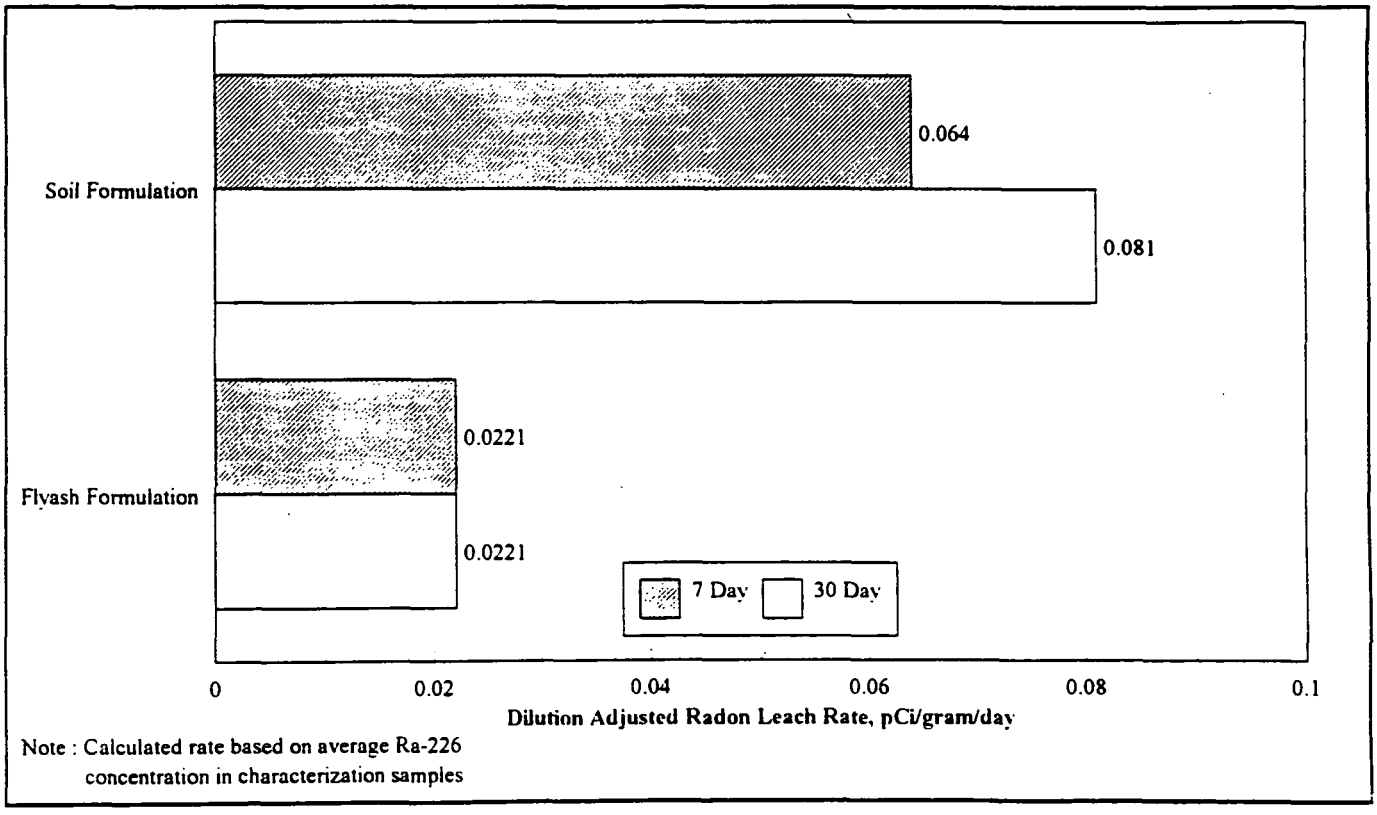

FIGURE 4-6 - PIT 2 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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WASTE PIT 3

Compositional Analysis

As vitrification feed material, Waste Pit 3 contains 48.22 mole percent glass formers and 51.78 mole percent flux. The former/flux ratio is 0.931 and satisfies the desired 0.5 or greater target. Additionally, compositional data reveal the presence of RCRA metals, uranium, and thorium at levels that might result in significant leaching in poor glass formulations.

Range-Finding Tests

Initial testing generated five samples that evaluated the performance of Waste Pit 3 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-15.

The as-is pit waste (P3-1) generated a low viscosity melt but cooled to a fused but nonvitreous granite-like mass with some visible crystals. Addition of sodium/flux in the Remedy Screening formulations was recommended to reduce the viscosity and allow more homogeneous processing.

Two waste/soil formulations (P3-2 and P3-3) produced low viscosity melts that cooled into excellent dark amber glasses. The higher waste loading formulation (P3-2) would be developed in Remedy Screening and the effect of reduction in sodium/flux addition evaluated.

Two waste/flyash formulations (P3-4 and P3-5) produced excellent glass phases with widely differing melt viscosity. P3-4 melted to a good pourable viscosity (V-3) and cooled into a homogeneous dark amber glass, while P3-5 melted into a nonpourable (V-1) glass with slag-like cap entrapping bubble pockets. Considering the combined sources and proportions of glass formers (waste and flyash) and fluxes (waste, flyash, and sodium addition) in each of these formulations, both exceed the 0.5 former/flux ratio, yet P3-5 lacks sufficient flux to lower melt viscosity. P3-5 was developed in Remedy Screening with various levels of flux added to enhance processability.

Remedy Screening Tests

This round of testing generated six samples that further refined the evaluation of soil, flyash, and

PIT 3
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P3-1 10500501	100	0	0	0	V-3	Fused, non-vitreous product
(Soil) P3-2 10501303	100	100	0	5.0	V-2/V-3	Good vitreous product
(Soil) P3-3 10501503	100	50	0	5.0	V-2/V-3	Good vitreous product
(Flyash) P3-4 10501903	100	0	50	5.0	V-3	Good vitreous product
(Flyash) P3-5 10502503	100	0	100	0	V-1	Vitreous with slag-like cap

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

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PIT 3
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P3-6 10502903	100	0	0	7.4	V-3/V-4	Near-vitreous, porcelain-like	3.3 U (MTCLP); 53 Na, 35 F (PCT)
(Soil) P3-7 10502603	100	50	0	5.2	V-2/V-3	Good vitreous product	5.9 U (MTCLP)
(Soil) P3-8 10502703	100	50	0	2.6	V-3	Good vitreous product	4.3 U (MTCLP)
(Flyash) P3-9 10502803	100	0	100	2.6	V-3/V-4	Near-vitreous porcelain	NA[d]
(Flyash) P3-11 10503005	100	0	100	7.0	V-3/V-4	Vitreous with crystals	0 U (MTCLP)
(Flyash) P3-12 10503006	100	0	100	7.5	V-2/V-3	Good vitreous product	0.5 U (MTCLP)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d]Not analyzed.

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sodium/flux additives. Table 4-15 presents these formulations.

One as-is vitrified test sample was generated (P3-6) using a 7.4 percent sodium addition. The result was a low viscosity melt that cooled to a black vitreous to slightly porcelain-like material in which green streaks were observed. Slight corrosive attack was observed in the firebrick crucible, which suggests that no higher level of sodium addition would be recommended. Leach testing was performed on this sample and 3.3 ppm uranium and 0.03 ppm cadmium were measured in the MTCLP. Low ppm levels of metals and anions were observed in the MPCT, the highest being 53 ppm sodium and 35 ppm fluorine.

Two waste/soil formulations (P3-7 and P3-8) produced low to medium viscosity melts that cooled to good quality, single-phase glasses. The lower sodium addition P3-8 formulation produced a higher viscosity melt. Leach testing on these samples indicated very similar performances: low to nondetectable levels of gross alpha/beta, metals, and anions. Uranium leachability in the MTCLP was 5.9 ppm for P3-7 and 4.3 ppm for P3-8, while uranium was nondetect in the MPCT for both.

Because both formulations produced satisfactory glasses in Remedy Screening, the sodium/flux addition would be kept the same while the soil loading was increased. It was anticipated that additional glass former from the soil would further improve the quality of glass produced while the additional flux from the soil would help lower the melt viscosity.

Three waste/flyash formulations resulted in medium (V-2/V-3) to high viscosity (V-1/V-2) melts that cooled to products ranging in character from borderline vitreous porcelain to vitreous with potentially crystalline streaks. From visual inspection, P3-12 appears to be the best quality glass although vitrification appears to have occurred nonuniformly through the monolith. Perhaps with increased flux content or increased stirring during processing, a more homogeneous melt could have been achieved. Leach testing was performed for P3-11 and P3-12. Low levels of uranium leaching (0.3 to 0.5 ppm) were observed in the MTCLP and low ppm levels of metals and anions were observed in the MPCT. P3-12, the high sodium/flux level formulation, was chosen for advanced phase testing because it demonstrated the lowest melt viscosity and leachability performance.

Remedy Selection Tests

The advanced phase Waste Pit 3 zone samples used the formulations listed in Table 4-16. The soil formulations, Formulation 1, produced very different products across the three pit zones. Zone 1 material vitrified with a low viscosity and cooled to a dark amber glass with a bubbled slag-like cap. This zone material would benefit from a higher sodium-flux addition to better process the incompletely vitrified slag phase. Zone 3 produced a nonporous, borderline-crystalline, vitreous material. Apparently, the soil formulation did not provide sufficient glass former. The Zone 3 material probably contained levels and kinds of formers significantly different from the composite material used in the Remedy Screening testing. The bulking factors for the zone waste/soil products were uniformly negative, from -46 to -76 percent, indicating significant volume reduction after processing.

The formulations for the advanced test remedy selection phase are listed in Table 4-16. The flyash formulation, Formulation 2, produced low and high viscosity melts among the three pit zones. The cooled products ranged from nonporous, near-vitreous to slag-like with entrapped gas bubbles to granite-like. This trend toward granite-like material is consistent with what was observed in remedy screening tests where no truly vitreous product could be achieved. The bulking factors for these products presented in Table 4-17 was uniformly negative, -50 percent to -67 percent, indicating a significant volume reduction after processing.

Results for Waste Pit 3 TCLP radionuclides for the two formulations are shown in Table 4-18. The metals in the TCLP leachates for the waste treated with the two vitrification formulas and the TC criteria for metals are shown in Table 4-19. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds. The leachability of the Formula 2 glass was as good as or better than that for Formula 1 for all radiological CPCs, with the exception of Ra-226.

The results of the PCT analysis showing the NLR are presented in Table 4-20. The NLRs for the three waste/soil zone glasses were all below 1 percent of the SRHLWC except for Na, K, B, and Li, which in the Zone 3 sample reached 18, 7, 61, and 29 percent of the criteria, respectively. The

waste/flyash glass average NLRs were below 1 percent of the SRHLWC except for Na and B, which had 109 and 14 percent, respectively. The leachability of Na exceeded the SRHLWC.

Waste Pit 3 Vitrification - Radon Emissions

Figures 4-7 and 4-8 both show radon leach and emanation rates much lower than the untreated waste or the calculated rate.

Waste Pit 3 Vitrification Testing - GTS Duratek/Catholic University of America

The preliminary results of the compositional analysis and vitrification testing by GTS Duratek are presented as part of the Waste Pit 4 results.

TABLE 4-16

VITRIFICATION--PIT 3
ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	100	0	5
2	100	0	100	16

TABLE 4-17

VITRIFICATION--ADVANCED PHASE--PIT 3
BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
1	1	-64	-61
2	1	-46	
3	1	-76	
1	2	-50	
2	2	-63	
3	2	-67	

TABLE 4-18

WASTE PIT 3 VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	ND	5.140	9.020
Plutonium-238	ND	ND	0.920
Plutonium-239/240	ND	1.220	1.340
Radium-226	9.620	2.770	7.240
Radium-228	13.030	ND	ND
Strontium-90	ND	7.090	ND
Technetium-99	867.000	14.540	ND
Thorium-228	6.440	9.520	2.710
Thorium-230	1.070	67.340	73.070
Thorium-232	ND	0.700	0.890
Uranium-234	74.900	127.870	22.980
Uranium-235/236	7.240	27.700	5.790
Uranium-238	181.250	127.610	32.400
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thoruim (Total)	ND	0.010	0.010
Uranium (Total)	0.390	0.380	0.100

TABLE 4-19

WASTE PIT 3 VITRIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Aluminum	3.432	16.071	17.643	
Antimony	0.184	0.014	ND	
Arsenic	0.298	0.056	0.028	5.000
Barium	0.312	2.035	0.460	100.000
Beryllium	0.007	0.009	0.010	
Boron	0.998	0.259	0.150	
Cadmium	0.054	0.015	0.012	1.000
Chromium	0.124	ND	ND	5.000
Cobalt	0.120	0.019	0.017	
Copper	0.475	0.294	0.327	
Cyanide	ND	ND	ND	
Lead	0.007	0.006	0.007	5.000
Manganese	49.812	1.012	0.537	
Mercury	0.001	ND	ND	0.200
Molybdenum	0.370	0.344	0.286	
Nickel	0.709	0.208	0.034	
Selenium	0.218	ND	0.003	1.000
Silver	0.092	ND	ND	5.000
Thallium	0.013	ND	ND	
Vanadium	0.729	0.346	0.510	
Zinc	0.397	0.140	0.175	

Table 4-20

TABLE 4-20

PIT 3 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	1	0.7	0.002	9	0.7	0.1	Not Calc'd	0.9	Not Calc'd
1	2	0.3	0.01	1.0	0.6	0.0	Not Calc'd	0.2	Not Calc'd
1	3	0.7	0.1	18	0.4	0.02	29	7	61
2	Average	1	0.03	109	1	Not Calc'd	Not Calc'd	1	14

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

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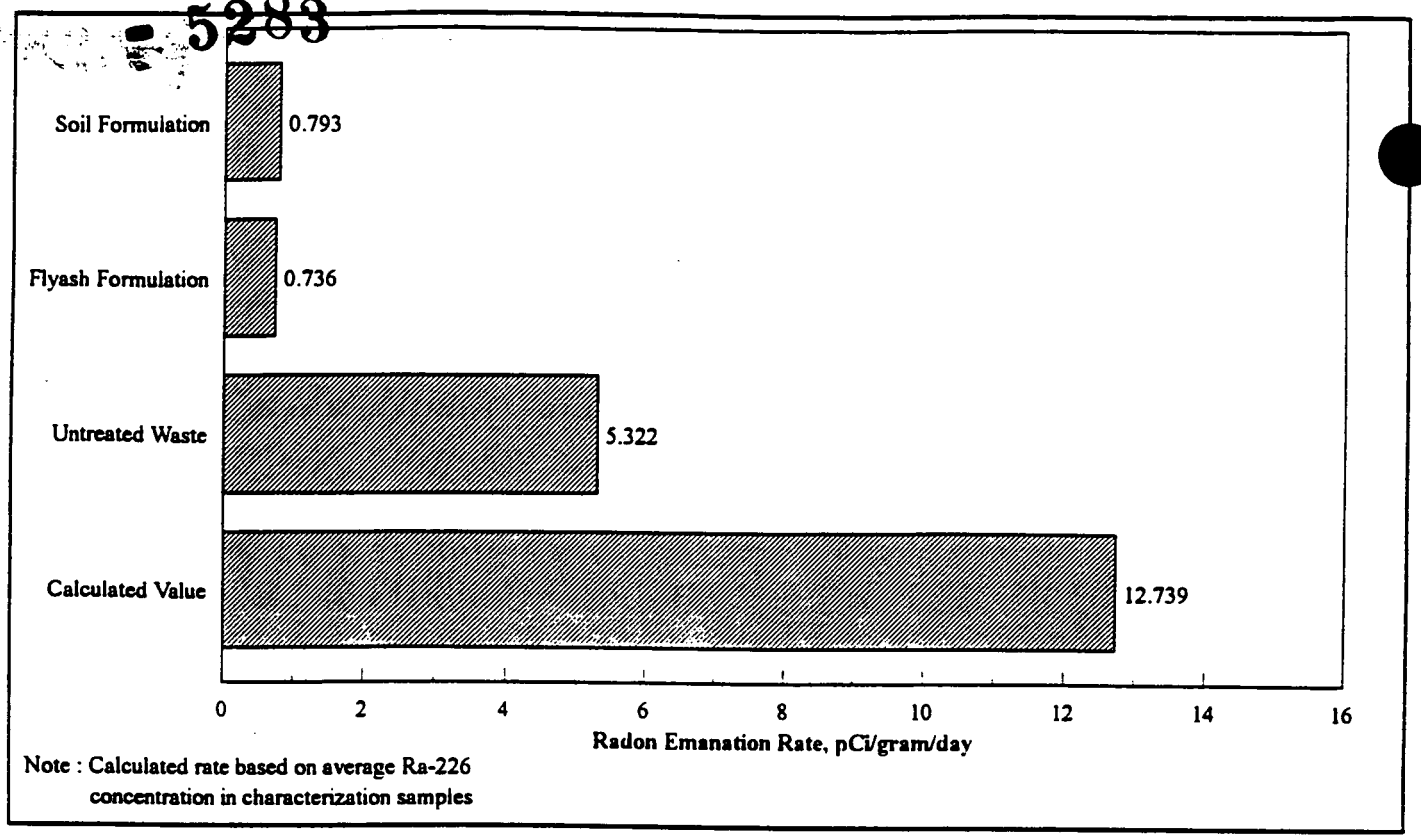

FIGURE 4-7 - PIT 3 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

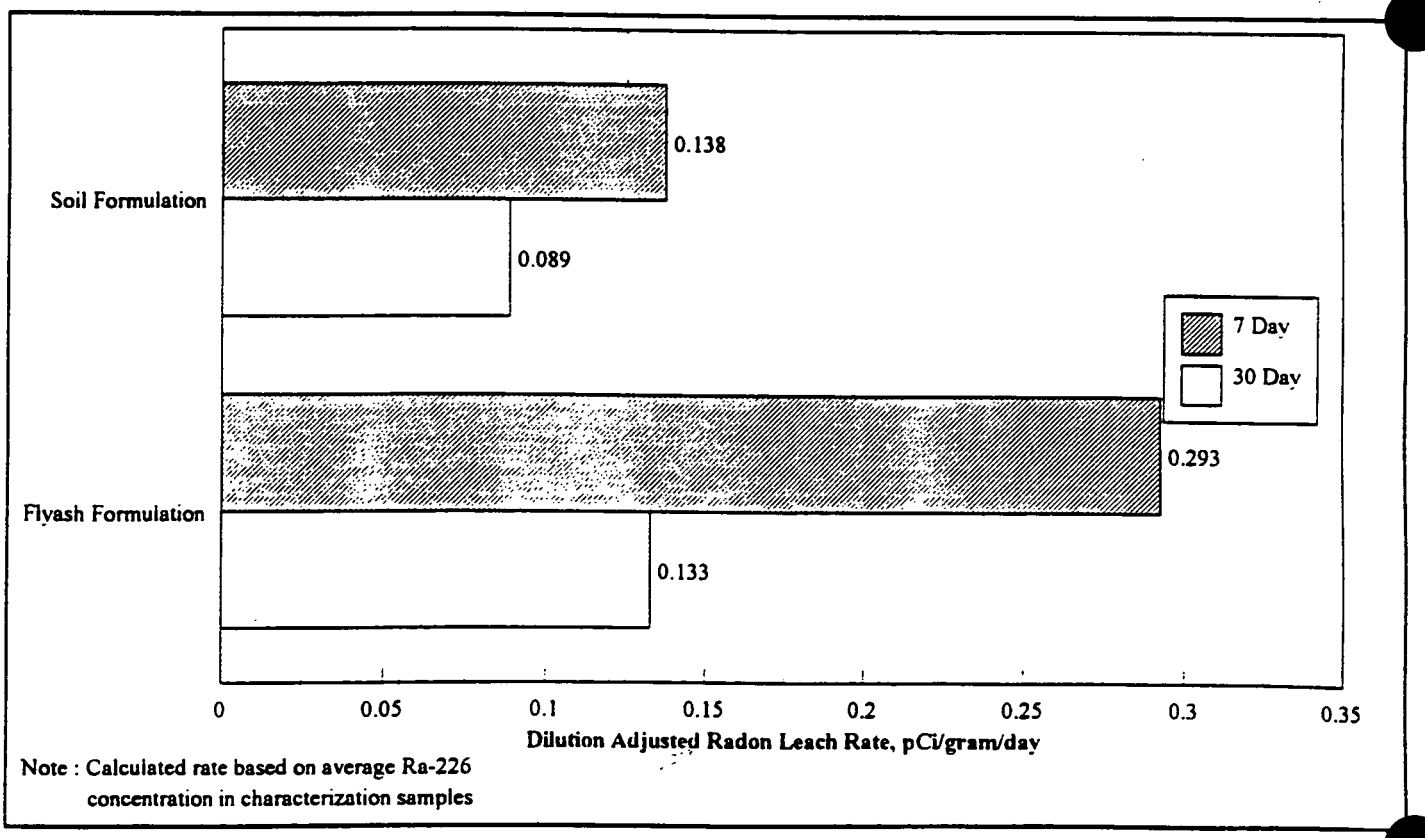

FIGURE 4-8 - PIT 3 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

0280

WASTE PIT 4

Compositional Analysis

As vitrification feed material, Waste Pit 4 contains 18.29 mole percent glass formers and 77.07 mole percent flux. The former/flux ratio is 0.237, below the desired 0.5 or greater target. Additionally, compositional data reveal the presence of RCRA metals, uranium, and thorium at levels that might result in significant leaching in poor glass formulations, especially the 4.63 mole percent/UO_3 present.

Range-Finding Tests

Initial testing generated five samples that evaluated the performance of Waste Pit 4 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-21.

The as-is pit waste (P4-1) produced a low viscosity (V-3) melt that cooled into a nonvitreous, crystalline granite material with a granulated surface cap. This result is due to the low concentration of glass formers in this waste. In Remedy Screening, the effect of increasing sodium/flux addition would be evaluated although no advantage would be expected.

Two waste/soil formulations (P4-2 and P4-3) were tested. They differed in their soil loadings, and P4-3, the higher loading formulation, produced an excellent glass, while P4-2 produced a heterogeneous vitreous/crystalline mixture. Both melts had good viscosities (V-3). P4-3 was investigated in Remedy Screening, to determine if a good glass could still be produced with reduced sodium/flux addition.

Waste/flyash formulations (P4-4 and P4-5) produced high viscosity melts (V-1) that cooled into very different products. P4-4, with lower flyash loading and 5 percent flux addition, produced a very porous, crystalline/granite-like material, while P4-5, the higher flyash loading without flux addition, produced a nonporous glass/porcelain material with slag cap. These differences reflect insufficient glass former in the first case and insufficient flux in the second. Remedy Screening testing would repeat the higher flyash loading P4-5 formulation, while investigating the effect of increasing sodium/flux addition.

Table 4-21

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PIT 4
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P4-1 10500401	100	0	0	0	V-3	Non-vitreous, crystalline granite
(Soil) P4-2 10501304	100	100	0	5.0	V-3	Vitreous, crystalline mixture
(Soil) P4-3 10501504	100	50	0	5.0	V-3	Good vitreous product
(Flyash) P4-4 10501904	100	0	150	5.0	V-1	Porous, crystalline granite
(Flyash) P4-5 10502504	100	0	200	0	V-1	Porcelain with slag cap

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

PIT 4
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P4-6 10502904	100	0	0	8.4	V-5 (melt down)	No material recovered	NA[d]
(As-Is) P4-7 10503007	100	0	0	5.2	V-5 (melt down)	Glossy, non-porous product	NA
(As-Is) P4-8 10503203	100	0	0	0	V-3/V-4	Coal-like product	NA
(As-Is) P4-9 10503208	100	0	0	2.1	V-5 (melt down)	Semi-glossy, encapsulated	NA
(Soil) P4-11 10502604	100	150	0	5.2	V-3	Glossy, non-porous glass	2.0 U (MTCLP)
(Soil) P4-12 10502704	100	150	0	2.6	V-3	Glossy, non-porous glass	24,000 alpha, 5150 beta, 67 U (MTCLP)
(Flyash) P4-13 10502804	100	0	200	2.6	V-1	Vitreous with slag-like cap	NA
(Flyash) P4-14 10503008	100	0	200	7.0	V-2/V-3	Porous slag with inclusions	3.6 U (MTCLP)
(Flyash) P4-15 10503009	100	0	200	5.7	V-3	Vitreous with crystal inclusions	3.6 U (MTCLP)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d] Not analyzed.

0283

Remedy Screening Tests

This second round of testing generated nine samples that further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-21 presents these formulations.

Four experiments with the as-is pit waste were performed with increasing loadings of sodium/flux to reduce the high melt viscosity. Nonporous products ranging from coal-like to glossy black resulted, all with very low viscosities. All but P4-8 resulted in crucible meltdown. These results reflect the inherent low glass former, high flux content of the waste and the corrosivity of such compositions under molten conditions. The further addition of sodium/flux only exacerbated the problem. The melting points of a significant portion of the waste's constituents (e.g., MgF, MgO, and CaO) all exceed 1250°C and may not have vitrified even with additional sodium flux. No leach tests were performed on these products.

Two waste/soil formulations were tested (P4-11 and P4-12), repeating the P4-3 formulation in P4-11 and reducing the sodium/flux addition by half for P4-12. Both formulations produced glossy, nonporous, single-phase vitreous products but their leachability performance differed significantly. The lower flux formulation (P4-11) leached considerably with 24,000 weight/weight (wt/wt) gross alpha and 5150 wt/wt gross beta), chromium (0.3 ppm), and uranium (U) (67 ppm) in the MTCLP. This poor leachability performance may be related to the observation of corrosive attack on the crucible during melt preparation. Such attack reflects unincorporated flux that can promote leachability. Due to the better quality of its vitrified product and leachability performance (e.g., 2 ppm uranium; nondetectable gross alpha/beta) formulation P4-12 was developed in the advanced phase testing.

Three waste/flyash formulations were tested during Remedy Screening. The range-finding waste/flyash formulation of choice (P4-5) was repeated with sodium/flux additions at 2.6 percent (P4-13), 5.7 percent (P4-14) and 7 percent (P4-15). The low flux formulation produced a very high viscosity (V-1) melt that cooled to a vitreous mass with slag-like cap, while the high flux formulation produced a pourable melt (V-2/V-3) that cooled to a porous slag with glossy nonporous inclusions. The medium flux formulation was prepared after observing the resulting products from the low and

high formulations. The medium flux melt had a pourable viscosity (V-3) and cooled to a glossy black nonporous product streaked with beige crystalline material that had not vitrified. This incomplete vitrification may be due to either composition (e.g., high CaO and MgO), inadequate processing (e.g., insufficient mixing or time at temperature) or both.

The leachability performance of the medium (P4-14) and high (P4-15) flux formulations were evaluated by MPCT and MTCLP and found to be nearly identical: uranium leached from MTCLP (3.6 ppm; 3.6 ppm), gross alpha/beta leached at the lowest level of detection (LLD) for both MTCLP and MPCT, and low ppm levels of metals and sulfate were observed in the MPCT.

The medium flux formulation (P4-14) was taken into the advanced phase testing due to its greater vitreous, although heterogeneous appearance.

Remedy Selection Tests

The advanced phase Waste Pit 4 zone samples used the formulations listed in Tables 4-22. The soil formulation, Formulation 1, produced low viscosity melts across the three zones that cooled to quite different products. Zones 1 and 2 products were nonporous, crystalline to vitreous with streaking of unvitrified material (e.g., yellow cake, green salt) through the interior. Remelts of these products produced darker, more homogeneous and single phase material. The Zone 3 product was light tan with crystalline, porous texture. More extensive furnace processing and sodium/flux addition would be required to improve the quality of these vitrified products. The bulking factors for these zone products shown in Table 4-23 were positive, from 17 to 32 percent, indicating a slight increase in volume. As with Waste Pit 1, this increase is partially due to incomplete vitrification of waste constituents.

The flyash formulation, Formulation 2, produced low to medium viscosity melts and cooled products fairly vitreous in character. Some slag-like coating and crystalline borders and inclusions were apparent, indicating that a longer processing time or higher sodium/flux addition is required. The bulking factors, as with the waste/soil products, were uniformly positive, from 57 to 68 percent.

Results for Waste Pit 4 TCLP radionuclides for the two formulations are shown in Table 4-24. The metals in the TCLP leachates from the waste treated with the two vitrification formulations and the TC criteria for metals are shown in Table 4-25. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds.

The results of the PCT expressed as NLRs are presented in Table 4-26. For both formulations, boron exceeded the SRHLWC. For the waste/soil product, sodium also exceeded the SRHLWC.

Waste Pit 4 Vitrification - Radon Emissions

Results of radon emissions testing are given in Figures 4-9 and 4-10.

TABLE 4-22

VITRIFICATION--PIT 4
ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	150	0	13
2	100	0	200	18

TABLE 4-23

VITRIFICATION--ADVANCED PHASE PIT 4
BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
1	1	32	37
2	1	20	
2	1	6	
3	1	17	
1	2	60	
2	2	68	
3	2	57	

TABLE 4-24

WASTE PIT 4 VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	3.630	5.380	9.410
Plutonium-238	ND	ND	1.460
Plutonium-239/240	ND	2.240	2.710
Radium-226	48.960	13.620	12.370
Radium-228	76.900	1108.930	ND
Strontium-90	19.680	8.400	ND
Technetium-99	95.910	34.440	ND
Thorium-228	ND	10.740	5.020
Thorium-230	ND	49.180	42.450
Thorium-232	ND	3.750	2.720
Uranium-234	8515.000	427.590	45.520
Uranium-235/236	1819.500	28.860	5.150
Uranium-238	67550.000	525.740	113.230
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thoruim (Total)	ND	0.190	0.020

TABLE 4-25

WASTE PIT 4 VITRIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.400	0.007	ND	
Arsenic	ND	0.015	0.020	5.000
Barium	3.744	1.330	0.402	100.000
Beryllium	0.047	0.005	0.005	
Boron	0.401	0.906	0.425	
Cadmium	0.046	ND	ND	1.000
Chromium	1.276	0.036	0.043	5.000
Cobalt	0.193	0.029	0.038	
Copper	0.439	0.130	0.063	
Cyanide	ND	ND	ND	
Lead	0.007	0.027	0.010	5.000
Manganese	28.344	3.155	0.200	
Mercury	ND	ND	ND	0.200
Molybdenum	0.111	0.022	ND	
Nickel	0.365	0.212	0.110	
Selenium	ND	ND	ND	1.000
Silicon	11.457	201.318	25.978	
Silver	0.706	0.014	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.508	0.130	0.033	
Zinc	0.484	0.689	0.152	

TABLE 4-26

PIT 4 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	1	0.4	0.1	4	0.6	0.1	48	4	50
1	2	0.5	0.02	23	1	0.0	50	3	78
1	3	1	0.02	128	2	0.2	Not Calc'd	6	Not Calc'd
1	2	2	0.004	90	1	0.1	14	75	>500
2	Average	0.2	0.05	46	0.7	Not Calc'd	Not Calc'd	10	142

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

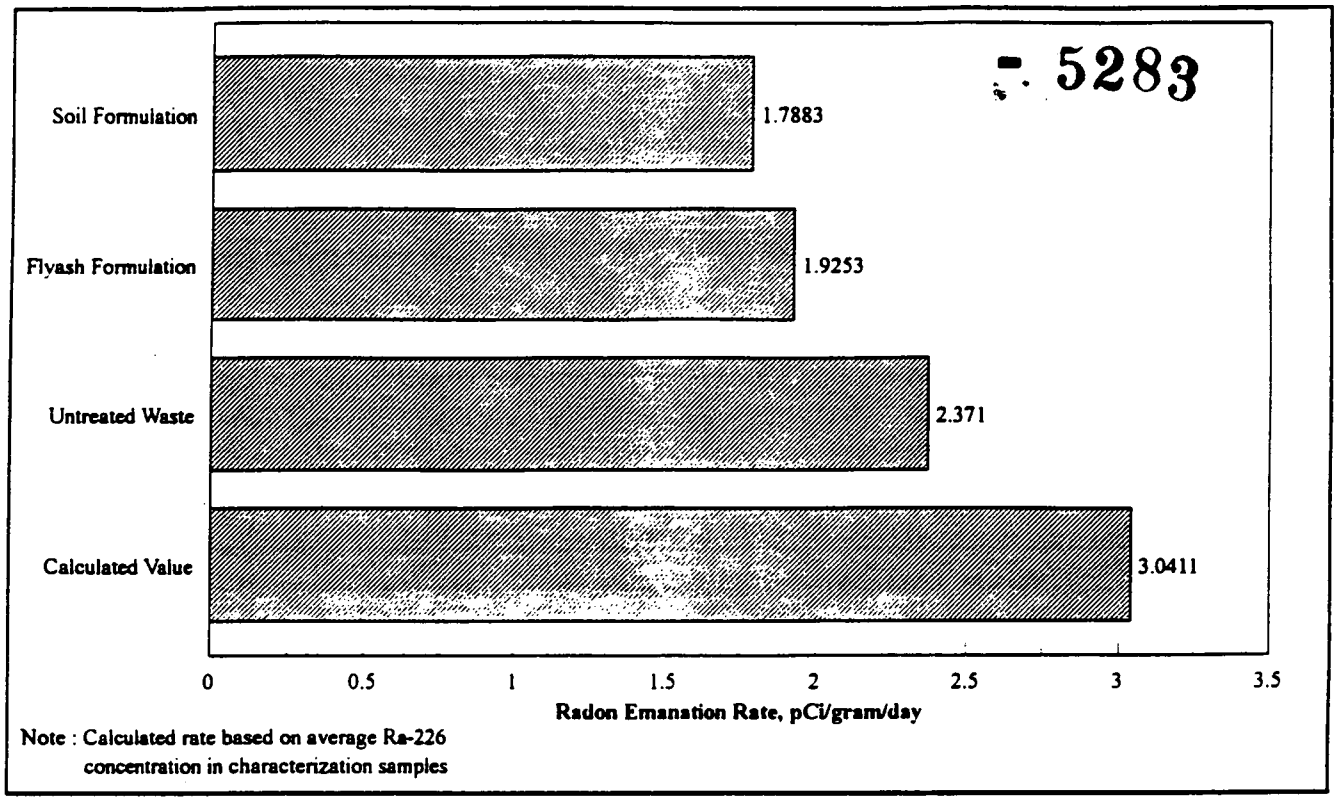

FIGURE 4-9 - PIT 4 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

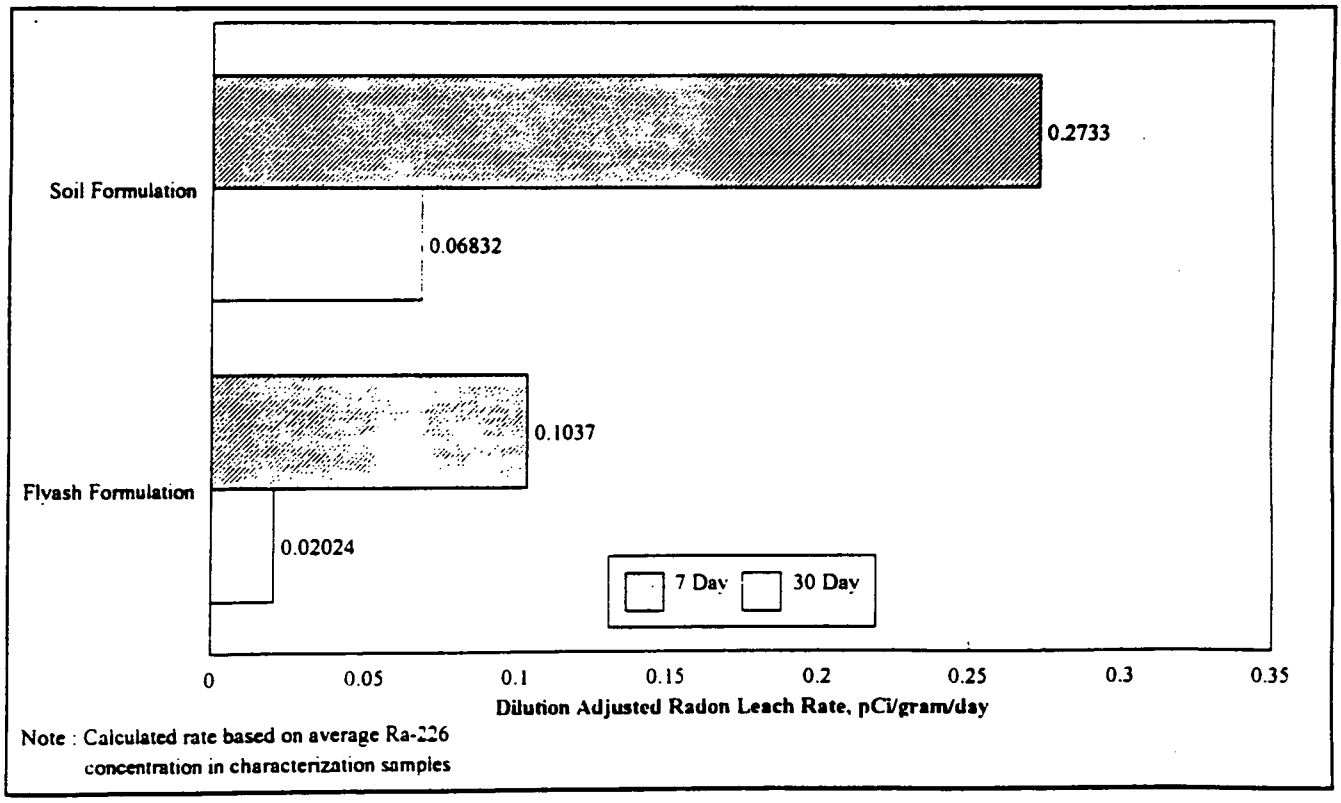

FIGURE 4-10 - PIT 4 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES 0291

WASTE PIT 4

Vitrification Testing Results - GTS Duratek/Catholic University of America

Analysis of Waste Pit 3 and Waste Pit 4 Materials

A 30 gallon drum of Waste Pit 3 material and a 30-gallon drum of Waste Pit 4 material were received at The Catholic University of America's Vitreous State Laboratory (VSL). The drum of Waste Pit 4 material, as received, was less than one-half full, with about 10 percent free water on the top. The sludge was black and extremely dense. The clay-like material was very difficult to separate; about 8 hours of mixing by two people using an electric stirrer was required in order to obtain a homogeneous sludge. Part of the difficulty in achieving a homogeneous mixture was due to the presence of black "plastic-like" materials within the sludge. The Waste Pit 3 sludge was a dry, clay-like material, grayish-black in color which was also difficult to stir. A single large stone (about 2 inches in diameter) was found in this material and was removed before using an electric stirrer to produce a homogeneous sludge. After these samples were homogenized as described above, samples were taken for subsequent analysis.

The compositions of the Waste Pit 3 and Waste Pit 4 materials were determined by acid dissolution followed by DCP, ICPMS, Ion Chromatography, Fluoride Electrode Analysis of the solutions, and also by Gamma Spectroscopy on the as-received material. The results of all of these techniques except gamma spectroscopy are summarized in Table 4-27. The first part of Table 4-27 shows the major components in terms of oxides and fluorides. While Waste Pit 4 is mainly MgF_2, a flux for glass-making, Waste Pit 3 is mainly composed of SiO_2, a glass former. This suggests that vitrifiable feeds can be formed by blending these two materials; results from such tests are given in the next section. While Waste Pit 4 contains much more fluoride than Waste Pit 3 (Pit 3 has below our detection limit of 1 wt. percent fluoride), the two materials contain similar amounts of sulfates --3.4 wt. percent.

From the DCP analysis, about 0.2 wt. percent uranium for the Waste Pit 3 sample was obtained and 2.4 wt. percent uranium for the Waste Pit 4 sample. Various uranium isotopes were examined, as well as Tc-99 and some heavy metals by ICPMS, as shown in the third part of Table 4-27. Samples

Table 4-27

Compositional Analysis of Pit 3 and Pit 4 Sludges

Oxides (wt. %)	Pit 3 (FE18)	Pit 4 (FE17)
Al_2O_3	11.0	3.0
B_2O_3	0.0	0.0
BaO	0.1	0.3
CaO	6.0	0.2
Cr_2O_3	0.0	0.0
Fe_2O_3	4.5	1.0
K_2O	2.0	0.0
Li_2O	0.1	0.0
MgO	4.0	0.0
MgF_2	0.0	85.0
MnO_2	0.2	0.1
Na_2O	0.0	0.1
NiO	0.0	0.0
SiO_2	70.0	7.8
SrO	0.0	0.0
TiO_2	0.6	0.0
U_3O_8	0.2	2.4
ZrO_2	0.0	0.1
Other	1.28	0
TOTAL	100	100.11
SO_4^{2-}	3.4	3.4

Radionucleides (ppm)	Pit 3 (Dried @ 450°C)	Pit 4 (Dried @ 450°C)	Pit 4 (Dried @ 1150°C)
Tc-99	< 0.2	< 0.2	< 0.2
U-235*	< 6	46	64
U-236*	< 1	1	1.4
U-238	1860	16,200	20,800
Heavy Metals (ppm)			
Pb	38	50	8
Cr	36	60	108
Hg	< 1	38	24

*Obtained Semi-Quantitatively (± 30%)

of Waste Pit 4 material dried at 450° C and at 1150° C were examined by ICPMS. The amount of U-238 for the Waste Pit 3 and Pit 4 samples were 0.2 wt. percent and 2 wt. percent respectively, both of them consistent with DCP results. No Tc-99 in either of the pit sludge samples (<0.2ppm) was detected.

Both Waste Pit 3 and Waste Pit 4 materials contain lead (Pb) and chromium (Cr), with Waste Pit 4 containing mercury (Hg) as well, as shown in Table 4-27. It is believed that Waste Pit 3 has less than 1 ppm of Hg. The amounts of Pb, Cr, and Hg for the Waste Pit 4 material dried at 450° C and at 1150° C are inconsistent with each other. The amount of Cr almosts doubles from the Waste Pit 4 sample dried at 450° C to the Waste Pit 4 samples dried at 1150° C. The amount of Cr in the Waste Pit 4 sample dried at 1150° C should be greater than that in the Waste Pit 4 sample dried at 450° C, but only by the weight lost in heating a sample from 450° C to 1150° C; 7.8 relative wt. percent (Table 4-27). Since the amount of Cr almost doubles rather than increases by 7.8 relative percent, the increase is most likely due to unrepresentative sampling. It should be noted that these analyses are based on rather small (100 mg) sub-samples (since a total dissolution must be effected with a manageable volume of reagent). From previous experience with sludges, a much more reliable method for analyzing these sludges (which are often inhomogeneous on the 100 mg scale) was to dry the material at 450° C, make a glass from it (about 400 g) using known amounts of chemical additives, and then analyze the resulting glass. Results from this type of analysis are presented in Table 4-28.

The amount of lead (Pb) and mercury (Hg) decreases in the Waste Pit 4 sample dried at 1150° C from the Waste Pit 4 sample dried at 450° C. This could be due to the loss of PbF_2 and HgF_2 since their boiling points are 1290° C and 650° C respectively, or it could also be due to unrepresentative sampling. By analyzing more Waste Pit 4 samples dried at 450° C and the glass samples made from Waste Pit 4 material, we should be able to report more representative concentrations of Pb, Cr, and Hg should be able to be reported.

The gamma spectroscopy of Waste Pit 3, Waste Pit 4, and the background contain similar peaks, Pb-212, Pb-214, U-235 and U-235/Th-230, and an array of overlappping peaks between 90 and 110

Compositional Analysis of Fernald Wastes Used for Glass Melts. Compositions Derived Mainly from Chemical Analysis of Resulting Glass Melts for Sludges. Composition of Soil Obtained After Drying Soil at 1150°C.

Components	Pit 3 (FE18)	Pit 4 (FE17)	Pit 5 (FE51)	Lockheed Soil Wash Concentrates (FE30+)
Al_2O_3	11.0	3.0	3.8	4.7
B_2O_3	0.0	0.0	0.4	0.1
BaO	0.1	0.3	0.0	0.0
CaO	6.0	0.2	46.0	49.7
Cr_2O_3	0.0	0.0	NA	NA
Fe_2O_3	4.5	1.0	7.1	2.8
K_2O	2.0	0.0	0.3	1.1
Li_2O	0.1	0.0	NA	NA
MgO	4.0	0.0	11.1	13.0
MgF_2	0.0	85.0	0	0.0
$MgSO_4$	-	-	16.8	-
MnO_2	0.2	0.1	NA	NA
Na_2O	0.0	0.1	1.4	0.5
NiO	0.0	0.0	NA	NA
SiO_2	70.0	7.8	9.2	26.8
SrO	0.0	0.0	NA	NA
TiO_2	0.6	0.0	0.2	0.3
U_3O_8	0.2	2.4	0.5	NA
ZrO_2	0.0	0.1	NA	NA
Other	1.28	0	3.25	1.06
TOTAL	100	100.11	100	100

Note: There are only small amounts of sulfates in Pit 3, Pit 4, and Lockheed soil (< 4 wt.%).
NA = Not Analyzed.

KeV. The main difference between the Waste Pit 3 and Waste Pit 4 materials is the intensity of these peaks; the vertical scale of the gamma spectrum of the Waste Pit 4 material is 16 times greater than that of the gamma spectrum of the Waste Pit 3 material. This is consistent with the radionuclide analysis by ICPMS which showed the various uranium isotopes an order of magnitude greater in the Waste Pit 4 material than in Waste Pit 3 material.

Table 4-29 presents the physical characterization data and the carbon content data for the Waste Pit 3 and Waste Pit 4 materials. The specific gravity of the Waste Pit 4 material, 3.39 g/cm^3 on a dried basis, is consistent with the fact that Waste Pit 4 is mainly composed of MgF_2 (specific gravity of MgF_2 is 3.0 g/cm^3). Likewise, the specific gravity of the Waste Pit 3 material, 2.82 g/cm^3 on a dried basis, is consistent with the fact that Waste Pit 3 is mainly composed of SiO_2 (specific gravity of SiO_2 is 2.5 g/cm^3). Both materials are very similar in weight loss and carbon content, but Waste Pit 4 material has a larger fraction of fine particles than Waste Pit 3 material; 86.4 wt. percent passes mesh 200 for Waste Pit 4 while only 49.1 wt. percent passes the same mesh for Waste Pit 3 material.

The composition of the Waste Pit 3 sample is somewhat surprising - the SiO_2 content is high (even greater than that of the native soil), the Mg and F contents are very low and the U content is low (in view of the fact that the Waste Pit 5 overflow was apparently directed to Waste Pit 3). Together, these results suggest that the Waste Pit 3 sample may be composed primarily of the cap material rather than the sludge itself. An analysis of a Waste Pit 3 sample reported by IT Corporation had about 22 percent CaO, 18 percent MgO (F was not analyzed) and 39 percent SiO_2

Crucible Melts from Waste Pit 3 and Waste Pit 4 Materials

Table 4-30 lists the 13 crucible melts completed thus far. The first five melts were used mainly to obtain the composition of the sludge, as discussed above. From previous experience, using a few hundred grams of a sludge, mixing it with additives, making a glass out of it, and then analyzing the glass, produced a much more representative compositional analysis than by analyzing th sludge itself. This is due to the fact that only 100 mg samples are used for chemical analysis while approximately 400 g samples are used for glass making. The resulting glass is much more reproducible, from one 400 g sample to the next, than are the smaller 100 mg samples.

Physical Characterization and Carbon Content of Pit 3 and Pit 4 Materials

	Pit 3	Pit 4
Specific Gravity[1] @ 20°C (gcm^{-3})		
As received	2.03	3.05
Dried at 110°C/18 hours	2.82	3.39
Carbon Content, % (As-received basis)		
TC	2.9	2.2
TOC	2.2	2.3
Sieve Analysis		
Sieve #10	97.3% Pas 2.7% Ret	98.9% Pas 1.1% Ret
#40	90.4% Pas 6.9% Ret	97.4% Pas 1.5% Ret
#60	80.3% Pas 10.1% Ret	95.4% Pas 2.0% Ret
#100	67.2% Pas 13.1% Ret	92.5% Pas 2.9% Ret
#200	49.1% Pas 18.2% Ret	86.4% Pas 6.1% Ret
Weight Loss, %		
110°C	21.4	21.2
450°C	26.8	28.5
850°C	31.8	29.9
1150°C	32.2	34.1

[1]ASTM D854 procedure was followed; "as-received" results refer to samples that were measured without predrying.

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TABLE 4-30
Glasses Made from Pit 3 and Pit 4 Sludges

Fernald Glass	F4-1	F4-2	F4-3	F4-4	F3-1	F4-5	F4-6	F4-7	F4-8	F4-9	F4-10	F4-11	F4-12	F4-13
Pit 4 (dried @ 450°C)	33	70	50	30	0	30	37	24	29.2	24	24	30.0	26.0	33.0
Pit 3 (dried @ 450°C)	0	0	0	0	76.9	55	45	38	29.2	40	40	30.0	38.0	45.0
Soil Fines (FE30+) (dried at 1150°C)	0	0	0	42	0	0	0	15	12.5	10	15	12.0	15.0	0.0
Pit 5 (FE51) (dried @ 450°C)	0	0	0	0	0	0	0	0	16.7	0	0	0	0	0
Total Waste Loading on Dried Basis	33	70	50	72	76.9	85	82	77	87.6	74	79	72	79	78
SiO_2	0	0	23	0	0	0	0	0	0	0	0	0.0	0.0	0.0
Na_2O	0	10	6	5	7.7	5	7	7	4.2	5	5	5.0	8.0	10(Na[illegible])
B_2O_3	55	20	8	9	15.4	10	11	11	8.3	11.0	11	11.0	12.0	12.0
Al_2O_3	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0	0.0
K_2O	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0	0.0
Fe_2O_3	0	0	0	0	0	0	0	0	0	5	0	0.0	0.0	0.0
CaO	0	0	13	14	0	0	0	5	0	5	5	0.0	1.0	0.0
Li_2O	12	0	0	0	0	0	0	0	0	0	0	0	0	0
Appearance upon cooling	green ceramic	green ceramic	green ceramic	brown opaque glass	opaque black glass/ceramic	opaque black & green with some undissolved chunks	light green ceramic	phase-separated glass.	Opaque black.	Opaque black.	Some undissolved chunks and crystallized glass.	Greenish glass.	Black Glass	Green brown glass.

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Crucible melts were begun to examine the viability of vitrifying Waste Pit 4 and Waste Pit 3 sludges with the F4-5 melt. For that glass, 30 wt. percent of Waste Pit 4 and 55 wt. percent of Waste Pit 3 were combined, obtaining a total waste loading of 85 wt. percent on a dried basis. The glass had undissolved material, most likely due to the high SiO_2 content from the Waste Pit 3 material. More homogeneous glasses were obtained by lowering the amount of Waste Pit 3 and Waste Pit 4. To increase the total waste loading, we added various amounts of soil wash concentrates from Lockheed Environmental laboratory studies for the MAWS program were added, and some Waste Pit 5 material. Total waste loadings varied from 72 wt. percent to 88 wt. percent.

All of the glasses were opaque, even the ones which showed no signs of crystallization. This may be due to the presence of reduced iron in the melt. The evidence for this is: (1)Analysis by SEM/EDX of one of the platinum (Pt)/gold (Au) crucibles which was attacked by these glass melts showed the presence of Pt/iron (Fe) alloy. (2)Preliminary colormetric analysis of dissolved F4-7 indicates a Fe^{2+}/Fe^{3+} ratio of 1.6, and (3) The glasses which do not crystallize after heat treatment at 1050° C for 2 hours produce clear glasses.

Table 4-28 shows the compositions of the sludges and soil-wash concentrates used in making the crucible melts. As mentioned above, most of the compositional anlysis of Waste Pit 3 and Waste Pit 4 materials were derived from the crucible melts themselves. Crucible melts were also used in obtaining the compositional anlysis of most of the Waste Pit 5 material. The soil-wash composition was obtained from soil dried at 1150° C for four hours.

Once these glasses were made, samples of each of them were crushed and sieved to pass through 200 mesh before dissolution and analysis; the resulting solutions were analyzed for fluoride and cations. The results of the fluoride anlaysis are presented in Table 4-31, along with the calculated fluoride content. In general, the analyzed and calculated fluoride contents agree within 10 relative percent, except for F4-1 and F4-2. It is believed that the saturation limit for fluoride in the glass matrix was exceeded in the melts containing nominally 35 wt. percent fluoride.

Table 4-31

Calculated and Analyzed Fluoride (wt. %) Contents of Glasses
Made from Pit 3 and Pit 4 Sludges

	F4-1	F4-2	F4-3	F4-4	F3-1	F4-7
wt. %F (calc.)	16.2	35.4	24.9	14.9	<1	12.0
wt. %F (analy.)	14.1	23.8	23.4	14.2	<1	11.4

	F4-8	F4-9	F4-10	F4-11	F4-12
wt. %F (calc.)	14.6	12.1	12.1	17.2	13.1
wt. %F (analy.)	13.9	11.3	9.8	18.7	12.5

The fluoride analyses presented in Table 4-31 were then used in combination with cation analysis by DCP to produce the analyzed content of the crucible melt glasses. Those results, along with the calculated compositions of the crucible melts, are presented in Table 4-32. The agreement between the analyzed and calculated columns is good, except for the F4-3 glass. It is believed that this is due to undissolved MgF_2 in the solution that was analyzed. Because of this low MgF_2 recovery, the initial data suggested that the Waste Pit 4 sample contained 75 wt. percent MgF_2. When glasses were melted with lower Waste Pit 4 loadings, it was determined that the Waste Pit 4 material actually contained 85 wt. percent MgF_2.

One important glass processing requirement is that the glass should have a liquidus significantly below the processing temperature. For formulations suitable for the 10 kg/d Duramelter test runs, the target is a liquidus temperature of below 1050° C. The liquidus temperature measurements are made by heat treating the glasses at 1050° C for 2 hours after a premelt at 100° C for one hour to melt all pre-existing nuclei. The results of these tests of 8 of the 13 crucible melts are given in Table 4-33. Three out of the eight glasses examined had a liquidus temperature below 1050° C: F4-7, F4-9 and F4-10. As noted in Table 4-33, F4-10 produced a somewhat inhomogeneous crucible melt. Thus, at present, F4-7 and F4-9 are the most viable glass formulations for the 10 kg/day continuos joule-heated melter tests.

Other processing parameters of concern are the melt viscosity and electrical conductivity. The viscosity and conductivity were measured for six of the crucible melts. Table 4-34 and 4-35 shows that the viscosity and conductivity of all of these crucible melts lie within the working range of the Duramelter joule-heated melter vitrification system. Some of the viscosity measurements are unstable around 1000° C, most likely as a result of the onset of crystallization.

Thus far, F4-7 and F4-9 are the most viable melts based on processing parameters. In addition to examining processing prarameters, several of these glasses have been subjected to TCLP leach testing. The results of TCLP tests on five of those crucible melts are presented in Table 4-36. All of the glasses passed the TCLP test. No data are presently available from PCT leach tests on these glasses, but based on earlier studies with Pit 5 glasses, the performance is expected to be good.

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Table 4-32

Calculated and Analyzed Compositions (wt.%) of Crucible Melts from Pit 3 and Pit 4 Sludges

	F4-1	F4-2	F4-3		F4-4		F3-1		F4-5	F4-6		F4-7		F4-8	F4-9	F4-10	F4-11	F4-12	F4-13	F4-14
Components	(calc.)	(calc.)	(calc.)	(anal.)	(calc.)	(anal.)	(calc.)	(anal.)	(calc.)	(calc.)	(anal.)	(calc.)	(anal.)	(calc.)	(calc.)	(calc.)	(calc.)	(calc.)	(calc.)	(calc.)
Al_2O_3	1.0	2.1	1.4	3.3	4.8	4.1	8.4	8.4	6.9	6.0	6.4	5.5	7.3	5.1	5.5	5.8	5.4	5.6	5.9	5.5
B_2O_3	56.5	21.2	8.3	7.6	9.7	9.4	16.5	16.3	10.8	11.8	11.3	11.6	10.9	8.8	11.7	11.7	13.3	12.7	12.9	9.5
BaO	0.1	0.2	0.2		0.2	0.1	0.1	0.1	0.2	0.2		0.1		0.1	0.1	0.1	0.1	0.1	0.2	0.1
CaO	0.1	0.1	13.6	10.1	19.5	23.2	4.6	4.2	3.4	2.8	3.6	15.4	12.9	14.8	12.9	15.6	9.3	11.2	2.7	17.5
Fe_2O_3	0.3	0.7	0.5	NA	2.0	2.3	3.4	3.9	2.8	2.4	1.5	2.4	2.4	2.9	7.6	2.4	2.2	2.4	2.3	2.4
K_2O	0.0	0.0	0.0	0.3	0.9	1.0	1.5	1.5	1.1	0.9	0.9	0.9	1.1	0.7	0.9	1.0	0.8	0.9	0.9	0.9
Li_2O	12.4	0.0	0.0	0.1	0.0	0.2	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MgF_2	26.6	58.0	40.8	31.9	24.6	23.3	0.0	0.0	25.3	31.1	NA	19.9	18.7	23.9	19.9	19.9	28.3	21.5	27.7	19.9
MgO	0.0	0.0	0.0	0.0	1.8	3.6	3.1	3.0	2.2	1.8	18.7	3.5	3.8	5.2	2.9	3.6	3.2	3.6	1.8	3.5
Na_2O	0.0	10.7	6.3	4.7	6.0	0.6	8.3	7.2	5.4	7.6	7.9	7.5	7.8	4.7	5.4	5.4	6.1	8.6	0.0	7.5
NaF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.7	0.0
Si_2O	2.4	5.3	27.7	26.2	29.6	29.1	53.5	50.6	40.8	34.2	26.0(?)	32.1	31.1	26.8	32.1	33.5	29.9	32.3	33.8	32.1
TiO_2	0.0	0.0	0.0	0.2	0.3	0.3	0.5	0.6	0.3	0.3	0.4	0.3	0.4	0.2	0.3	0.3	0.2	0.3	0.3	0.3
U_3O_8	0.8	1.6	1.2	1.2	0.7	0.9	0.2	0.2	0.8	1.0	1.1	0.6	0.7	0.8	0.6	0.6	0.9	0.7	0.9	0.6
Excess Fluoride	-	-	-	3.9	-	0	-	-	-	-	-	-	0	-	-	-	-	-	-	-

NA - Not Analyzed

Note: The analyzed compositions consist of both fluoride analysis and cation analysis (DCP), unless indicated by NA for MgF_2 row, in which case fluoride has not been analyzed. When both fluoride and the cations are analyzed, the fluoride and magnesium are reported as MgF_2. If fluoride is the limiting agent, the rest of the Mg is reported as MgO. If Mg is the limiting agent, the excess fluoride is put in the excess fluoride row.

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Table 4-33

Heat Treatment of Glasses Made From
Pit 3 and Pit 4 Sludges

	F4-3	F4-4	F4-5	F4-6	F4-7	F4-9	F4-10	F4-11
After heat treatment at 1050°C for 2 hrs	< 3% fluorophlogopite	~ 20% fluorophlogopite	~ 3% fluorophlogopite	~ 15% crystals; mainly fluorophlo-gopite.	Clear. No crystals by SEM.	Clear. No crystals.	Clear. No crystals.	Surface crystals.

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Viscosity (Interpolated to Standard Temperatures) of
Pit 3 and Pit 4 Crucible Melts. (Poise)

Temperature (°C)	F4-4	F4-7	F4-8	F4-9	F4-10	F4-11
950	Unstable	43.1	NA	NA	NA	Unstable
1000	Unstable	17.2	Unstable	20.7	Unstable	Unstable
1050	4.7	9.1	Unstable	8.1	19.9	2.4
1100	2.9	5.8	2.4	4.6	11.5	1.8
1150	1.9	4.0	1.8	3.2	7.2	1.4
1200	1.3	3.1	1.4	2.5	4.8	1.1

NA = Not Analyzed

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Table 4-35

Conductivity (Interpolated to Standard Temperatures) of Pit 3 and Pit 4 Crucible Melts
(Siemens/cm)

Temperature (°C)	F4-4	F4-7	F4-8	F4-9	F4-10	F4-11
950	NA	NA	NA	NA	NA	NA
1000	0.11	0.15	0.03	0.09	0.07	0.05
1050	0.20	0.21	0.20	0.16	0.10	0.07
1100	0.30	0.26	0.31	0.22	0.14	0.08
1150	0.41	0.32	0.37	0.28	0.19	0.11
1200	0.52	0.37	0.42	0.33	0.26	0.13

NA = Not Analyzed

Table 4-36

Leach Data for Glasses Made from
Pit 3 and Pit 4 Materials
RCRA Metals (ppm).

	As	Se	Cd	Hg	Ag	Pb	Cr	Ba
F4-4	0.94	0.52	0.01	0.01	0.01	1.63	0.09	0.83
F4-7	0.54	0.43	0.01	0.19*	0.00	1.49	0.05	0.48
F4-8	0.11	0.06	0.02	0.07	0.01	1.26	0.06	1.69
F4-9	0.50	0.39	0.01	0.16**	0.02	1.09	0.05	0.03
F4-10	0.37	0.02	0.01	0.13	0.02	1.07	0.30	0.13
EPA Limit	5	1	1	0.2	5	5	5	100

* Spike of 0.2 ppm Hg gave 0.35 ppm Hg
** Spike of 0.2 ppm Hg gave 0.36 ppm Hg

Preliminary Assessment of Waste Pit 3 and Waste Pit 4 Vitrification

From the study thus far, both the F4-7 and F4-9 formulations would be viable candidates for vitrification of Waste Pit 3 and Waste Pit 4 sludges. Both glasses have acceptable viscosity and conductivity, have liquidus below 1050° C, and pass the TCLP test. Both the F4-7 and F4-9 blends as prepared in crucible melts appear to be somewhat reduced (with respect to redox state) after melting at 1150° C for one hour. This is unlikely to be the case for continuous melter operations, however, since residence times are much longer and oxygen availability is often greater; this will be confirmed in the 10 kg/day continuous melter test runs. In fact, it was found that heat treatments for an additional three hours at elevated temperatures (1050-1100° C) is enough to produce oxidized glass. The components for F4-7 and F4-9 blends, on both dried and wet (as recieved) basis, are given in Table 4-37. These formulations are composed of 74-77 wt. percent waste on a dried basis, and 80-83 wt. percent waste on a wet (as received) basis.

Viable Glasses for Melter Runs

Components	F4-7 (Dried basis)	F4-7 (Wet basis)	F4-9 (Dried basis)	F4-9 (Wet basis)
Pit 4	24	23.1	24	23.9
Pit 3	38	36.5	40	39.9
Soil Fines (FE30+)	15	23.0	10	15.8
Na_2O	7	5.3	5	3.9
B_2O_3	11	8.3	11	8.6
Fe_2O_3	0	0	5	3.9
CaO	5	3.8	5	3.9
Total	100	100	100	99.9

WASTE PIT 5

Compositional Analysis

As vitrification feed material, Waste Pit 5 contains 12.94 mole percent glass formers and 87.06 mole percent flux. The former/flux ratio is 0.149, below the desired 0.5 or greater target. Additionally, compositional data reveal the presence of RCRA metals, uranium, thorium, and anions at levels that might result in significant leaching in poor glass formulations.

Range-Finding Tests

Initial testing generated four samples that evaluated the performance of Waste Pit 5 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-38.

The as-is formulation (P5-1) did not vitrify substantially during furnace processing. The resulting material was not fused, appearing more like charred black chunks of powdery "soil." The waste material did not liquify during the 2 hours it was heated at 1250°C, which may be due to the fact that the melting points of a significant portion of the waste's constituents (e.g., MgF, MgO, and CaO) all exceed 1250°C. A major benefit of sodium/flux addition is that it can lower the melting point of glass former/flux mixtures. The potential for vitrification of the as-is Waste Pit 5 material at 1250°C with addition of sodium/flux was investigated during Remedy Screening.

Two waste/soil formulations (P5-2 and P5-3) were processed with very different results for melt and cooled product. P5-2 exhibited a low viscosity (V-3) melt but cooled to a fused to porcelain-like mass with a less porous surface cap. P5-3 with a higher soil loading but identical sodium/flux addition, produced a high viscosity melt (V-1) and upon cooling, a fused, granite-like mass. The addition of both soil and sodium/flux effected liquification of the Pit 5 waste and the production of fused but heterogeneous monoliths. It was anticipated that further addition of sodium/flux would result in more homogeneous and more vitreous product and this was investigated during Remedy Screening.

TABLE 4-38

PIT 5
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P5-1 10500601	100	0	0	0	(did not melt)	Charred chunks, soil-like
(Soil) P5-2 10501305	100	100	0	5.0	V-3	Fused, porcelain with cap
(Soil) P5-3 10501505	100	150	0	5.0	V-1	Fused, granite product
(Flyash) P5-4 10501905	100	0	200	5.0	V-1	Good glass but non-pourable

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

PIT 5
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P5-6 10502905	100	0	0	3.0	(did not melt)	Non-fused, charred solids	2340 alpha, 10,200 beta, 354 Na (PCT); 1.7 Cr (MTCLP)
(As-Is) P5-7 10503010	100	0	0	18.0	V-3	Glass with phase sep.	216 Al, 539 Na (PCT); 5.5 Cr, 0.7 Se (MTCLP)
(Soil) P5-8 10502605	100	200	0	5.2	V-1	Granite-like product	NA[d]
(Soil) P5-9 10502705	100	250	0	8.5	V-3	Bi-phase glass	30 Ca, 33 Na (PCT)
(Soil) P5-11 10503011	100	250	0	8.0	V-3	Bi-phase glass	30 Cd, 33 Na (PCT)
(Flyash) P5-12 10502805	100	0	250	8.8	V-1	Slag-like product	NA
(Flyash) P5-13 10503012	100	0	250	14.0	V-1	Slag-like product	NA
(Flyash) P5-14 10503013	100	0	250	18.0	V-2/V-3	Bi-phase glass	25 Ca, 74 Na,24 Si (PCT); 0.7 Cr (MTCLP)
(Flyash) P5-15 10503204	100	0	250	16.0	V-2/V-3	Bi-phase glass	31 Al, 126 Na, 32 Si (PCT); 0.7 Cr (MTCLP)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d] Not analyzed.

One waste/flyash formulation (P5-4) was tested that produced a homogeneous, nonporous glass but with a very high melt viscosity (V-1). Only further addition of sodium/flux was required to reduce the melt viscosity because the product was already a good glass.

Remedy Screening Tests

This second round of testing generated nine samples that further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-38 presents these formulations.

Two pit waste-only formulations with sodium/flux addition (P5-6 and P5-7) were tested in an attempt to lower the melting point of waste constituents and achieve a more vitreous product. A 3 percent sodium/flux level for P5-6 resulted in a nonfused, charred black material with an extremely porous texture. Leach testing of this formulation indicated that gross alpha at 2230 wt/wt and gross beta at 10,200 wt/wt, cadmium (189 ppm), and sodium (354 ppm) leached appreciably in the MPCT, while in the MTCLP the gross beta (1200 wt/wt) and chromium (1.7 ppm) were detected.

An 18 percent sodium/flux addition to the waste (P5-7) resulted in a pourable (V-3) melt that cooled to a phase-separated product. The outer surface of the monolith was coated with a porous, sulfur-like material through which in some areas a purely vitreous, transparent inner mass was visible. It is hypothesized that the high concentration of anions (fluorine, chlorine, SO_4, and PO_4) formed a separate, nonvitrified phase while, aided by the significant sodium/flux addition, the glass formers vitrified into the glass phase. Leach testing of this formulation revealed aluminum (216 ppm) and sodium (539 ppm) in the MPCT, and chromium (5.5 ppm) and selenium (0.7 ppm) in the MTCLP. Radionuclides (alpha, beta, and uranium) were at LLD in both.

In the as-is Remedy Screening, it appears that high levels of sodium/flux addition cannot bring some of the waste constituents into the vitrifying melt. The addition of soil and flyash helped make some progress towards this, but were unable to totally overcome this limitation.

Three waste/soil formulations were tested involving higher soil and sodium/flux loadings than tested during range-finding phase. P5-8 at 5.2 percent sodium/flux addition produced a very high viscosity

(V-1) melt that cooled to a porous, granite-like mass. No leach testing was done on this sample. P5-11 at 8 percent sodium/flux addition produced a pourable (V-3) melt that cooled to a bi-phasic monolith. Only the outer crucible-contacting surfaces exhibited the vitreous, sulfur-like second phase. The vitreous mass was an excellent glass. Leach testing of this sample indicated some leaching of cadmium (30 ppm), and sodium (33 ppm) in the MPCT and arsenic (1.0 ppm) in the MTCLP. Radionuclides (alpha, beta, and uranium) were at LLD for both. The effect of further raising the sodium/flux addition was investigated in P5-9. At 8.5 percent sodium/flux addition, a good glass was also produced with the same vitreous, sulfur-like second phase. Leach testing of this product revealed an essentially identical level of leaching for gross alpha/beta, metals, and anions.

The problem of a bi-phasic product could not be resolved with sodium/flux or soil addition. Because nothing more seemed to be gained from increasing flux addition from 8 percent to 8.5 percent, the 8 percent formulation (P5-11) was chosen for use in the advanced phase testing.

Four experiments were performed with waste/flyash mixtures to reduce the viscosity of the P5-4 range-finding formulation. Sodium/flux additions at 8.8 percent, 14 percent, 16 percent, and 18 percent were tested. At 8.8 percent and 14 percent additions, very high viscosity (V-1) melts were produced that cooled into slag-like masses with either a spongy-porous (P5-13) or fibrous texture (P5-12). Both products are very heterogeneous in texture and color of constituents. No leach testing was performed on these samples.

At 16 percent and 18 percent flux addition, melt viscosity reduced to pourable (V-2/V-3) and much more complete phase separation was effected. P5-15 exhibited only a small bottom rim of vitreous, sulfur-like second phase, while P5-14 still had layers of the yellow second phase interspersed throughout it. Leach testing of these two samples detected low levels of metals and anions in the MPCT and MTCLP. P5-15 leached aluminum (31 ppm), silicon (32 ppm), and sodium (126 ppm) in the MPCT, and chromium (0.7 ppm) and uranium (0.3 ppm) in the MTCLP. P5-14 leached cadmium (25 ppm), silicon (24 ppm), and sodium (74 ppm) in the MPCT, and chromium (2.0 ppm) and uranium (0.2 ppm) in the MTCLP. Both were LLD for gross alpha/beta.

From the performance of the four test waste/flyash formulations, it was decided that the waste/flyash ratio was sound and that this formulation should be developed in the advanced phase testing.

Remedy Selection Tests

The advanced phase Waste Pit 5 composite sample used the soil and flyash formulations listed in Table 4-39. The soil formulation (Formulation 1) produced a low viscosity melt that cooled to a nonporous, dark amber glass that was streaked with yellowish-brown, incompletely vitrified material. This glass product was identical to that produced during Remedy Screening. The bulking factor, as shown on Table 4-40, was -88 percent, indicating that a significant volume reduction occured during furnace processing.

The flyash formulation (Formulation 2) produced a low viscosity melt that cooled to a multiphase, semiporous product identical to that produced during Remedy Screening. Its bulking factor was -69 percent.

Results for Waste Pit 5 TCLP radionuclides for the two formulations are shown in Table 4-41. The metals in the TCLP leachates for the waste treated with the two vitrification formulations and the TC criteria for metals are shown in Table 4-42. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds. The concentrations of the radionuclides were compared. Formula 2 had the better results. Specific exceptions where Formulation 1 was better were Pu-238, Ra-228, and Sr-90. For all other radiological constituents of concern, Formulation 2 had lower concentrations, or both formulations had NDs.

The results of the PCT expressed as NLRs are presented in Table 4-43. The waste/soil composite glass sample leached at levels typically < 1 percent of the SRHLWC for the metals of interest. The worst metals were Na and K at 9 and 10 percent of the SRHLWC, respectively. The waste/flyash composite exceeded the SRHLWC for Na, K, and B.

Table 4-39

VITRIFICATION--PIT 5
ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	299	0	35
2	100	0	299	100

Table 4-40

VITRIFICATION--ADVANCED PHASE PIT 5
BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
Composite	1	-88	-78
Composite	2	-69	

TABLE 4-41

WASTE PIT 5 VITRIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	ND	ND
Neptunium-237	NA	2.690	ND
Plutonium-238	NA	ND	0.490
Plutonium-239/240	NA	1.320	ND
Radium-226	NA	97.700	49.200
Radium-228	NA	ND	7.980
Strontium-90	NA	7.400	10.400
Technetium-99	NA	18.000	ND
Thorium-228	NA	2.760	0.750
Thorium-230	NA	171.000	39.100
Thorium-232	NA	1.140	ND
Uranium-234	NA	106.000	38.900
Uranium-235/236	NA	6.890	1.940
Uranium-238	NA	209.000	74.900
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thoruim (Total)	NA	0.010	ND
Uranium (Total)	NA	0.620	0.220

* See Table 4-6

\+ See Table 4-6

TABLE 4-42

WASTE PIT 5 VITRIFICATION TCLP
METEL DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS
Antimony	0.082	0.011	0.007	
Arsenic	0.027	0.304	0.039	5.000
Barium	3.904	3.480	1.630	100.000
Beryllium	0.006	0.009	0.010	
Cadmium	0.003	ND	ND	1.000
Chromium	0.014	0.029	0.137	5.000
Cobalt	0.032	0.020	0.083	
Copper	1.916	0.139	ND	
Cyanide	ND	ND	ND	
Lead	0.035	0.038	ND	5.000
Manganese	2.307	1.380	1.000	
Mercury	0.002	ND	ND	0.200
Molybdenum	0.190	1.040	1.350	
Nickel	0.296	0.066	0.299	
Selenium	ND	ND	ND	1.000
Silver	0.099	ND	ND	5.000
Thallium	0.223	ND	ND	
Vanadium	0.815	1.620	0.219	
Zinc	0.326	0.338	0.200	

* See Table 4-6

\+ See Table 4-6

Table 4-43

PIT 5 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	Composite	1	0.2	9	0.6	0.1	Not Calc'd	10	Not Calc'd
2	Composite	4	0.5	>500	2	Not Calc'd	Not Calc'd	476	>500

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

Waste Pit 5 Vitrification - Radon Emission

Figures 4-11 and 4-12 both show radon leach and emanation rates lower than the untreated waste or the calculated rate.

Vitrification Testing Results - GTS Duratek/Catholic University of America

Compositional Analysis

Characterization results for Waste Pit 5, Waste Pit 6, and Clearwell sludges, Fernald soil, and Fernald fly ashes (referred to as Fly Ash 1 and Fly Ash 2, respectively) are presented in this section. A summary of compositional conclusions for these samples is given in Table 4-44.

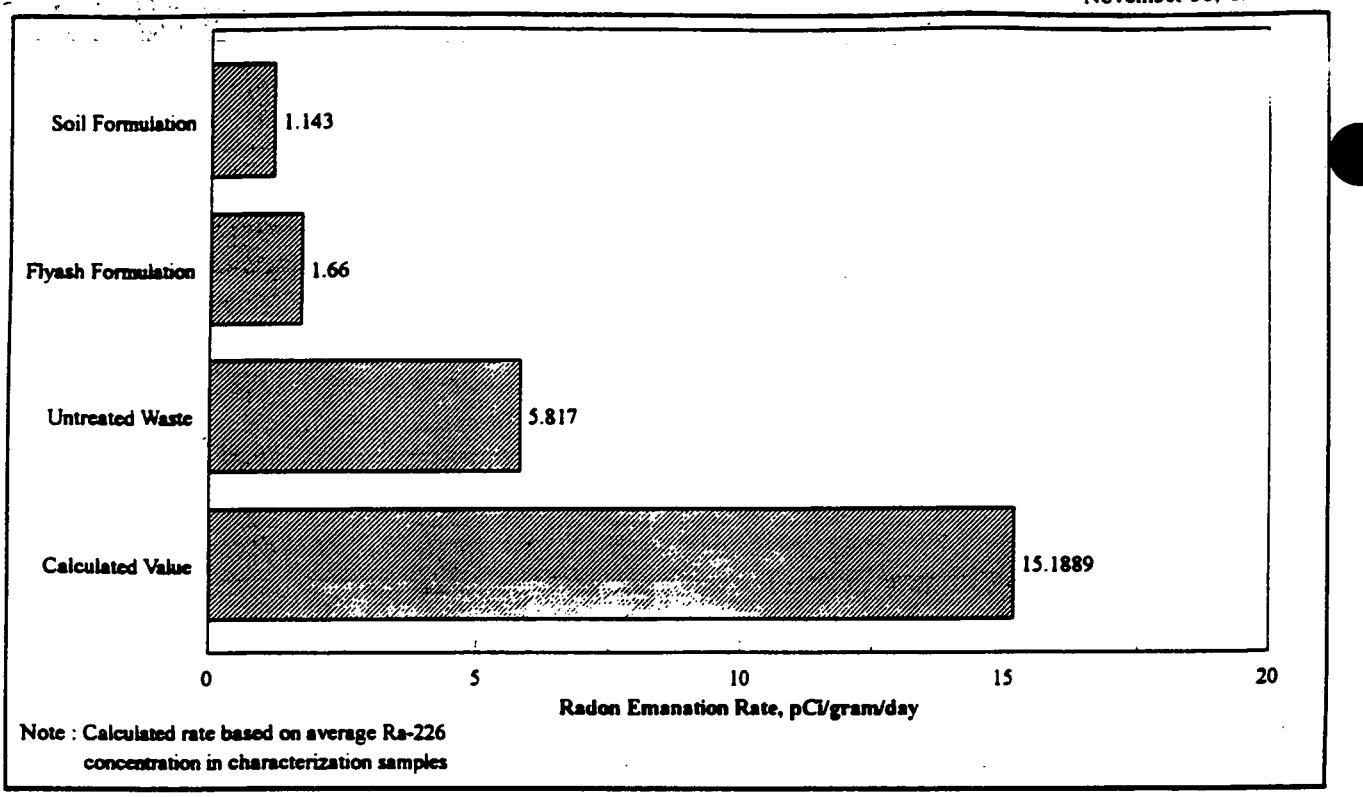
The Waste Pit 5 material was highly stratified with approximately 25 percent by volume free water. The Waste Pit 6 material contained approximately 20 percent by volume free water with a solid phase very much stiffer than the Waste Pit 5 sample. Unlike the Waste Pit 5 sample, several chunks of material ranging in size up to about 2 cm were found in the Waste Pit 6 sample.

The individual containers were thoroughly mixed before collecting any samples for analysis or vitrification.

Physical Characterization and Carbon Content

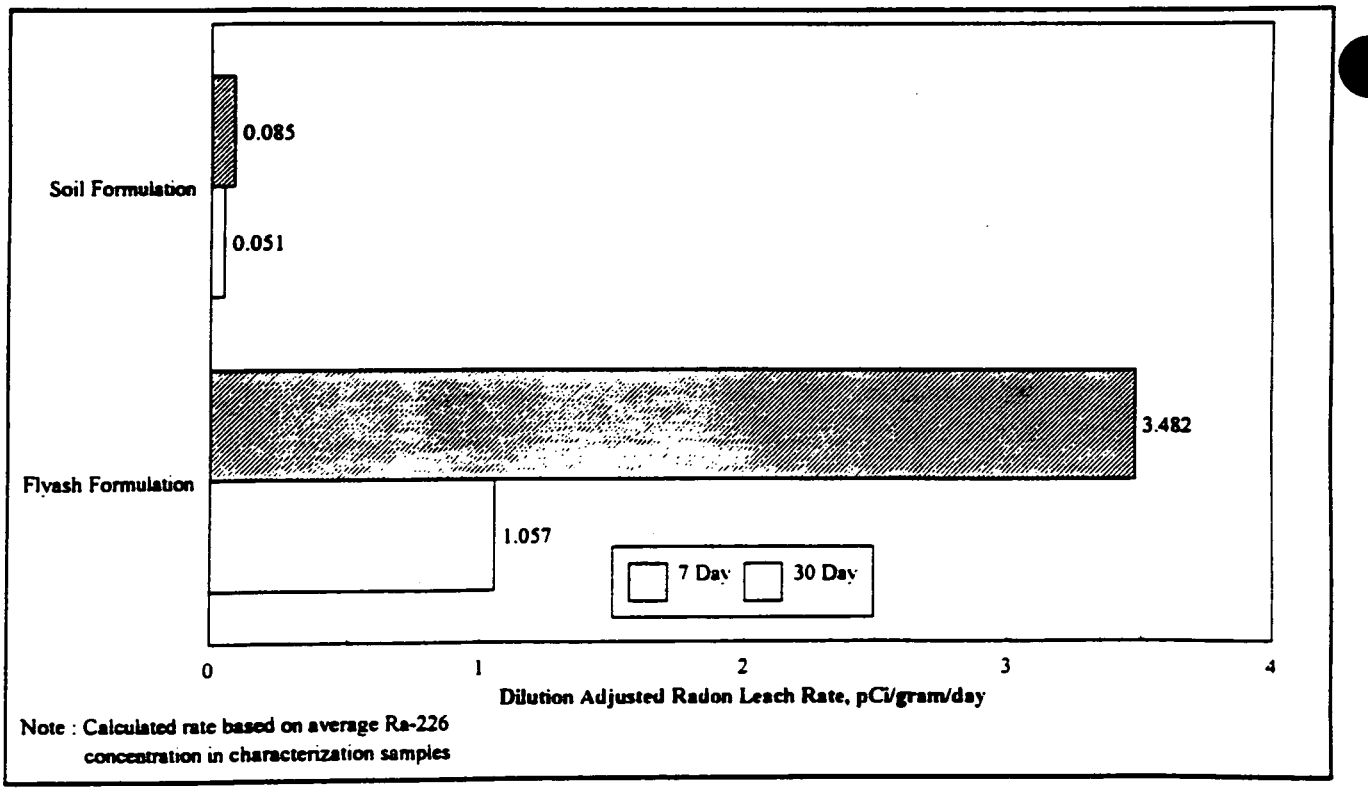
Specific Gravity: Specific gravity measurements were made on as-received samples and samples dried at 110°C for 18 hours. These data are listed in Table 4-45 along with results on weight loss as a function of temperature, particle size distribution, and carbon content. Waste Pit 5 and Waste Pit 6 show large increases in specific gravity due to the amount of water lost (67 and 34 wt percent, respectively). Both fly ashes show much smaller changes in specific gravity on drying, increasing from 1.5 g/ml to 1.8 g/ml.

Carbon Content: The total carbon, organic carbon, and inorganic carbon contents, were analyzed for all as-received samples (Table 4-45). Total carbon contents of each of the sludges and the soil are all less than 5 percent, with less than half of that composed of organics. Fly Ash 1 has 18 percent



FL/FEMP/OU1TR/45-7A

FIGURE 4-11 - PIT 5 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES



FL/FEMP/OU1TR/45-7B

FIGURE 4-12 - PIT 5 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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Summary of FEMP Waste Compositions

BASIS = DRIED AT 1150°C FOR 4 HOURS						
	Pit 5 (wt%)	Pit 6 (wt%)	Clearwell (wt%)	Soil (wt%)	Fly Ash (wt%) FEMP 920729-052	Fly Ash (wt%) FEMP 920729-053
	DCP and Fluoride Analysis	DCP and Fluoride Analysis	DCP and Fluoride Analysis	DCP Analysis	DCP Analysis	DCP Analysis
Al_2O_3	2.11	0.82	6.54	7.58	33.16	25.61
B_2O_3	0.08	0.05	0.05	0.13	0.2	0.13
BaO	1.88	0.01	0.30	0.04	0.08	0.31
CaO	37.19	3.38	25.52	22.14	1.12	3.55
Cr_2O_3	0.07	0.01	0.03	0.05	0.00	0.15
Fe_2O_3	3.18	0.4	3.34	3.4	4.71	13.53
K_2O	0.30	0.25	1.58	2.01	2.46	0.00
Li_2O	0.34	0.03	0.18	0.25	0.05	0.03
MgF_2	37.6	83.9	6.29	--	--	--
MgO	1.33	0	0.63	5.34	0.78	1.77
MnO_2	0.12	0.01	0.37	0.17	0.02	0.12
Na_2O	0.95	0.1	0.48	1.03	0.46	0.61
NiO	0.07	0.03	0.02	0.06	0.01	0.00
P_2O_5	0.24	0.08	0.81	0.00	0.17	NA
SiO_2	13.98	3.68	46.97	56.7	55.1	52.65
SrO	0.06	0.01	0.03	0.04	NA	0.12
TiO_2	0.22	0.07	0.40	0.51	1.65	1.38
ZrO_2	0.25	0.25	0.03	0.05	0.04	0.03
Total	99.97	93.09	93.60	99.50	100	100

Table 4-44
(Continued)

Radionucleides (ppm)	Pit 5	Pit 6	Clearwell	Fly Ash 1
Tc-99	0.38	<0.02	0.05	0.41
Th-232	730	12	97	99
U-233	<0.02	<0.02	0.44	0.03
U-234	0.38	1.2	0.04	<0.04
U-235	49	160	6.5	0.52
U-236	1.2	3.1	0.17	0.08
U-238	3400	102,700	1900	93
Heavy Metals (ppm)				
Pb	120	42	270	120
Hg	0.8	0.03	1.3	11
Tl	7.8	0.3	2.2	6.0
Cd	4.5	<0.02	1.0	<0.02

Fernald Sludge, Soil and Fly Ash Physical Characterization and Carbon Content Data

	Pit 5	Pit 6	Clearwell	Soil[5]	Fly Ash 1	Fly Ash 2
Specific Gravity @ 20°C[1]						
As received	1.264	1.845	1.575	2.508	1.559	1.537
Dried at 110°C/18 hours	2.848	3.223	1.943	2.542	1.802	1.853
Carbon Content, % (As-received basis)						
TC	2.0	0.55	3.4	4.5	18.4	56
TOC	0.26	0.31	0.97	1.9	18.8	37
Sieve Analysis[3]: Sieve #10	99.98% Pas 0.02% Ret	99.70% Pas 0.30% Ret	97.26% Pas 2.74% Ret	76.95% Pas 23.05% Ret	92.68% Pas 7.32% Ret	83.74% Pas 16.26% Ret
#40	94.06% Pas 5.92% Ret	94.74% Pas 4.96% Ret	81.78% Pas 15.48% Ret	61.61% Pas 15.34% Ret	69.68% Pas 23.00% Ret	61.49% Pas 22.25% Ret
#60	89.51% Pas 4.55% Ret	89.04% Pas 5.70% Ret	73.14% Pas 8.64% Ret	56.10% Pas[4] 5.51% Ret[4]	61.40% Pas 8.28% Ret	48.33% Pas 13.16% Ret
#100	78.17% Pas 11.34% Ret	81.80% Pas 7.24% Ret	67.60% Pas 5.44% Ret	43.53% Pas 12.57% Ret	51.94% Pas 9.46% Ret	36.82% Pas 11.51% Ret
#200	65.01% Pas 13.16% Ret	70.66% Pas 11.14% Ret	62.38% Pas 5.32% Ret	36.68% Pas 6.85% Ret	39.47% Pas 12.47% Ret	22.64% Pas 14.18% Ret
Weight Loss[2], %						
110°C	67.47	33.73	42.55	8.56[6]	19.28	25.20
450°C	70.57	35.60	44.79	2.53	33.08	32.67
850°C	76.24	36.55	55.24	18.22	37.93	56.66
1150°C	77.39	38.86	55.90	26.41	37.93	54.95

REMARKS:

[1]ASTM D854 procedure was followed; "as-received" results refer to samples that were measured without pre-drying.

[2]All samples were dried in a Pt crucible except for the fly ash samples which were dried in Inconel crucibles.

[3]The sieve analyses of the samples are based on 50g samples of Pit 6 and Clearwell, and a 42g sample of Pit 5 sludge; all were oven-dried at 110°C. ASTM D422 procedure was followed.

[4]These are values for sieve #50, not #60.

[5]The specific gravity and carbon content analyses were done on soil reconstituted from fractions resulting from sieving through mesh #10, 30, 40, 50, 100, and 200 due to shortage of material.

[6]Drying of soil sample for this stage (110°C) was done for 20 hours instead of 18 hours.

0323

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carbon; all in the form of organics. Fly Ash 2 has 56 percent carbon; composed of 37 percent organic, and 19 percent inorganic carbon.

Particle Size Analysis: Each sample was dried at 110°C for 18 hours, then sieved (Table 4-45). Sixty to 70 percent of the sludges passed mesh #200 (<75 micron). The soil and fly ashes were coarser, with 20 percent to 40 percent passing mesh #200 (<0.075 mm).

Weight Loss: Weight loss data are shown in Table 4-45 and Figure 4-13. The Waste Pit 5 sample consists mostly of water, losing about 67 percent of its weight after drying at 110°C for 18 hours and 77 percent of its weight on drying at 1150°C for four hours. The weight loss from 110°C to 1150°C is most likely due to bound water, carbonates, and hydroxides released as CO_2 and H_2O. Clearwell sludge and Pit 6 sludge contain less water, as indicated by weight losses of 43 percent and 34 percent, respectively. Fly Ashes 1 and 2 lose 38 percent and 55 percent of their weight respectively after drying.

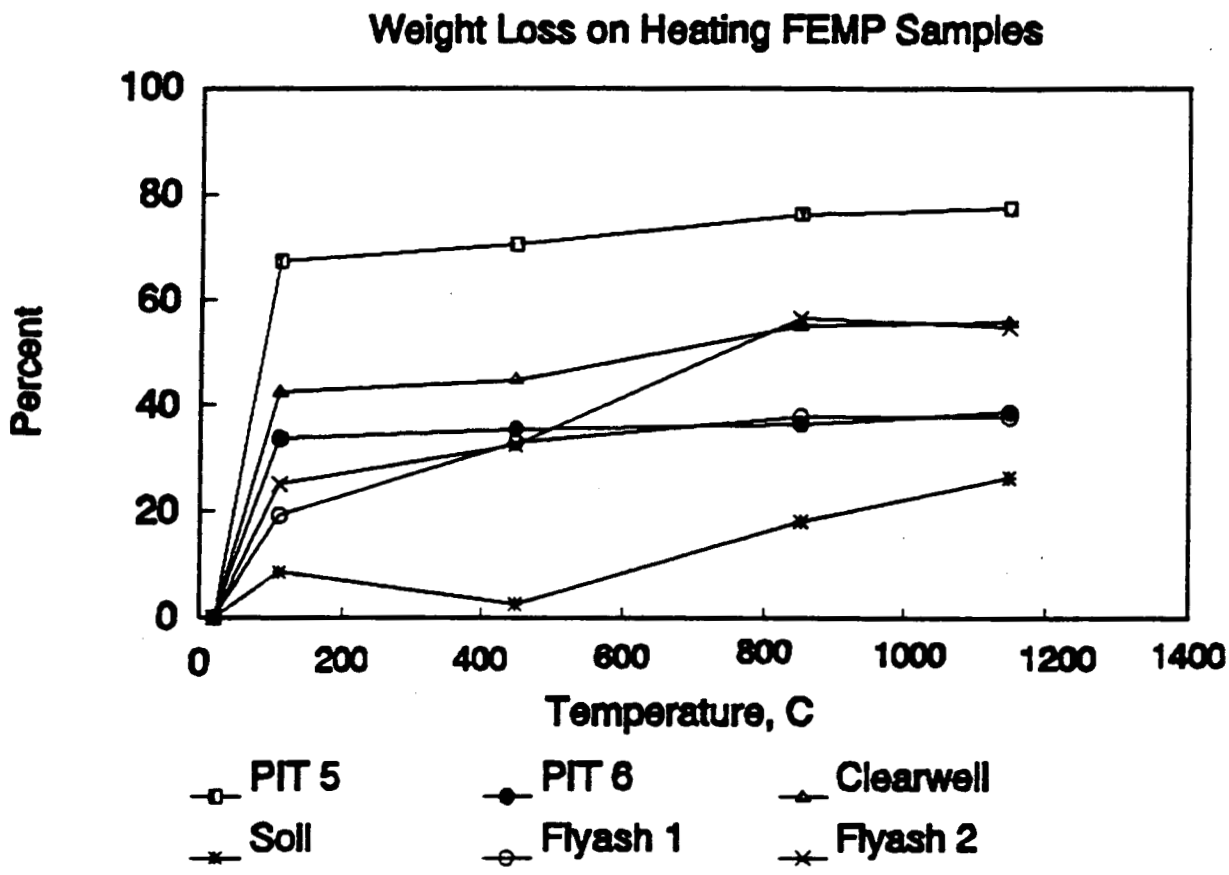
Total carbon measurements indicate Fly Ash 2 contains 56 percent total carbon. In comparison, a 55 percent weight loss for Fly Ash 2 after drying the as-received sample at 1150°C for four hours. This would indicate the weight loss is due to loss of carbon (presumably by combustion and loss as CO_2). Since it is very unlikely any form of carbon present in these samples would combust at 110°C, the weight loss after drying at 110°C/18 hours is assumed to be mainly due to water. Using this logic and the weight loss data, the carbon content should be no more than 30 percent (i.e. equal to the weight loss on drying the 110°C/18 hour sample to 1150°C/4 hour), whereas 56 percent total carbon was obtained. Since the five carbon content measurements for the fly ash were in agreement to within ± 7 percent, the most likely explanation is the samples are heterogeneous on a small scale (since only 50 mg samples are used for the carbon content measurements). In contrast, the weight loss data reflect the behavior of much larger samples (of the order of 100g).

Compositional Results

Results from analyses of sludges, soil, and fly ashes by total dissolution followed by DCP emission spectroscopy are summarized in Table 4-46. Unnormalized and normalized data are shown for each

Figure 4-13

Weight Loss of Sludges, Soil and Fly Ashes on Heating



Elemental analysis of FEMP sludges, soil, and fly ash after drying at 1150°C for 4 hrs, and total dissolution, followed by DCP emission spectroscopy. The results are quoted on an oxide basis. (*Note: fluoride is not determined by this analysis*)

BASIS = DRIED AT 1150°C FOR 4 HOURS												
Components as Oxides	Pit 5 (wt.%)		Pit 6 (wt.%)		Clearwell (wt.%)		Soil (wt.%)		Fly Ash FEMP 920729-052 (wt.%)		Fly Ash FEMP 920729-053 (wt.%)	
	unnorm	norm	unnorm	norm	unnorm	norm	unnorm	norm	unnorm	norm	unnorm	norm
Al_2O_3	2.11	2.43	0.82	1.28	6.54	7.16	7.27	7.58	31.7	33.16	23.94	25.61
B_2O_3	0.08	0.10	0.05	0.09	0.05	0.05	0.13	0.13	0.19	0.2	0.12	0.13
BaO	1.88	2.15	0.01	0.01	0.30	0.33	0.04	0.04	0.08	0.08	0.29	0.31
CaO	37.19	42.64	3.38	5.32	25.52	27.94	21.24	22.14	1.08	1.12	3.32	3.55
Cr_2O_3	0.07	0.08	0.01	0.02	0.03	0.03	0.05	0.05	0.00	0.00	0.14	0.15
Fe_2O_3	3.18	3.64	0.40	0.63	3.34	3.65	3.26	3.4	4.5	4.71	12.64	13.53
K_2O	0.30	0.35	0.25	0.39	1.58	1.73	1.93	2.01	2.35	2.46	0.00	0.00
Li_2O	0.34	0.39	0.03	0.05	0.18	0.19	0.24	0.25	0.05	0.05	0.03	0.03
MgO	25.66	29.41	54.29	85.55	4.7	5.15	5.13	5.34	0.74	0.78	1.65	1.77
MnO_2	0.12	0.13	0.01	0.02	0.37	0.41	0.16	0.17	0.02	0.02	0.11	0.12
Na_2O	0.95	1.09	0.10	0.15	0.48	0.52	0.98	1.03	0.44	0.46	0.57	0.61
NiO	0.07	0.08	0.03	0.05	0.02	0.02	0.06	0.06	0.01	0.01	0.00	0.00
P_2O_5	NA	NA	0.08	0.13	0.81	0.89	NA	NA	0.16	0.17	NA	NA
SiO_2	13.98	16.03	3.68	5.80	46.97	51.43	54.4	56.7	52.69	55.1	49.21	52.65
SrO	0.06	0.07	0.01	0.01	0.03	0.04	0.04	0.04	NA	NA	0.12	0.12
TiO_2	0.22	0.25	0.07	0.11	0.4	0.43	0.49	0.51	1.57	1.65	1.29	1.38
ZrO_2	0.25	0.29	0.25	0.40	0.03	0.03	0.05	0.05	0.03	0.04	0.02	0.03
TOTAL	86.46	100	63.47	100	91.35	100	95.47	100	95.61	100	93.45	100

NA = Not Analyzed

compositional analyses. Recoveries for Waste Pit 5 and Waste Pit 6 samples were 72 percent and 63 percent, respectively. These low recoveries are due to the presence of fluoride. For the Clearwell sludge, 91 percent recovery was obtained on an oxide basis; part of the remainder is due to the presence of some fluoride and sulfate.

The same digestion solution used for the DCP analysis of Waste Pit 5 was also analyzed by ion chromatography for chloride and sulphate which indicated there is no chloride (within the detection limit) and only small amounts of sulfate present in Pit 5 and Clearwell sludges. The ASTM C169 procedure for fluoride analysis was also performed on samples of the pit sludges. Compositions corrected for fluoride loss are given in Table 4-47.

Gamma Spectroscopy

The gamma spectra obtained from sludges and fly ashes and background spectrum show the Th-234 peak at 63.3 KeV, including some combination of U-235 and Th-230 at 185.9 KeV, are present in all sludges and fly ashes spectra. All of the spectra show activity due largely to Pb-212 and Pb-214 except for Waste Pit 6 sludge where the peaks are much closer to the background. The peaks in the region between 65 and 120 KeV have too many possibilities for the source of the emitter to permit an unambiguous assignment. Quantitative analysis by conversion of the gamma spectra to absolute activities was not possible due to the difficulty in making geometrical and self-screening corrections for these materials.

Analysis by ICPMS

Samples of dried sludges and fly ash were subjected to total acid dissolution and the solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICPMS). Results are shown in Table 4-48. Table 4-49 compares results for Waste Pit 5 samples dried at 450°C with samples dried at 1150°C. Based on the weight loss data in Table 4-45, an increase of about 30 percent would be expected in the levels of all components unless they are volatilized at 1150°C. Significant decreases are seen for Tc-99, Pb, and especially thallium. All of these species are known to have relatively high volatilities; the presence of fluorides would tend to enhance this effect. Surprisingly, mercury

now considerably closer to 100%.

Table 3.6 Composition of Pit 5 and Pit 6 and Clearwell Obtained by Including Fluoride Analysis Data

BASIS = DRIED AT 1150°C FOR 4 HOURS						
Components as Oxides	Pit 5 (wt.%)		Pit 6 (wt.%)		Clearwell (wt%)	
	unnorm	corrected using fluoride	unnorm	corrected using fluoride	unnorm	corrected using fluoride
Al_2O_3	2.11	2.11	0.82	0.82	6.54	6.54
B_2O_3	0.08	0.08	0.05	0.05	0.05	0.05
BaO	1.88	1.88	0.01	0.01	0.30	0.30
CaO	37.19	37.19	3.38	3.38	25.52	25.52
Cr_2O_3	0.07	0.07	0.01	0.01	0.03	0.03
Fe_2O_3	3.18	3.18	0.4	0.4	3.34	3.34
K_2O	0.30	0.30	0.25	0.25	1.58	1.58
Li_2O	0.34	0.34	0.03	0.03	0.18	0.18
MgF_2	----	37.6	----	83.95	----	6.29
MgO	25.66	1.33	54.29	0	4.7	0.63
MnO_2	0.12	0.12	0.01	0.01	0.37	0.37
Na_2O	0.95	0.95	0.1	0.1	0.48	0.48
NiO	0.07	0.07	0.03	0.03	0.02	0.02
P_2O_5 (d)	0.24	0.24	0.08	0.08	0.81	0.81
SiO_2	13.98	13.98	3.68	3.68	46.97	46.97
SrO	0.06	0.06	0.01	0.01	0.03	0.03
TiO_2	0.22	0.22	0.07	0.07	0.40	0.40
ZrO_2	0.25	0.25	0.25	0.25	0.03	0.03
Total	86.46	99.97	63.47	93.09	91.35	93.60
Excess Fluoride (a)		0		0.24		0
Measured fluoride (b)	15.5		39.5		2.4	
Corrected fluoride (c)	22.9		51.4		3.8	

(a) The measured fluoride content (corrected for loss between 450°C and 1150°C) is listed as MgF_2 to the extent allowed by the measured Mg analysis; these entries represent the excess fluoride obtained by this procedure;

(b) The measured fluoride content at 1150°C; See Table 3.5;

(c) The fluoride content at 1150°C, corrected for loss between 450°C and 1150°C;

(d) Phosphorus was not analyzed in the 6-4-92 sample of Pit 5; the value listed here is the average of the measurements made on 9-11-92 and 2-23-93 samples. See Table 3.7.

Table 4-48

ICPMS results on Pit 5, Pit 6, and Clearwell sludges, and Fly Ash 1. All samples were dried at 450°C before acid dissolution and analysis.

BASIS = DRIED AT 450°C FOR 4 HOURS				
Radionucleides (ppm)	Pit 5	Pit 6	Clearwell	Fly Ash 1
Tc-99	0.38	<0.02	0.05	0.41
Th-230	0.88	0.07	0.06	0.06
Th-232	730	12	97	99
U-233	<0.02	<0.02	0.44	0.03
U-234	0.38	1.2	0.04	<0.04
U-235	49	160	6.5	0.52
U-236	1.2	3.1	0.17	0.08
U-238	3400	102,700	1900	93
Heavy Metals (ppm)				
Pb	120	42	270	120
Hg	0.8	0.03	1.3	11
Tl	7.8	0.3	2.2	6.0
Cd	4.5	<0.02	1.0	<0.02

Table 4-49

ICPMS results on dried Pit 5 sludge samples after acid dissolution

Radionucleides (ppm)	Pit 5 Dried at 450°C for 4 hours	Pit 5 Dried at 1150°C for 4 hours
Tc-99	0.38	0.12
Th-232	730	1300
Th-230	0.88	1.3
U/Th-234	0.38	0.65
U-233	<0.02	0.11
U-235	49	83
U-236	1.2	2.3
U-238	3400	3800
Heavy Metals (ppm)		
Pb	120	48
Hg	0.8	1.4
Tl	7.8	0.26
Cd	4.5	8.0

seems to be well retained at 1150°C. These results are consistent with glass melting and off-gas analysis data, except that solubility in the glass melt strongly moderates these losses for all species other than thallium.

Crucible Melts from Waste Pit 5 Materials

Forty crucible melts (F5-9 was never melted) containing various amounts of dried Waste Pit 5 sludge, whole soil, Fly Ash 1, and additives were made in order to determine the compositional range suitable for vitrification. In addition, a series of surrogate non-radioactive glass melts was also made to better understand the important role of fluoride in these melts. Predrying of Waste Pit 5 sludge samples before vitrification was used to increase the mass of glass produced from each crucible loading. The fly ash was oxidized to burn off all forms of carbon to prevent damage to the Pt crucibles used. For the F5-37 crucible melt, as-received fly ash (wet) was used. A summary of the forty melts and the analyses performed is given in Table 4-50.

The blends were melted in clay crucibles for the first six melts until evidence of silicon and aluminum contamination from the clay crucibles was discovered. All melts after F5-6 were performed using Pt/Au crucibles except F5-35, F5-36, and F5-37 for which inconel crucibles were used. The weight percent data in Table 4-50 are based on dry weights; both sludge and soil had been dried at 450°C (five hours for sludge and four hours for soil) before vitrification and fly ash samples were dried at 1150°C for four hours. The blends were usually melted at 1150°C for one hour with continuous stirring for the last 0.5 hour. The glass melts were then removed from the furnace and cooled to room temperature.

Results: The first four melts used uncontaminated soil from the Weldon Spring site since the Fernald soil samples were unavailable; Fernald soils were used in all subsequent crucible melts. Figure 4-14 shows the waste loading for each crucible melt on a dry and a wet basis.

Compositional analyses of glasses made from surrogate materials melted in clay crucibles indicates silicon and aluminum leach out of the clay crucibles into the glass, whereas surrogate glasses melted

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Summary of Crucible Melts made from FEMP Pit 5 and Data Collected (see notes for key)

Name	Pit 5		Soil	Fly Ash	Additives	Fluoride Analysis	XTAL	Vis	Con	TCLP	PCT	DCP Analysis
F5-1	CL	70	30WS	0	0		•	•	•			•
F5-2	CL	40	40WS	0	20							•
F5-3	CL	70	30WS	0	0		•	•	•			
F5-4	CL	40	40WS	0	20							
F5-5	CL	41.7	41.7	0	16.6		•			•	•	•
F5-6	CL	70	30	0	0							
F5-7	Pt/Au	50	40	0	10		•	•	•	•	•	•
F5-8	Pt/Au	40	40	0	20		•	•	•	•	•	•
F5-10	Pt/Au	45	45	0	10					•	•	•
F5-11	Pt/Au	45	40	0	15			•	•			•
F5-12	Pt/Au	60	14	0	26	•	•	•	•			•
F5-13	Pt/Au	60	14	0	26	•	•	•	•			•
F5-14	Pt/Au	60	14	0	26		•	•	•			•
F5-15	Pt/Au	60	14	0	26		•	•	•			•
F5-16	Pt/Au	60	17	0	23			•	•			•
F5-17	Pt/Au	60	14	0	26			•	•	•	•	•
F5-18	Pt/Au	55	14	0	31			•	•			
F5-19	Pt/Au	55	14	0	31					•	•	•
F5-20	Pt/Au	50	14	0	31	•	•	•	•	•	•	
F5-21	Pt/Au	50	14	0	31							•
F5-22	Pt/Au	40	20	0	40		•	•	•	•	•	•
F5-23	Pt/Au	35	20	0	45	•	•	•	•	•	•	•
F5-24	Pt/Au	30	39	0	31	•		•	•	•	•	•
F5-25	Pt/Au	30.9	40.2	0	28.9	•	•	•	•	•	•	•
F5-26	Pt/Au	28.5	37.1	0	34.4		•	•	•			•

Table 4-50
(Continued)

Name	Pit 5	Soil	Fly Ash	Additives	Fluoride Analysis	Crystal	Visc	Con	TCLP	PCT	DCP Analysis
F5-27	Pt/Au 28.7	37.3	0	34							•
F5-28	Pt/Au 55	14	0	31		•			*	*	
F5-29	Pt/Au 55	14	0	31					*	*	
F5-30	Pt/Au 55	14	0	31					*	*	
F5-31	Pt/Au 52	0	0	48	*	*	*	*			*
F5-32	Pt/Au 52	0	0	48	*	*	*	*	*	*	*
F5-33	Pt/Au 50	7	0	43	*		*	*			*
F5-34	Pt/AU 49	7	16	28		•	*	*			*
F5-35	IN 49.81	7.11	16.31	26.77	*				*	*	*
F5-36	IN 50	15	0	35	*				*	*	*
F5-37	IN 45.8	13.7	22.2 (wet)	18.3					*	*	*
F5-38	Pt/Au 50	15	15	20							
F5-39	Pt/Au 48	14	15	23			*	*	*	*	
F5-40	Pt/Au 47.1	13.5	14.5	24.9			*	*	*	*	
F5-41	Pt/Au 51	30	0	19	•		*	*			

CL = melted in clay crucibles.
Pt/Au = melted in platinum/gold crucibles.
IN = melted in inconel crucibles
* = analysis completed
WS = Weldon Spring site soil was used
XTAL = Crystallization data
Vis = Melt viscosity data
Con = Electrical conductivity data
DCP = Glass composition analysis by dissolution followed by DCP spectroscopy

The numbers for Pit 5, soil, fly ash, and additives are in weight percent.

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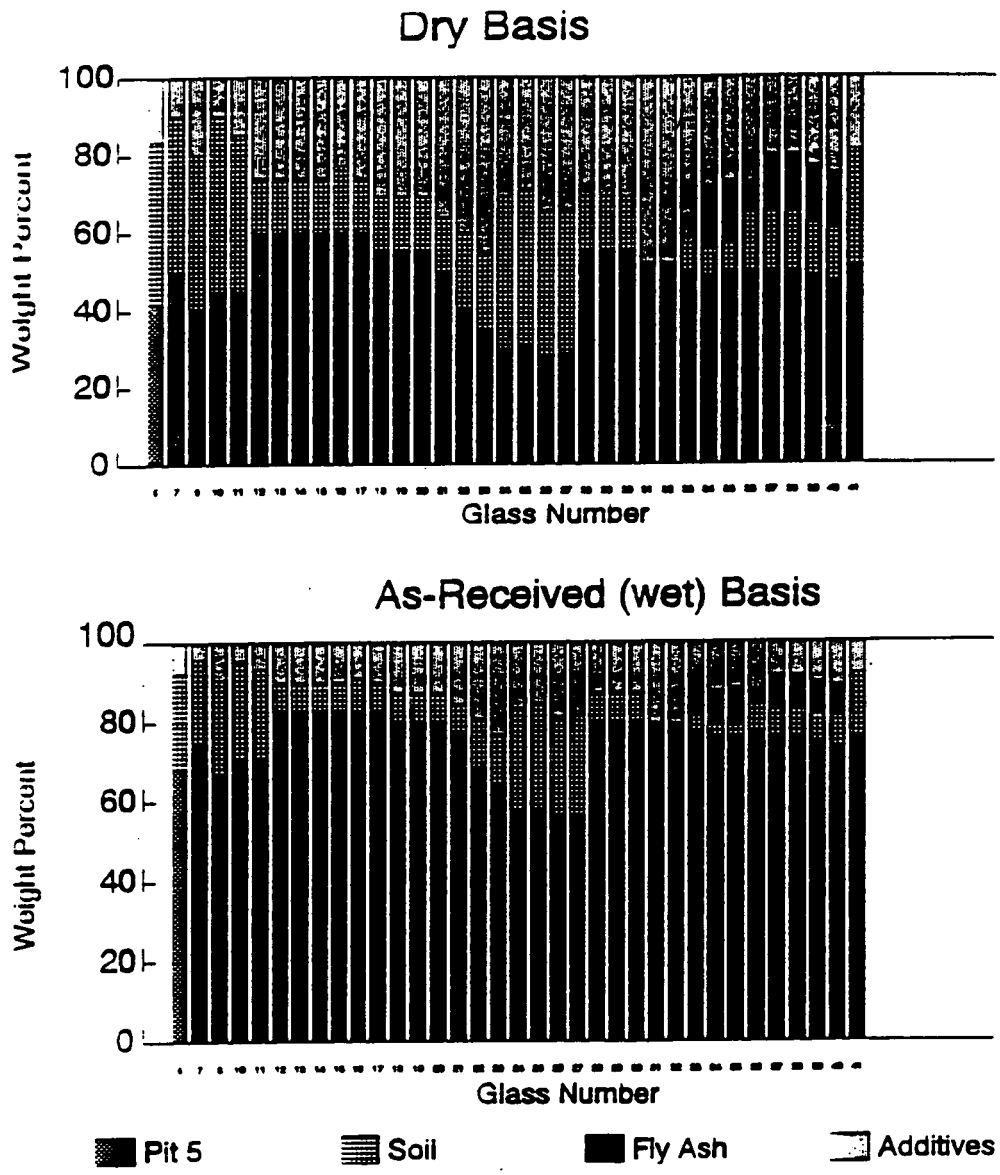
Figure 4-14



Waste Loadings of FEMP Pit 5 Crucible Melt Glasses

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in Pt/Au crucibles showed no such contamination. For this reason, Pt/Au crucibles were used for all remaining glass melts, except F5-35, F5-36, and F5-37 for which inconel crucibles were used.

The batch composition used for each melt and the appearance of the glass upon cooling are summarized in Table 4-51. Objectives of the batch composition variations included: varying sludge-to-soil ratio; effect of fly ash; effect of various additives such as SiO_2, Na_2O, B_2O_3, Al_2O_3, K_2O and Fe_2O_3; and effect of fluorine.

For the first glasses melted, appearance upon cooling was the initial determination of a glass quality. Opaque greenish glasses were initially identified as poor glasses, however, it was determined this appearance was due to phase separation (i.e. glass-in-glass separation as distinct from crystallization). Increasing the cooling rate suppresses this phase separation effect. In a production situation it would therefore be preferable to make small, rapidly cooled glass pieces (e.g. gems, marbles, or beads) rather than large glass monoliths.

The general effect of replacing boron with sodium can be seen from the appearance of the glasses F5-18, F5-29, and F5-30 after melting. As the amount of boron decreases (and sodium increases) the amount of crystallization increases, until at 0 percent boron, a ceramic-like material is produced. It appears about 6 wt. percent boron is needed to suppress crystallization.

Compositional Analysis of Glass Melts: Table 4-52 shows the analyzed compositions of 29 of the 40 glass melts, along with the calculated compositions of all of the melts (except those made with Weldon Spring soil). Compositions were calculated by using the normalized DCP analysis of the soil and fly ash, and the unnormalized DCP analysis of Waste Pit 5 along with the fluoride analysis (see Table 4-44). The calculated and analyzed compositions are generally in good agreement. The analyzed column uses DCP analysis in which the measured Mg content was converted to wt. percent as MgF_2. This assumes no fluoride loss during the melting, which is not strictly true. Glasses which show poor agreement between calculated and analyzed compositions are heterogeneous glasses (except F5-26) such as F5-23B (the B means the second melt of F5-23) and F5-27. Both F5-23B and F5-27 contained white powders surrounded by glass suggesting a SiO_2 solubility problem, either kinetic or

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Glass Batch Compositions used for Crucible Melts and Appearance upon Cooling. Entries are weight percent on a dry basis.

Fernald Glass	F5-5	F5-7	F5-8	F5-10	F5-11	F5-12	F5-13	F5-14	F5-15	F5-16
Pit 5	41.7	50	40	45	45	60	60	60	60	60
Soil	41.7	40	40	45	40	14	14	14	14	17
Fly Ash	0	0	0	0	0	0	0	0	0	0
SiO_2	0	0	0	0	0	14	14	17	14	14
Na_2O	8.3	5	10	5	5	5	3	0	0	0
B_2O_3	8.3	5	10	5	10	7	6	6	6	6
Al_2O_3	0	0	0	0	0	0	3	3	6	3
K_2O	0	0	0	0	0	0	0	0	0	0
Fe_2O_3	0	0	0	0	0	0	0	0	0	0
CaO	0	0	0	0	0	0	0	0	0	0
Appearance upon cooling	glassy, black	opaque on top, glassy in middle	glassy, brown	green on bottom pores on top	heterogeneous, undissolved chunks	glassy, brown	glassy, brown	opaque green	very glassy	opaque, greenish brown

Fernald Glass	F5-17	F5-18	F5-19	F5-20	F5-21	F5-22	F5-23	F5-24	F5-25	F5-26
Pit 5	60	55	55	50	50	40	35	30	30.9	28.5
Soil	14	14	14	14	14	20	20	39	40.2	37.1
Fly Ash	0	0	0	0	0	0	0	0	0	0
SiO_2	14	14	14	19	14	20	22	11.5	11.9	10.9
Na_2O	0	5	0	5	5	6	6	5.5	5.7	5.2
B_2O_3	3	6	6	6	6	5	7	7	7.2	11.7
Al_2O_3	9	6	6	6	11	5	6	4	4.1	3.8
K_2O	0	0	5	0	0	0	0	0	0	0
Fe_2O_3	0	0	0	0	0	4	4	3	0	2.8
CaO	0	0	0	0	0	0	0	0	0	0
Appearance upon cooling	green on bottom, opaque brown on top	glassy	Not melted at 1150°C. Caramel/ green after heating to 1200°C	dark green & opaque remelt in clay gives glassy brown	opaque, brown with white chunks	glassy brown	heterogeneous; green, brown, black, & white; F5-23B still has white powder	glassy brown	glassy brown	glassy brown

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Table 4-51
(Continued)

Fernald Glass	F5-27	F5-28	F5-29	F5-30	F5-31	F5-32	F5-33	F5-34	F5-35	F5-36
Pit 5	28.7	55	55	55	52	52	50	49	49.81	50
Soil	37.3	14	14	14	0	0	7	7	7.11	15
Fly Ash	0	0	0	0	0	0	0	16	16.31	0
SiO_2	11	14	14	14	22	22	19	10	10.21	14
Na_2O	7.1 (NaF)	5	8	11	7	7 (NaF)	7	6.5	4.9	6
B_2O_3	6.7	3	3	0	9	9	9	9	9.12	8
Al_2O_3	6.2 (AlF_3)	6	6	6	6	6	5.5	0	0	4
K_2O	0	0	0	0	0	0	0	0	0	0
Fe_2O_3	2.8	3	0	0	1	1	1	1	1.02	3
CaO					3	3	1.5	0.84	1.52	0
Appearance upon cooling	heterogeneous, white,green, and blue	lots of crys	bits of crys in glass	homogeneous rock	glassy brown	opaque green	glassy brown	opaque green	glassy black	shiny black

Fernald Glass	F5-37	F5-38	F5-39	F5-40	F5-41
Pit 5	45.8	50	48	47.1	51
Soil	13.7	15	14	13.5	30
Fly Ash	22.2 (wet)	15	15	14.5	0
SiO_2	5.5	6	6	5.8	7
Na_2O	3.7	4	8 (NaF)	9.6 (NaF)	5 (NaF)
B_2O_3	7.3	8	7.5	8	7
Al_2O_3	0	0	0	0	0
K_2O	0	0	0	0	0
Fe_2O_3	1.8	2	1.5	1.5	0
CaO	0	0	0	0	0
Appearance upon cooling	opaque black	opaque green	opaque blue & green	opaque green	opaque green

Analyzed and Calculated Compositions (wt%) of FEMP Crucible Melt Glasses

(analysis is from DCP results with the assumption that all of the Mg is combined with fluoride, calculated is batch composition)

	F5-5	F5-5	F5-7	F5-7	F5-8	F5-8	F5-10	F5-11	F5-11	F5-12	F5-12	F5-13	F5-13
Components	(calc)	(anal)	(calc)	(anal)	(calc)	(anal)	(calc)	(calc)	(anal)	(calc)	(anal)	(calc)	(anal)
Al_2O_3	3.9	5.0	4.0	3.7	3.70	3.7	4.3	3.8	4.3	2.1	2.3	5.7	5.3
AlF_3	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA	0.0	NA
B_2O_3	10.1	7.6	6.2	6.1	12.0	11.5	6.2	12.2	13.4	8.3	7.9	7.2	6.7
BaO	0.7	0.7	0.9	0.8	0.71	0.8	0.8	0.8	0.8	1.1	1.0	1.1	1.0
CaO	23.5	22.7	26.5	24.4	22.4	22.8	25.8	24.4	24.2	23.5	21.8	23.5	21.2
Fe_2O_3	2.6	3.0	2.9	3.2	2.5	2.9	2.9	2.7	3.8	2.2	2.9	2.2	2.6
K_2O	0.9	0.9	0.9	1.5	0.9	1.3	1.0	0.9	0.0	0.4	0.5	0.4	0.5
MgO	2.1	*	2.1	*	2.1	*	2.4	2.1	*	0.7	*	0.7	*
MgF_2	15.7	20.6	19.2	25.1	14.9	21.5	17.2	17.0	21.5	22.2	28.1	22.2	28.4
Na_2O	8.6	8.9	5.9	5.7	10.6	10.8	5.9	5.8	5.7	5.5	5.1	3.6	3.1
NaF	0.0	NA	0.0	NA	0.0	NA	0	0.0	NA	0	NA	0.0	NA
SiO_2	28.5	28.4	29.15	26.20	27.1	24.1	31.3	28.1	25.5	32.0	28.7	32.0	38.3
U_3O_8	0.3	0.4	0.3	0.4	0.3	0.5	0.3	0.3	NA	0.4	NA	0.4	NA

* Assumes that all of the Mg is combined with fluoride rather than oxygen
NA = not analyzed

Table 4-52
(Continued)

Components	F5-14 (calc)	F5-14 (anal)	F5-15 (calc)	F5-15 (anal)	F5-16 (calc)	F5-16 (anal)	F5-17 (calc)	F5-17 (anal)	F5-18 (calc)	F5-18 (anal)	F5-18 (anal)	F5-19 (calc)	F5-20 (calc)	F5-20 (anal)
Al_2O_3	5.7	5.2	9.3	8.4	6.0	5.7	12.9	11.1	9.1	8.3	8.9	9.1	8.9	9.5
AlF_3	0.0	NA	0.0	NA	0.0	NA	0.0	NA	0.0	NA	NA	0.0	0.0	NA
B_2O_3	7.2	6.6	7.2	6.5	7.2	6.4	3.6	3.3	7.1	6.7	7.1	7.1	7.0	7.2
BaO	1.1	1.0	1.1	1.0	1.1	1.0	1.1	1.0	1.0	1.0	0.9	1.0	0.9	0.9
CaO	23.5	21.0	23.5	21.2	24.3	21.3	23.5	20.9	21.5	19.3	21.7	21.5	19.6	18.4
Fe_2O_3	2.2	2.6	2.2	2.70	2.3	2.8	2.2	2.7	2.1	2.4	2.6	7.9	1.9	2.4
K_2O	0.4	0.5	0.4	0.3	0.5	0.4	0.4	0.3	0.4	0.4	0.0	0.4	0.4	0.3
MgO	0.7	*	0.7	*	0.9	*	0.7	*	0.7	*	*	0.7	0.7	*
MgF_2	22.2	27.9	22.3	27.5	22.4	27.7	22.2	27.5	20.1	24.6	27.3	20.1	18.0	22.3
Na_2O	0.7	0.4	0.7	0.5	0.7	0.5	0.7	0.5	5.4	5.0	5.5	0.6	6.1	6.0
NaF	0.0	NA	0.0	NA	0.0	NA	0.0	NA	0.0	NA	NA	0.0	0.0	NA
SiO_2	35.6	31.9	32.0	28.4	33.9	30.6	32.0	30.0	30.9	28.8	29.1	30.9	35.7	31.4
U_3O_8	0.4	NA	0.4	NA	0.4	NA	0.4	NA	0.4	NA	NA	0.4	0.3	NA

* Assumes that all of the Mg is combined with fluoride rather than oxygen
NA = not analyzed

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Table 4-52 (Continued)

Components	F5-20	F5-21	F5-22	F5-22	F5-23	F5-23	F5-23B	F5-23B	F5-23BRW	F5-24BR	F5-24	F5-24	F5-25	F5-25
	(anal) (remelt in clay)	(calc)	(calc)	(anal)	(calc)	(anal)	(calc)	(anal)	(anal)	(anal)	(calc)	(anal)	(calc)	(anal)
Al_2O_3	9.9	14.7	7.9	7.9	8.8	8.6	8.8	7.2	8.1	7.9	8.0	7.4	8.3	7.5
AlF_3	NA	0.0	0.0	NA	0.0	NA	0.0	NA	NA	NA	0.0	NA	0.0	NA
B_2O_3	7.4	7.0	5.7	5.5	7.9	7.7	7.9	7.3	4.8	7.9	8.2	8.2	8.4	7.9
BaO	0.9	0.9	0.7	0.7	0.6	0.6	0.6	0.6	0.4	0.7	0.5	0.6	0.5	0.6
CaO	18.5	19.6	17.3	17.7	15.4	14.8	15.4	14.1	8.0	14.9	18.2	18.1	18.8	17.3
Fe_2O_3	2.3	1.9	6.3	8.7	6.1	6.3	6.1	11.7	3.8	6.2	5.6	5.8	2.2	2.4
K_2O	0.5	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.7	0.4	0.8	0.8	0.8	0.8
MgO	0.0	0.7	1.0	*	1.0	*	1.0	*	*	*	1.9	*	2.0	*
MgF_2	22.6	18.0	14.3	18.7	12.3	16.3	12.3	15.3	9	16.3	10.9	16.6	11.3	16.6
Na_2O	5.6	6.4	7.4	7.5	7.3	7.2	7.3	6.6	6.9	7.1	7.0	7.0	7.32	7.2
NaF	NA	0.0	0.0	NA	0.0	NA	0.0	NA	NA	NA	0.0	NA	0.0	NA
SiO_2	31.0	29.9	38.3	35.2	39.5	37.9	39.5	32.8	54.5	37.6	38.0	34.4	39.4	37.4
U_3O_8	NA	0.3	0.3	NA	0.2	NA	0.2	NA	NA	NA	0.2	NA	0.2	NA

* Assumes that all of the Mg is combined with fluoride rather than oxygen
NA = not analyzed

Table 4-52
(Continued)

Components	F5-26	F5-26	F5-27	F5-27B	F5-27G	F5-27W	F5-28	F5-29	F5-30	F5-31	F5-31
	(cal)	(anal)	(cal)	(blue)+ (anal)	(green)+ (anal)	(white)+ (anal)	(calc)	(calc)	(calc)	(cal)	(anal)
Al_2O_3	7.5	8.3	3.2	5.9	5.9	4.8	9.1	9.1	9.1	7.7	7.0
AlF_3	0.0	NA	8.2	NA	NA	NA	0.0	0.0	0.0	0.0	NA
B_2O_3	13.5	4.0	7.8	7.9	8.1	3.7	3.5	3.5	0.0	10.2	9.5
BaO	0.5	0.6	0.5	0.6	0.6	0.2	1.0	1.0	1.0	0.9	0.9
CaO	17.1	18.1	17.3	18.4	18.4	5.7	21.5	21.5	21.5	20.3	18.0
Fe_2O_3	5.2	6.2	5.2	5.6	5.6	3.4	5.6	2.0	2.0	2.6	3.0
K_2O	0.8	0.9	0.8	0.7	0.7	1.0	0.4	0.4	0.4	0.1	0.4
MgO	1.8	*	*	*	*	*	0.7	0.7	0.7	0.0	*
MgF_2	10.3	17.8	10.3	16.7	16.9	5.7	20.1	20.1	20.1	18.3	21.4
Na_2O	6.6	4	0.6	6.5	6.6	4.7	6.5	10.0	13.5	8.3	8.5
NaF	0.0	NA	8.2	NA	NA	NA	0.0	0.0	0.0	0.0	NA
SiO_2	35.8	39.8	36.1	30.4	30.2	63.0	30.9	30.93	30.9	31.2	30.7
U_3O_8	0.2	NA	0.2	NA	NA	NA	0.4	0.4	0.4	0.3	NA

* Assumes that all of the Mg is combined with fluoride rather than oxygen; NA = not analyzed
+ Separate fractions from the same melt

Table 4-52
(Continued)

Components	F5-32	F5-32	F5-33	F5-33	F5-33	F5-33	F5-34	F5-34	F5-34	F5-35	F5-35	F5-36	F5-36
	(calc)	(anal)	(calc)	(anal)	(anal)	(anal)	(calc)	(anal)	(anal)	(calc)	(anal)	(cal)	(anal)
Al_2O_3	7.7	7.8	7.7	6.9	6.9	6.1	7.5	6.6	7.4	7.6	7.4	6.6	6.9
AlF_3	0.0	NA	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA
B_2O_3	10.2	10.6	10.4	10.1	10.0	9.3	10.4	8.9	10.1	10.5	10.2	9.3	8.7
BaO	0.9	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9
CaO	20.3	20.2	19.0	18.1	16.8	15.1	18.8	15.5	18.1	19.8	19.0	19.8	19.0
Fe_2O_3	2.6	3.3	2.8	3.2	3.4	2.8	3.6	3.7	4.1	3.7	4.3	5.4	5.7
K_2O	0.1	0.1	0.3	NA	0.4	0.2	0.7	1.1	NA	0.7	NA	0.4	NA
MgO	0.0	*	0.3	*	*	*	0.5	*	*	0.5	*	0.8	*
MgF_2	18.3	21.5	17.9	21.1	20.1	18.4	17.5	18.4	21.4	17.7	21.2	18.1	20.5
Na_2O	0.4	6.3	8.5	8.6	8.9	7.8	8.0	7.2	7.9	6.2	6.1	7.5	7.4
NaF	7.9	NA	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA
SiO_2	31.2	29.9	31.7	28.3	32.1	27.9	31.3	27.3	28.1	31.8	27.9	30.5	27.8
U_3O_8	0.3	NA	0.3	NA	NA	NA	0.3	NA	NA	0.3	NA	0.3	NA

Components	F5-37	F5-37	F5-37B	F5-38	F5-39	F5-39	F5-40	F5-40	F5-41	F5-41
	(calc)	(anal)	(anal)	(cal)	(cal)	(anal)	(calc)	(anal)	(calc)	(anal)
Al_2O_3	7.8	8.2	2.9	7.8	7.6	7.2	7.3	7.7	3.2	3.6
AlF_3	0.0	NA	NA	0.0	0.0	NA	0.0	NA	0.0	NA
B_2O_3	9.3	9.6	0.1	9.3	8.7	7.5	9.2	8.7	8.5	8.1
BaO	0.9	0.9	0.0	0.9	0.8	0.8	0.8	1.0	0.9	1.1
CaO	20.0	19.9	0.3	20.0	19.0	17.9	18.5	16.7	24.2	20.1
Fe_2O_3	5.1	4.3	0.4	5.05	4.3	4.6	4.3	5.5	2.5	3.0
K_2O	0.8	NA	0.2	0.84	0.8	0.8	0.7	0.9	0.7	0.7
MgO	0.9	*	*	0.89	0.8	*	0.8	*	1.6	*
MgF_2	18.1	23.4	0.3	18.08	17.2	20.5	16.9	20.3	19.1	23.7
Na_2O	5.3	5.5	0.5	5.30	0.6	7.9	0.6	7.9	0.7	4.7
NaF	0.0	NA	NA	0.0	9.2	NA	11.1	NA	6.0	NA
SiO_2	30.8	29.5	7.6	30.81	29.8	28.1	28.8	24.0	31.6	26.2
U_3O_8	0.3	NA	NA	0.3	0.3	0.3	0.3	0.3	0.3	0.3

* Assumes that all of the Mg is combined with fluoride rather than oxygen; NA = not analyzed

thermodynamic. Repeating this melt from a separate batch of dried sludge, soil, and additives gave the same undissolved white powders, as did remelting with more vigorous stirring. Both F5-23BRW (the white portion of F5-23B remelted) and F5-27W (the white part of F5-27) are very rich in silicon. The green part of F5-27 (F5-27G) and the blue part of F5-27 (F5-27B) have the same composition since the difference in appearance between them is due to different cooling rates.

This inability of SiO_2 to dissolve into pit waste mixtures was seen five times. For F5-23B and F5-27, the evidence was the observation of macroscopic powders rich in SiO_2. For F5-24, F5-25, and F5-26, the evidence of undissolved SiO_2 was seen with SEM/EDX. A targeted Si/Mg mole ratio higher than about 2.5 showed evidence of SiO_2 insolubility. This limit upon the amount of SiO_2 soluble in the FEMP waste produces an upper limit on the viscosity of FEMP glasses since SiO_2 is the major ingredient responsible for increasing viscosity.

The combined raw materials of sludge, soil, and additives react with clay crucibles at 1150°C, but not with Pt/Au crucibles. Attempts were made to use inconel crucibles since they are much less expensive than Pt/Au crucibles. The first two attempts were on F5-35 and F5-36 which produced glasses which appeared to be good upon cooling. Inconel crucibles were therefore used to test the formation of glass from as-received fly ash (F5-37). The large amounts of carbon in both FEMP fly ashes present a problem for Pt/Au crucibles since carbon can reduce iron at 1150°C, which in turn alloys with the Pt/Au crucible to form a Pt/Fe alloy which destroys the crucible. Melting a blend containing as-received fly ash in an Inconel crucible produced an opaque black glass; the crucible was visibly corroded. Using SEM/EDX, spinel (Cr/Fe crystals) was detected in all three melts made in Inconel crucibles. No spinel was found in any of the other glasses suggesting spinel formation was due to Cr dissolved from the Inconel crucible.

Since vitrification involves heating to 1150°C for one hour, there is the possibility of considerable fluoride loss from the melt during vitrification. This is an important consideration for continuous melting operations. Table 4-53 shows the calculated and analyzed fluoride content of a number of FEMP glasses from crucible melts, along with the percentage of fluoride lost during vitrification, based on the calculated numbers. It appears 20-30 percent of the original fluoride content is lost

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Fluoride Analysis of FEMP Glasses and % of Fluoride Lost During Melting

	Calculated	Analyzed (average)	% loss
F5-25	6.87	6.6	0.04
F5-31	11.54	8.0	31
F5-32	15.23	11.20	26
F5-33	11.02	8.6	22
F5-34	10.78	7.1	34
F5-35	11	8.95	19
F5-36	11	7.25	34
F5-41	14.39	9.5	34

during vitrification for blends targeted to contain 10-15 wt. percent fluoride. Hence, the amount of fluoride shown in Table 4-53 in the analyzed columns (which is based solely on the Mg content by assuming all Mg is present as MgF_2) is expected to be about 20-30 percent too high for most glasses.

Viscosity and Conductivity: Both viscosity and electrical conductivity data as functions of temperature are needed in order to assess the processability of FEMP glasses. Melt viscosity has a major effect on processing rates and the melt electrical conductivity determines power dissipation in joule-heated melting systems.

Conductivity and viscosity were measured at typically four temperatures to span the range of likely processing parameters. Collecting viscosity and conductivity at 1500°C, was not necessary because viscosities were very low (< 10 poise) at 1150°C and there was rapid fluoride loss above 1150°C; thus higher processing temperatures would be impractical. The electrical conductivity data were fitted to Arhenius equations while the viscosity data were fitted to Vogel-Fulcher equations (Arhenius with allowance for the rapid rise in viscosity on approach to the glass transition temperature).

Results: Tables 4-54 and 4-55 show viscosity and conductivity measurements of 23 FEMP glasses. Entries marked "unstable" indicate readings were unstable due to crystallization for those glass melts. Glass melts marked with an asterisk used the same glass for both viscosity and conductivity measurements.

Most of the FEMP glasses fall into the range of 1-10 Poise at a temperature of 1150°C (Table 4-54). Attempts to increase the viscosity were limited by the solubility of SiO_2 in typical pit waste blends. The use of the Duramelter system, however, permits melting of these low-viscosity, high-waste loading feeds, as shown in Figure 4-15.

The conductivity of the FEMP glasses range from about 0.1 S/cm to 0.6 S/cm for a typical processing temperature of 1150°C. The viscosity-conductivity behavior of typical FEMP glasses is shown for comparison with constraints associated with high-level nuclear waste in Figure 4-15. High-

Viscosity (Interpolated to Standard Temperatures) of FEMP Crucible Melt Glasses (Poise)

Temp. (°C)	F5-7*	F5-8*	F5-11	F5-12	F5-13	F5-14*	F5-15*	F5-16	F5-17
950	unstable	unstable	NA	unstable	unstable	NA	NA	NA	⌉
1000	5.5	4.4	5.7	5.2	unstable	unstable	unstable	13.7	| unstable
1050	3.0	2.8	3.6	3.3	2.2	8.5	8.9	7.3	⌋
1100	2.1	1.9	2.4	2.1	3.6	5.0	4.5	4.4	5.4
1150	1.7	1.3	1.7	1.4	3.1	3.3	2.4	3.0	3.7

Temp.(°C)	F5-18*	F5-20*	F5-22*	F5-23*	F5-24*	F5-25*	F5-26*	F5-31*
950	NA	NA	unstable	NA	unstable	97.2	⌉	18.4
1000	12.9	44.1	unstable	86.2	60.9	45.0	|	10.3
1050	6.2	15.4	26.1	43.1	31.6	23.6	|unstable	6.1
1100	3.9	8.5	14.9	22.9	18.2	13.6	⌋	3.8
1150	2.8	5.8	9	12.9	11.3	8.4	~ 32	2.4

NA = Not analyzed
* = Same sample used for viscosity and conductivity measurements

Conductivity (Interpolated to Standard Temperatures) of FEMP Crucible Melt Glasses (Siemens/cm)

Temp.	F5-7*	F5-8*	F5-11	F5-12	F5-13	F5-14*	F5-15*	F5-16	F5-17
950°C	unstable	0.14	NA	0.12	unstable	NA	NA	NA	NA
1000°C	0.16	0.22	0.09	0.19	unstable	0.09	0.04	0.04	NA
1050°C	0.24	0.32	0.14	0.28	0.20	0.15	0.11	0.09	0.06
1100°C	0.34	0.43	0.20	0.39	0.31	0.22	0.19	0.16	0.09
1150°C	0.45	0.54	0.28	0.52	0.41	0.33	0.28	0.26	0.11

Temp.	F5-18*	F5-20*	F5-22*	F5-23*	F5-24*	F5-25*	F5-26*	F5-31*	F5-32*
950°C	NA	NA	NA	NA	NA	0.03	unstable	NA	0.10
1000°C	0.08	0.09	0.04	0.04	0.04	0.04		NA	0.13
1050°C	0.18	0.12	0.09	0.07	0.07	0.07		NA	0.17
1100°C	0.25	0.17	0.14	0.11	0.13	0.10	0.04	~0.34	0.27
1150°C	0.30	0.23	0.20	0.14	0.24	0.14	0.09	NA	0.57

* = Same sample used for viscosity and conductivity measurements
NA = Not analyzed

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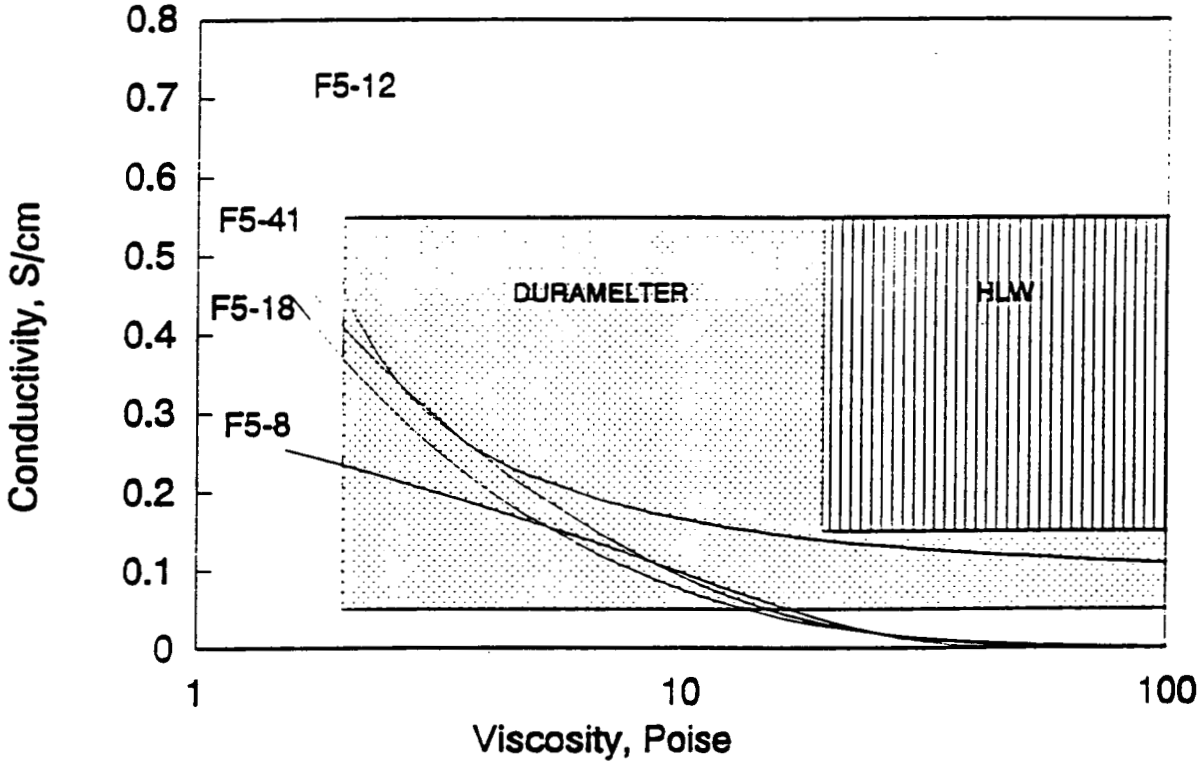


Glass Conductivity-Viscosity Behavior in Relation to Melter Processing Constraints. Fitting equations were used to extrapolate measurements made over the approximate ranges of 1-5P and 0.1-0.5 S/cm.

waste-loading FEMP glasses would not be processable using the constraints imposed by conventional joule-heated melter technology but are processable using a Duramelter system.

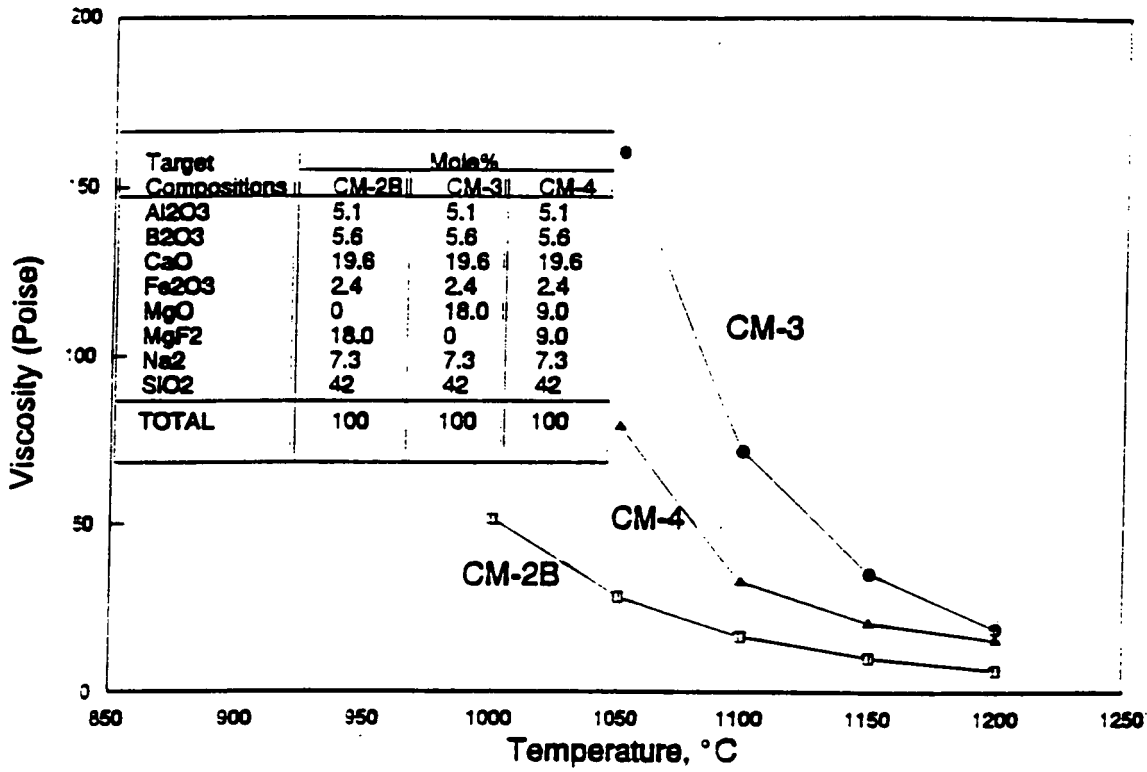
Effect of Fluoride Loss on Conductivity and Viscosity Measurements

When measuring viscosity and conductivity, the glasses are heated to high temperatures (1000-1200°C) which invariably leads to some fluoride loss. This loss was measured in three ways: measurable amounts (40 ppm) of hydrogen fluoride (HF) released to the gas phase when glass is at ~ 1150°C; increases in conductivity and viscosity over a few days of measurement; and the reduction in fluorine concentration in the glass after completion of the conductivity and viscosity measurements.

The loss of fluoride to the atmosphere during viscosity and conductivity measurements was not detected early in this study. The same glass sample was used for viscosity and conductivity measurements with no particular concern for the length of time the glass was at high temperatures during these measurements. After discovery of the fluoride loss, viscosity and conductivity procedures were changed to use as-melted glass for each measurement and the measurement time was minimized. As a result, data obtained with this new procedure are more accurate. There were some viscosity and conductivity data obtained after the new procedure was instituted in which the same glass sample was used for both viscosity and conductivity measurements due to limitations on the amount of sample left but the time the sample was at high temperatures was noted so the amount of fluoride lost during the measurements could be estimated. Data for the samples denoted by asterisks in Table 4-54 and 4-55 are less accurate than the other data since the same sample was used for viscosity and conductivity measurements and fluoride loss was more significant.

A series of surrogate melts was made to further elucidate the role of fluoride in these compositions. In this series, CM-2B, CM-3, and CM-4, the molar concentrations of all components were held constant except for fluoride and oxygen. The effect of fluoride on viscosity and conductivity of glass melts can be seen in Figures 4-16 and 4-17. The target composition (in mole percent) of these glasses is given in Figure 4-16. The data shows the extent of the effect of increasing fluoride on decreasing

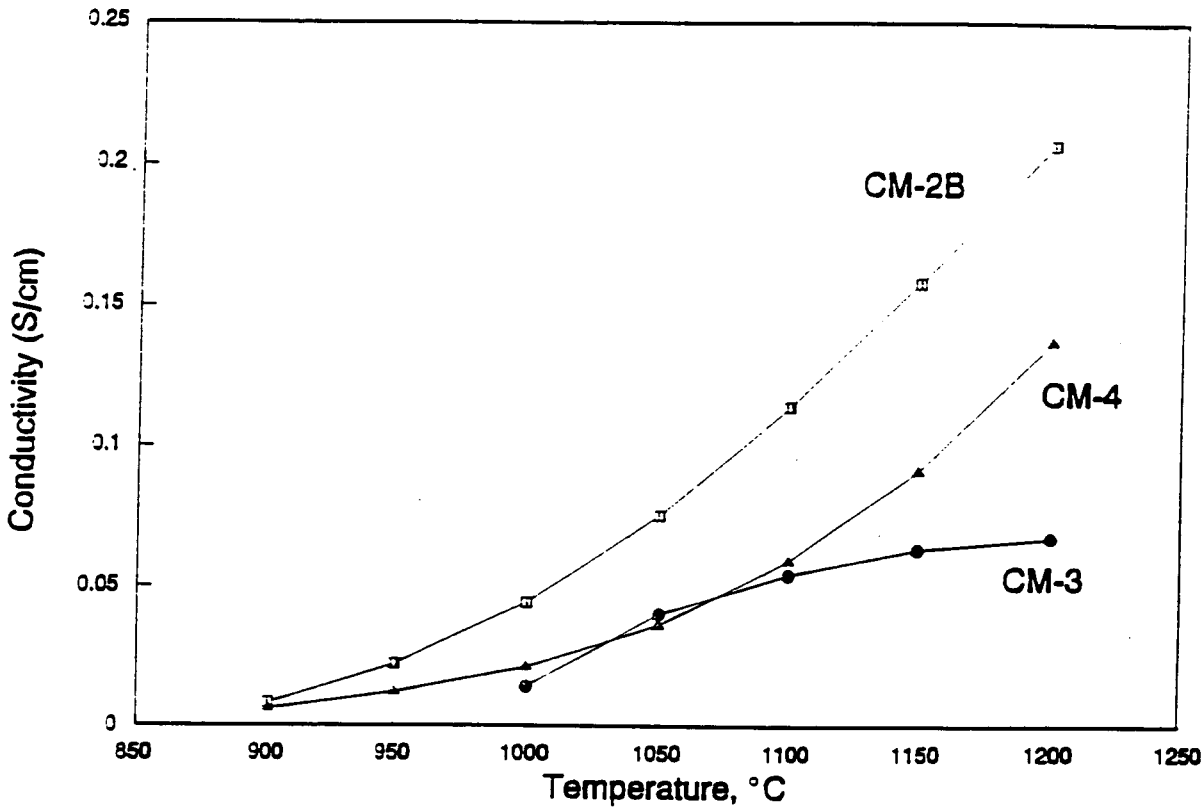
Figure 4-16



Target Compositions	Mole% CM-2B	CM-3	CM-4
Al2O3	5.1	5.1	5.1
B2O3	5.6	5.6	5.6
CaO	19.6	19.6	19.6
Fe2O3	2.4	2.4	2.4
MgO	0	18.0	9.0
MgF2	18.0	0	9.0
Na2	7.3	7.3	7.3
SiO2	42	42	42
TOTAL	100	100	100

Viscosity vs. temperature for three glasses showing that fluoride reduces melt viscosity.

Figure 4-17



Conductivity vs. temperature for three glasses showing that fluoride increases melt conductivity.

the viscosity and increasing the conductivity. Fluoride breaks the oxygen linkages in the glass network which leads to a decrease of the viscosity and an increase in the ease with which cations can move which results in an increase in the conductivity.

Modelling: The effect of fluoride and various cations on the viscosity and conductivity of FEMP glass melts was modelled using least-squares regression analysis to determine the components responsible for the major variations in the data. These models were used to predict glass compositions with processable viscosities and conductivities.

Leach Testing

Twenty FEMP glasses were subjected to the EPA TCLP leaching procedure for inorganics. Leachate solutions were analyzed for the eight listed metals (As, Se, Cd, Hg, Ag, Pb, Ba, and Cr) by DCP. Results are listed in Table 4-56 along with the EPA regulatory limits. All glasses passed the TCLP. The TCLP extracts were also analyzed by ICP-MS to determine radionuclide concentrations for the longer-lived isotopes. Results are shown in Table 4-57.

While all glasses pass the EPA TCLP test, TCLP is not the best measure of long-term glass durability. The more aggressive PCT test has been adopted as the benchmark test for distinguishing differences in the leach resistance of high-level nuclear waste glasses. A large data base on the PCT performance of high-level waste glasses is available and collection of such data for FEMP glasses permits a direct comparative evaluation of the glass durability. Results of the PCT tests are tabulated in Table 4-58. The 20 glasses were tested in four sets, each of which included a standard glass (West Valley Reference 5). The results fall within the range of values measured on the Reference 5 glass in several hundred tests conducted over the past few years.

Experience from the high-level waste vitrification program has shown boron concentrations provide the best upper bound on overall glass leach rates; next best are usually lithium and sodium. The high-level waste Waste Acceptance Specifications require reporting of only these three elemental concentrations in the PCT leachate. Since there are very small amounts of lithium in the FEMP glasses and silicon is a major matrix component, results have focussed on boron, sodium, and silicon

Table 4-56

TCLP Leach Data for FEMP Glasses - RCRA metals (ppm)

	As	Se	Cd	Hg	Ag	Pb	Ba	Cr
F5-5	0.57	0.43	0.00	0.01	0.00	0.89	4.06	0.00
F5-7	0.17	0.00	0.00	0.00	0.00	0.86	4.03	0.00
F5-8	0.25	0.17	0.00	0.10	0.00	1.00	4.60	0.03
F5-10	0.64	0.40	0.00	0.07	0.00	1.01	6.02	0.06
F5-17	0.87	0.66	0.00	0.15	0.02	0.99	12.42	0.12
F5-19	0.26	0.23	0.01	0.02	0.01	0.94	2.80	0.01
F5-20	0.54	0.00	0.00	0.06	0.00	0.89	3.70	0.00
F5-22	0.08	0.21	0.00	0.03	0.00	0.90	9.90	0.02
F5-23	0.55	0.16	0.01	0.19	0.01	0.91	9.63	0.04
F5-24	0.34	0.10	0.01	0.03	0.00	0.84	7.52	0.00
F5-25	0.52	0.00	0.02	0.07	0.00	1.12	7.57	0.10
F5-28	0.40	0.31	0.01	0.05	0.01	1.04	4.18	0.02
F5-29	0.10	0.26	0.01	0.10	0.00	0.94	0.69	0.01
F5-30	0.28	0.24	0.01	0.00	0.00	0.69	0.26	0.00
F5-32	0.12	0.38	0.03	0.13	0.02	1.11	5.98	0.03
F5-35	0.56	0.32	0.01	0.06	0.01	0.99	4.62	0.09
F5-36	0.39	0.49	0.00	0.06	0.00	1.05	2.24	0.00
F5-37	0.54	0.11	0.00	0.05	0.00	1.18	1.45	0.01
F5-39	0.31	0.27	0.00	0.00	0.00	0.86	2.11	0.01
F5-40	0.15	0.20	0.03	0.18	0.01	1.04	12.49	0.04
EPA Limit	5	1	1	0.2	5	5	100	5

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Table 4-57 TCLP Leach Data for FEMP Glasses - Radionuclide Concentrations (ppb)

Radionuclides (ppb)	F5-5	F5-7	F5-8	F5-17	F5-19	F5-20	F5-22	F5-23	F5-24	F5-25
Tc-99	0.16	0.14	0.14	0.10	0.16	0.12	0.15	0.11	0.04	0.03
Th-232	10	8.0	22.7	305	0.52	7.1	94.5	107	30.1	240
U-234	< 0.01	0.05	0.02	0.32	0.31	0.21	0.18	0.17	0.15	0.16
U-233	0.04	0.02	< 0.02	0.91	< 0.02	0.04	0.27	0.22	0.10	< 0.02
U-235	0.64	5.6	3.8	43.7	36	33.7	25	24	18	24
U-236	0.008	0.15	0.09	1.1	0.86	0.83	0.61	0.56	0.49	0.59
U-238	93	891	573	5700	4600	4300	3000	2800	2000	2700

Radionuclides (ppb)	F5-28	F5-29	F5-30	F5-32	F5-35	F5-36	F5-37	F5-39	F5-40
Tc-99	0.03	0.18	0.41	0.09	0.06	0.06	0.09	0.30	0.09
Th-232	7.0	0.75	0.06	0.17	4.1	0.45	0.60	0.54	11
U-234	0.36	0.03	0.02	0.19	0.22	0.34	0.04	0.30	0.23
U-233	0.03	0.03	< 0.02	< 0.02	< 0.02	0.02	< 0.02	0.02	0.05
U-235	49	0.33	0.16	26	33	37	0.93	40	32
U-236	1.2	0.03	< 0.02	0.67	0.74	1.0	< 0.02	1.0	0.79
U-238	5500	38	18	3100	3900	4200	120	4400	9400

PCT Results of FEMP Glasses (ppm)

(7 days, 90°C, 100-200 mesh)

	F5-5	F5-7	F5-8	F5-10	F5-17	F5-19	F5-20	F5-22	F5-23	F5-24
B	144.5	96.66	239.4	98.43	69.91	47.00	97.78	16.09	28.01	19.16
Si	11.72	6.32	7.43	7.30	5.94	9.39	11.83	18.96	21.93	24.29
Na	503.1	296.3	651.4	288.4	19.37	13.95	217.6	54.24	71.95	44.56
pH	11.43	11.19	11.37	11.07	8.85	9.7	9.58	10.09	9.43	10.04
Al	2.57	0.67	1.22	0.77	0.30	2.72	0.96	1.23	1.02	1.13
Ba	2.12	1.64	1.91	1.10	0.91	3.07	1.61	1.15	0.58	0.64
Ca	30.20	46.67	52.7	51.34	66.25	68.66	40.70	56.80	47.86	47.20
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
K	46.88	45.92	49.06	47.49	9.80	111.5	14.41	3.62	4.48	5.49
Mg	0.03	0.07	0.00	0.00	1.40	0.06	0.07	0.01	0.08	0.03
Ti	0.06	0.03	0.09	0.07	0.05	0.00	0.05	0.03	0.00	0.02
Li	0.89	0.88	1.14	0.65	0.55	0.51	0.37	0.22	0.20	0.19
Mn	0.00	0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.00	0.01
Zr	0.03	0.01	0.15	0.10	0.08	0.00	0.04	0.19	0.00	0.05
P	0.54	0.59	0.93	0.56	0.37	0.00	0.75	1.03	0.63	0.87
Ni	0.08	0.03	0.22	0.12	0.18	0.10	0.22	0.06	0.00	0.05
Cr	0.25	0.01	0.02	0.30	0.05	0.63	0.09	0.00	0.00	0.00
Sr	0.32	0.45	0.45	0.43	0.27	0.24	0.21	0.09	0.11	0.12
Ag	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.02	0.00	0.00
As	4.88	2.77	3.78	2.63	0.15	0.00	0.04	0.69	1.24	0.74
Cd	0.00	0.00	0.11	0.00	0.10	0.06	0.10	0.03	0.00	0.09
Hg	0.69	0.08	0.27	1.65	0.67	2.65	0.38	0.97	0.06	0.00
Pb	0.00	0.27	0.30	0.17	0.05	0.23	0.00	0.07	0.00	0.00
Se	7.92	0.00	1.56	1.41	0.00	0.00	0.00	0.82	0.00	0.55

	F5-25	F5-28	F5-29	F5-30	F5-32	F5-35	F5-36	F5-37	F5-39	F5-40
B	23.40	81.84	135.1	13.48	397.4	296.7	369.3	455.7	331.1	315.0
Si	24.44	7.80	18.57	78.71	8.54	6.92	5.53	6.93	9.42	6.64
Na	54.79	349.5	891.3	4588	477.9	464.5	754.2	713.7	759.3	597
pH	10.14	10.91	11.59	12.25	9.10	9.67	10.08	9.62	9.46	9.34
Al	1.16	2.17	5.16	1.00	0.52	0.29	2.42	1.26	0.35	0.44
Ba	0.89	0.49	0.09	0.09	0.39	1.25	1.35	1.23	0.08	0.25
Ca	60.47	37.22	8.01	0.55	16.36	38.14	60.51	46.03	2.44	4.93
Fe	0.00	0.01	0.00	0.04	0.00	0.00	0.00	0.01	0.03	0.00
K	6.27	9.60	4.85	169.1	4.45	45.9	14.36	44.82	39.14	36.73
Mg	0.05	0.01	0.08	0.08	0.40	0.21	0.05	0.12	0.26	0.43
Ti	0.02	0.01	0.03	0.06	0.02	0.01	0.03	0.01	0.02	0.08
Li	0.22	0.70	0.45	0.48	0.20	0.56	0.29	0.35	0.59	1.05
Mn	0.00	0.01	0.04	0.00	0.01	0.05	0.02	0.02	0.02	0.03
Zr	0.01	0.09	0.07	0.03	0.01	0.03	0.01	0.04	0.05	0.08
P	1.42	1.01	3.56	0.30	0.06	0.43	0.50	0.74	0.49	3.82
Ni	0.01	0.02	0.03	0.68	0.00	0.06	0.03	0.02	0.23	0.13
Cr	0.00	0.00	0.00	0.28	0.00	0.39	0.14	0.11	0.08	0.00
Sr	0.15	0.15	0.00	0.00	0.12	0.31	0.39	0.40	0.23	0.07
Ag	0.14	0.00	0.01	0.08	0.00	0.00	0.00	0.00	0.08	0.00
As	1.85	4.33	4.08	7.41	7.90	2.14	0.65	0.00	0.03	0.34
Cd	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hg	1.30	1.25	0.34	3.21	1.05	1.68	2.46	1.83	0.77	0.65
Pb	0.01	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.09
Se	0.00	0.46	0.00	4.86	0.81	0.28	7.82	2.88	1.06	1.24
										2.66

for comparative purposes. These leachate concentrations are plotted as the normalized concentrations (i.e. solution concentration normalized to that in the glass (Jantzen and Bibler, 1989)) for the 20 FEMP glasses in Figures 4-18 and 4-19. The normalized leach rates, in units of $g/m^2/day$, for each set of five glasses are compared to the present high-level waste glass acceptance standard, the Savannah River SRL-EA glass (Jantzen, Bibler, and Beam, 1992). Figure 4-18 shows all glasses have normalized leach rates below the SRL-EA standard glass for boron, sodium, and silicon, except for F5-30. The F5-30 melt produced a ceramic microcrystalline material with no evidence of a glassy phase due to the lack of boron.

Phase Stability

The stability of the vitreous phase with respect to crystallization impacts both the production process and leach resistance. Crystal formation during vitrification can cause melter clogging. Crystallinity in the final waste form may affect the leach resistance. In this section, the extent of crystal formation after various heat treatments, and the role of fluoride on the microstructure of FEMP glasses is examined.

Results of 20-hour and 2-hour Heat Treatments: The FEMP glasses were first heat treated at 1050°C for 20 hours. The temperature was selected based on the minimum reasonable margin between the typical processing temperature for joule-heated melting (1150°C) and the glass liquidous temperature (maximum temperature at which crystals will form from the melt). The time was judged to be representative of severe process upsets. The crystals repeatedly appearing in FEMP glasses are forsterite ($2(MgO) \cdot SiO_2$) diopsidic augite ($MgO \cdot CaO \cdot 2(SiO_2)$), and fluorophlogopite ($K_2Mg_6[Si_6Al_2O_{20}]F_4$).

A serious disadvantage in conducting such long heat treatments with high-fluoride FEMP glasses is the loss of fluoride which occurs. This complicates interpretation of the data since the observed crystal formation may be influenced by the changing melt composition as well as by the heat treatment. These data are directly relevant, however, in terms of evaluating the effects of long idling times in the vitrification system which would also lead to both fluoride loss and heat treatment effects.

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Figure 4-18

Results from PCT tests on FEMP glasses compared to the high-level waste standard glass (SRL-EA)

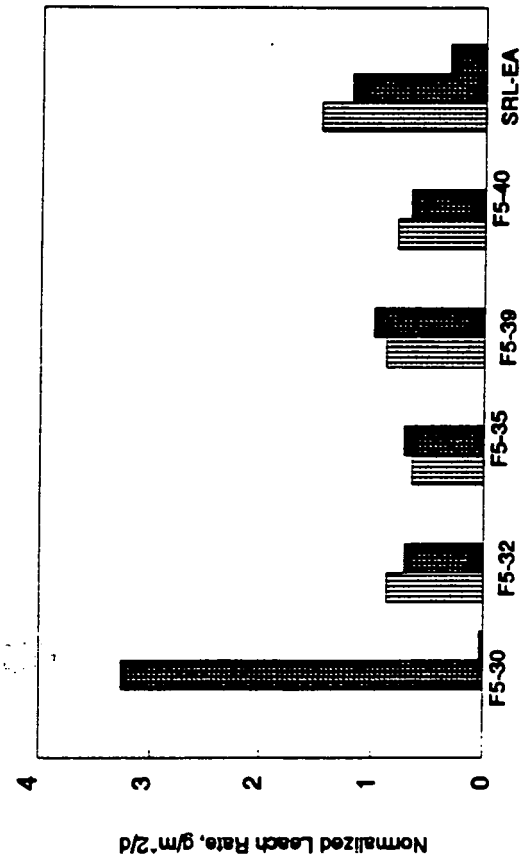
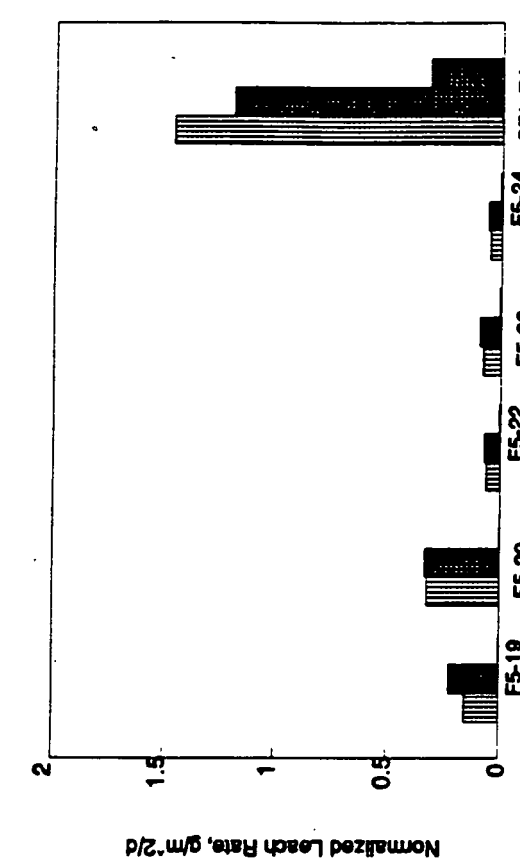


Figure 4-19



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After some experimentation, a heat treatment time of two hours was selected. Table 4-59 summarizes heat treatment results for two-hour heat treatments on nine glasses. Compositions selected for the continuous joule-heated melter runs have a liquidous temperature of 1050°C or below.

Effect of Fluoride on the Microstructure of FEMP Glasses: Increasing fluoride concentration decreased viscosity and increased conductivity. The same fluoride variational study glasses, CM-2B, CM-3, and CM-4, were used to determine the effect of fluoride on the liquidous temperature. Table 4-60 shows the compositions as mole percent for CM-2B, CM-3, and CM-4. The aim of the study was to hold all components constant except fluoride and oxygen. The oxide compositions were obtained by DCP analysis and the fluoride content was analyzed by a modified form of ASTM C169. Some fluoride loss occurred during the melting process since the calculated fluoride values are higher than the analyzed values. However, the trend of increasing fluoride from CM-3 to CM-4 to CM-2B is still preserved. These samples were heat treated for two hours at various temperatures to determine the approximate liquidous temperature as a function of fluoride concentration. The study of CM-2B, CM-3 and CM-4 was further simplified by the fact that diopsidic augite was the only crystal formed from this series of melts. By examining the amount of diopsidic augite in the three glasses, it can be seen the liquidous temperature decreases with increasing fluoride in the glass. The results shown in Table 4-61 suggest fluoride suppresses crystallization, but this can only be true of crystals which do not contain fluoride. In fact, the formation of fluoride-containing crystals such as fluorophlogopite would be favored by increasing the fluoride concentration in the melt. The effect of fluoride on the formation of other crystals was studied using F5-15. This type of analysis was done for FEMP glass F5-15 after various heat treatments. In addition to SEM/EDS, fluoride analysis was performed after each heat treatment in order to correlate the observed microstructure to fluoride content. The results are summarized in Table 4-62, where the amount of each type of crystal found and the wt percent of fluoride analyzed is shown for each heat treatment. Though the analyzed fluoride content fluctuates within each premelt time (most likely due to the different surface-to-volume ratio during heat treatments), the trend is that of decreasing fluoride with increasing premelt time. From Table 4-62, decreasing fluoride concentration decreases the amount of fluorophlogopite, while increasing the

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Table 4-59 Liquidous Temperature of FEMP Glasses as Determined by 2 Hr Heat Treatments (1 hour premelt at 1100°C)

	HT @ 985°C for 2 hrs	HT @ 1000°C for 2 hrs	HT @ 1050°C for 2 hrs	Liquidous Temp
F5-12	NA	NA	No crystals	Below 1050°C
F5-33	NA	NA	No crystals	Below 1050°C
F5-34	NA	NA	No crystals	Below 1050°C
F5-35	Phase Separated Glass	NA	NA	NA
F5-36	Phase Separated Glass	NA	Made ceramic	Above 1050°C
F5-37	NA	< 10% Crystals	Surface crystals	Above 1050°C
F5-39	NA	NA	Brown glass with inclusions	NA
F5-40	NA	NA	Phase separated glass	Below 1050°C
F5-41	NA	(for 3 hrs) Many Crystals	No crystals	Below 1050°C

NA = Not analyzed
HT = Heat treatment

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Table 4-60 **Calculated and Analyzed Compositions of CM-2B, CM-3, and CM-4. The analyzed compositions are from DCP measurements which do not determine fluoride content, therefore Mg is listed as MgO rather than MgF_2; fluoride entries were determined by separate analysis.**

Compositions (mole %)	CM-2B (calc)	CM-2B (analy)	CM-2B (analy)	CM-3 (calc)	CM-3 (analy)	CM-4 (calc)	CM-4 (analy)
Al_2O_3	5.1	4.40	4.34	5.1	4.55	5.1	4.46
B_2O_3	5.6	5.54	5.54	5.6	5.67	5.6	5.38
CaO	19.6	19.29	19.87	19.6	19.65	19.6	19.93
Fe_2O_3	2.4	2.49	2.69	2.4	2.47	2.4	2.46
MgF_2	18.0	NA	NA	0.0	NA	9.0	NA
MgO	0.0	16.3	16.47	18.0	16.89	9.0	16.86
NaF	0.0	NA	NA	0.0	NA	0.0	NA
Na_2O	7.3	7.64	7.85	7.3	7.8	7.3	7.54
SiO_2	42	44.35	43.23	42	42.97	42	43.37
Total	100	100	100	100	100	100	100
Fluoride (wt%)	10.4 %	8.8%	8.8%	0%	0%	5.4%	4.0%

NA = Not Analyzed

Table 4-61 The volume % of diopsidic augite in CM glasses with different thermal histories. All were premelted at 1200°C for one hour and then heat treated for two hours at the temperature indicated.

Wt. % Fluoride (measured)	0%	4.0%	8.8%
	Volume % of Diopsidic Augite		
	CM-3	CM-4	CM-2B
No heat treatment	0	0	0
1100°C, 2 hrs	16	0	0
1050°C, 2 hrs	26	22	0
1000°C, 2 hrs	41	33	6

Table 4-62

Microstructure and Fluoride Concentration in Heat-treated F5-15 (volume %)

Premelt (hrs) at 1150°C	1				2				4				20			
Heat treatment (hrs) at 1000°C	1	2	4	20	1	2	4	20	1	2	4	20	1	2	4	20
Fluorophlogopite	1.0	5.3	5.9	8.7	2.2	4.4	4.0	2.5	0.7	Tr	5.1	Tr	Tr	0.9	Tr	Tr
Forsterite	Tr	0	Tr	Tr	Tr	Tr	Tr	0	Tr	5.7	Tr	Tr	7.0	9.8	16	5.3
Pargasite	Tr	1	7	17	3	11	1	25	6	20	15	28	0	0	0	38
Augite	0	0	0	0	0	0	0	0	0	0	0	0	1	3	26	0
Fluorite	0	0	Tr	Tr	0	0	0	0	Tr	0	Tr	Tr	0	0	0	0
*	Tr	Tr	Tr	Tr	Tr	0	Tr	Tr	0	0	0	0	0	0	0	0
Total	1	7	13	26	5	16	5	28	7	26	20	28	8	14	42	43
wt % of fluoride	10.4	8.8	9.3	10.0	9.0	8.1	10.1	7.8	7.7	6.0	8.8	7.1	3.3	5.8	4.2	6.5

Tr = Trace amount

* = Unidentified fluorosilicate

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amount of forsterite, pargasite, and augite. Adding up all of the various crystals detected by SEM/EDS, the total amount of crystals increases as the fluoride concentration decreases from about 10 percent to about 5 percent. This trend of increasing crystallization with decreasing fluoride content in the range of 10 percent to 0 percent fluoride had been seen with the cold melt studies.

Fluoride can have a positive effect on FEMP glasses since it lowers the liquidous temperature of many non-fluoride containing crystals. In addition, the fluoride containing crystals only appear in trace amounts at about 10-11 percent fluoride. This range of fluoride content corresponds to about 70-80 percent Waste Pit 5 sludge loading on a wet basis.

Phase Separation: Many of the FEMP glasses phase separated if cooled slowly. This phase separation is quite distinct from the crystallization behavior discussed above. This involves the separation of a second glass phase of different composition from the bulk (i.e. rather like oil dispersed in water). The phase separation produced opaque greenish glasses. When these glasses were examined using SEM, small particles of less than 0.2 micron were found to be dispersed throughout the glass matrix which provides strong support for phase separation being responsible for the opaque appearance.

Although many of the FEMP glasses phase separated upon cooling, the problem of phase separation can be avoided in large-scale production by ensuring rapid cooling. Glass "gems" (or marbles or beads) could therefore be cooled rapidly to ensure production of a homogeneous, non-phase separated glass waste form.

Continuous Joule-Heated Melter Tests

Crucible melt studies demonstrate a number of the FEMP glasses meet the requirements for processability and leach resistance. Crystallization is one of the most constraining factors for these melts and it was determined that 10-11 wt. percent fluoride can effectively suppress crystallization. This fluoride content corresponds to 70-80 percent Waste Pit 5 sludge on a wet basis which effectively sets the high end of Pit 5 waste loadings possible. Two glass compositions were tested using a Duramelter joule-heated vitrification system, with a nominal glass output rate of 10 kg/day.

These small-scale continuous melter tests provide essential information which cannot be obtained from crucible melts. Such studies are necessary: (1) to determine the off-gas release and potential off-gas system needs and performance, (2) to examine the effect of cold caps on both throughput rates and in mitigation of off-gas release, and (3) to demonstrate the recycle of the fluoride and other components lost to the off-gas system. The last point is especially important because significant amounts of fluoride are lost when the pit wastes or glasses are heated to temperatures above 1000°C. The fluoride recycle system used a NaOH scrubber solution which combines with the off-gas stream to form NaF in solution. The system operates so the NaF can be removed from the scrubber solution as a solid in slurry form which is then used as an additive for the next batch of feed. This stream provides part of the sodium required for the batch.

Results: These runs successfully demonstrated FEMP Pit 5 waste could be processed in a Duramelter joule-heated vitrification system, the nominal processing rate of 10 kg of glass per day was exceeded, over 99 percent of the uranium and thorium were contained within the glass before recycle of the scrubber sludge (i.e. volatilization of UF_6 is not a problem), and the glasses are leach resistant.

Extensive system tests were performed with fluoride-containing surrogate feeds covering a range of compositions (Table 4-63). These runs were performed to test a variety of system modifications made for high-fluoride feeds prior to radioactive operations. Over 160 kg of glass was produced in these runs.

Table 4-64 lists two types of feed used for the radioactive 10 kg/day melter runs with actual FEMP wastes. The feeds are based on (but not identical to) crucible melts F5-12 and F5-39, which were processable and leach resistant. (The results of leach tests on F5-12, while believed reliable, were performed before QA approval of CUA procedures by FEMP and are not reported.) The major component of the feeds is Waste Pit 5 sludge, with the main variation between Micro-F1 feed and Micro-F2 feed being the amount of soil added to the feed, which increases the amount of calcium and silicon from the waste streams. A further difference between Micro-F1 and Micro-F2 is the larger

Table 4-63 Range of Surrogate Feed Compositions Used in Micromelter (wt%)

	Wt%
Al_2O_3	3.1 - 7.7
B_2O_3	8.5-9.6
BaO	0.7 - 1.0
CaO	19.1 - 24.8
Fe_2O_3	2.5 - 5.0
K_2O	0.7 - 1.0
MgO	0 - 1.7
MgF_2	16.7 - 20.4
Na_2O	0 - 10.4
NaF	5.1 - 9.6
SiO_2	29.4 - 32.5
TiO_2	0 - 0.4

Table 4-64 Feeds Used for 10 Kg/Day Melter Runs

	Micro-F1		Micro-F2	
	Mass	Wt%	Mass	Wt%
Pit 5 Sludge	6.94 kg	71.8%	6.73 kg	73.2%
Fernald Whole Soil	0.46 kg	4.8%	1.33 kg	14.5%
H_3BO_3	0.59 kg	6.1%	0.50 kg	5.4%
SiO_2	0.60 kg	6.2%	0.30 kg	3.3%
$Fe(OH)_3$ Slurry (88% water)	0.55 kg	5.7%	0	0%
Recovered NaF (40% water)	0.53 kg	5.5%	0.34 kg	3.7%

amount of iron in Micro-F1. Both feeds used NaF recycled from the off-gas scrubber; as such, it is not an additive but part of the waste for vitrification. Multiple batches of each of these feeds were made.

Glasses produced from Micro-F1 and Micro-F2 feeds were called MIC3-54A and MIC3-56A, respectively. Their analyzed compositions, using combined DCP and fluoride analyses, are shown in Table 4-65.

Micro-F1 and Micro-F2, produced stable slurries which fed into the melter well and processed without major difficulties. The feed rate was typically 40-60 ml/min which produced approximately 500 g glass per litre of feed. The overall glass production rate during these two runs was 21 kg/day, well in excess of the nominal 10 kg/day design basis. The maximum cold cap formation (i.e. fraction of melt surface occluded by unreacted feed) was estimated at 80 percent. The major constraint on exceeding a production rate of 21 kg/day was the feed system; a more reliable feed system would permit higher production rates (rates of up to 45 kg/day were sustainable between clogging events over relatively short periods of time). This is not a significant process problem for scaled up systems. No unusual events such as foaming were noted during the continuous melter runs.

Temperature and electrode power ranges used during these runs were summarized. An approximate average value of 0.7 kW hr/kg was obtained, somewhat smaller than expected in view of the large water content of the feeds.

Glasses produced from Micro-F1 and Micro-F2 feeds behaved well in the melter and showed no evidence of crystallization in the melt pool at processing temperatures. Some difficulties in draining the glass were probably due to crystallization in the drain tube which was at a temperature of below 1000°C.

Table 4-66 summarizes the viscosity and conductivity measurements were made on samples of glass produced in these runs. Melt viscosities were about 1.7 to 3.5 Poise over the processing temperature range of 1100°C to 1150°C the .

Table 4-65 DCP and Fluoride Analysis of MIC3-54A and MIC3-56A Glasses Produced in 10 kg/d Continuous Melter Runs (wt%)

	MIC3-54A		MIC3-56A	
	DCP Analysis (w/o fluoride)	Analysis (with fluoride)	DCP Analysis (w/o fluoride)	Analysis with fluoride
Al_2O_3	5.8	5.8	4.9	4.9
B_2O_3	9.3	9.3	9.9	9.9
BaO	0.9	0.9	0.9	0.9
CaO	18.2	18.2	15.9	15.9
Cr_2O_3	0.2	0.2	0.4	0.4
Fe_2O_3	4.1	4.1	4.9	4.9
K_2O	1.0	1.0	0.7	0.7
Li_2O	0.3	0.3	0.2	0.2
MgO	11.8	5.1	13.0	5.7
MgF	NA	10.3	NA	11.3
MnO_2	0.1	0.1	0.1	0.1
Na_2O	8.3	8.3	7.5	7.5
NiO	0.2	0.2	0.5	0.5
P_2O_5	0.3	0.3	0.3	0.3
SiO_2	31.3	31.3	29.9	29.9
SrO	0.02	0.02	0.03	0.03
TiO_2	0.1	0.1	0.1	0.1
U_3O_8	0.65	0.65	0.55	0.55
ZrO_2	0.1	0.1	0.1	0.1
Total	92.67	96.27	89.88	93.88
Measured Fluoride	6.3%		6.9%	

NA = Not Analyzed

Table 4-66 Viscosity and Conductivity Measurements Interpolated to Standard Temperatures for MIC3-54A and MIC3-56A Glass Produced from 10 kg/day Continuous Melter Runs.

	Viscosity (Poise)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
MIC3-54A	NA	9.35	4.85	3.5	2.9
MIC3-56A	NA	7.5	4.4	2.7	1.7
	Conductivity (S/cm)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
MIC3-54A	0.05	0.09	0.13	0.19	0.26
MIC3-56A	NA	0.10	0.16	0.22	0.27

NA = Not Analyzed

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TCLP testing of the MIC3-54A and MIC3-56A glass shows both pass the EPA limits for all eight metals, as shown in Table 4-67.

Off-Gas Analysis: A major factor determining overall system performance and the performance required of the off-gas system, is the natural distribution of the hazardous and radioactive elements between the glass and vapor phases in the melter. A variety of analyses were performed to quantify the distribution of various elements between the glass and the off-gas system, and within the off-gas system, between the scrubber solutions and the solid phase recycled to the melter feed batch.

Results show there is on the order of 1000-fold more uranium contained in the glass than in the off-gas system. This is particularly important in view of the high fluoride concentrations in these melts, since it indicates the volatilization of uranium as UF_6 is not significant. Thorium-232 retention in the glass is approximately 10^4 times that in the off-gas system. Other isotopes of thorium would be expected to behave similarly. Approximately 50 percent of the Tc-99 is retained in the glass and the majority of the fraction accumulated in the off-gas system is found in the NaF sludge recycled back to the feed batch.

The distribution of other elements between the glass melt and the off-gas system is summarized in Table 4-68. Results show the demands placed on off-gas system performance in order to meet emission standards are not great. On the other hand, fluoride is present in much higher concentrations and a significant fraction is volatilized. Thus, the ability to capture and effectively recycle the fluoride is one of the major features required of the off-gas system for FEMP Waste Pit 5 vitrification. The Duramelter system employed for the 10 kg/day continuous melter tests captured and successfully recycled the fluoride. The concentrations of HF in the final off-gas stream were reduced to below 1 ppm (the OSHA limit for the workplace is 3 ppm).

Concentrations of heavy metals and radionuclides in the final off-gas stream even before HEPA filtration were uniformly low - typically either below the detection limit or in the few - ppb range.

Table 4-67

TCLP Data for Glasses Produced from 10 kg/day Continuous Melter Runs

	As	Se	Cd	Hg	Ag	Pb	Ba	Cr
MIC3-54A	0.39	0.52*	0.01	0.15	0.02	1.40	4.47	1.49
MIC3-56A	0.30	0.46*	0.02	0.11	0.02	1.37	8.13	0.11
EPA Limit	5	1	1	0.2	5	5	100	5

* Se data were below the standard deviation of the measurement

Table 4-68 Percentage Distribution, by Weight, of Elements between Glass, Scrubber Liquid, and Scrubber Solids after Completion of 10 kg/day Melter Runs

	Wt.%		
Component	Glass	Scrubber Liquid	Scrubber Solid
Ba	99.77	0.06	0.16
Cd	99.65	0.34	0.00
Cr	97.43	1.81	0.75
Hg	92.68	1.28	6.04
Ni	99.8	0.00	0.17
Pb	99.73	0.099	0.16
Sb	99.54	0.31	0.15
Al	99.47	0.034	0.49
B	97.76	1.88	0.35
Ca	99.55	0.00	0.45
Cs	99.71	0.00	0.28
Fe	99.60	0.014	0.38
Li	99.27	0.095	0.63
Mg	99.75	0.001	0.24
Mn	99.61	0.00	0.38
Mo	99.11	0.62	0.27
Nd	99.93	0.011	0.05
P	99.66	0.13	0.21
Rb	99.48	0.20	0.32
Si	99.63	0.067	0.30
Sn	99.82	0.054	0.12
Sr	99.34	0.032	0.63
Ti	99.3	0.013	0.61
W	99.33	0.15	0.51
Zr	99.95	0.024	0.02

Comparison to test objectives

Glass formulations for FEMP Waste Pit 5 sludges were developed which exhibit high leach resistance, acceptable melt viscosity and electrical conductivity, acceptable liquidous temperatures, and high waste loadings.

The processability of these formulations was demonstrated by test runs on a laboratory Duramelter vitrification system with a nominal glass production rate of 10 kg/day; significantly higher production rates proved possible with these feeds. Fluoride loss from the melt is an important factor for FEMP wastes which must be carefully addressed by potential vitrification (or any thermal) process technologies. However, the Duramelter system test runs successfully demonstrated the concept of fluoride capture in the off-gas system and recycle to the feed batch with fluoride emissions below regulatory levels. Measurements of elemental distributions between the glass melt and the off-gas system show very high intrinsic retention of heavy metals and radionuclides in the glass melt.

The study demonstrated the following:

- Waste Pit 5 sludge could be processed with 77-88 wt. percent waste loading in a Duramelter joule-heated vitrification system
- Approximately 99.9 percent of the uranium and thorium was contained within the glass before recycle of the scrubber sludge (i.e. volatilization of UF_6 is not a problem)
- Heavy metals and radionuclides are effectively retained within the glass melt minimizing off-gas problems
- Fluoride can be captured in the off-gas system and recycled into the feed batch as NaF
- Fluoride emissions were below regulatory levels

Overall volume reduction calculations for Waste Pit 5 sludge (taking into account all materials added to produce a vitrifiable blend, including soil and/or fly ash) yield a volume reduction of about 80 percent.

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WASTE PIT 6

Compositional Analysis

As vitrification feed material, Waste Pit 6 contains 24.63 mole percent glass formers and 74.07 mole percent flux. The former/flux ratio is 0.333, which is below the desired 0.5 or greater target. Additionally, compositional data reveal the presence of chromium, uranium, and thorium at levels that might result in significant leaching in poor glass formulations, especially with uranium at 6.69 percent (as UO_3).

Range-Finding Tests

Initial testing generated four samples that evaluated the performance of Waste Pit 6 composite material to vitrify as-is, with soil, and with site flyash. The formulations are presented in Table 4-69.

The as-is formulation (P6-1) produced a good vitreous product with a low viscosity (V-3/V-4) melt. Streaks of a greenish-yellow material were observed throughout the monolith. During Remedy Screening, the ability of sodium/flux addition to help incorporate this second phase material into the vitrified mass was investigated.

Two waste/soil formulations (P6-2 and P6-3) generated excellent glasses with pourable melts. The higher soil loading formulation (P6-3) produced a completely vitreous, single-phase product, while the lower soil loading formulation (P6-2) exhibited a nonvitreous skin where it contacted the crucible walls. During Remedy Screening, the P6-3 formulation was be modified to determine if a good glass could be produced with reduced sodium/flux addition.

Only one waste/flyash formulation (P6-4) was tested. The melt viscosity was very high (V-1) and the cooled product was granite-like with a dark, crystalline cap. It was reasoned that this formulation contained insufficient glass former content so during Remedy Screening the flyash loading would be increased.

TABLE 4-69

PIT 6
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P6-1 10500801	100	0	0	0	V-3/V-4	Vitreous with inclusions
(Soil) P6-2 10501306	100	100	0	5.0	V-3	Excellent glass product
(Soil) P6-3 10501506	100	150	0	5.0	V-3	Excellent glass product
(Flyash) P6-4 10501906	100	0	150	5.0	V-1	Granite-like with crystalline cap

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

TABLE 4-69 (Continued)

PIT 6
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P6-6 10502906	100	0	0	8.5	V-3/V-4	Vitreous, bi-phase glass	19 K, 14 Si,58 Na, 123 F (PCT); 15 U (MTCLP)
(Soil) P6-7 10502606	100	150	0	5.2	V-3	Good vitreous product	3.7 U (MTCLP); 27 Ca, 14 Si, 31 F
(Soil) P6-8 10502706	100	150	0	2.6	V-3	Good vitreous product	15,800 alpha, 4460 beta, 1.4 U (MTCLP); 45 Ca, 23 Si, 31 F, 8 SO_4
(Flyash) P6-9 10502806	100	0	200	2.6	V-3	Good vitreous product	1.8 U, 0.1 Cr (MTCLP); 5 Al, 11 Si, 3.5 F (PCT)
(Flyash) P6-11 10503014	100	0	200	5.2	V-2/V-3	Non-vitreous and porous	2.7 U (MTCLP); 11 Si, Al, Cd, Mg and F all <5

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.

Remedy Screening Testing

This second round of testing generated five samples which further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-69 presents these formulations.

The as-is range-finding formulation was modified by the addition of 8.5 percent sodium/flux addition. The resulting formulation (P6-6) produced a low viscosity (V-3/V-4) melt that cooled to a vitreous black-amber mass in which greenish-yellow streaks of a second phase material were still present. Leach testing of this product indicated that some leachability of uranium (15 ppm) in the MTCLP, and silicon (14 ppm), sodium (58 ppm), and fluoride (123 ppm) in the MPCT was evident. Gross alpha/ beta was at LLD in both.

Two waste/soil formulations (P6-7 and P6-8) tested the ability of the P6-3 range-finding formulation to produce a good glass with reduced sodium/flux addition. P6-7 was an unmodified retest of the P6-3 formulation. It produced a low viscosity (V-3) melt that cooled to a transparent glossy black, nonporous glass. Leach testing of this glass indicated leaching of uranium (3.7 ppm) and chromium (0.2 ppm) in the MTCLP, and cadmium (27 ppm), silicon (14 ppm), and fluoride (31 ppm) in the MPCT. Gross alpha/beta were at LLD for both tests. P6-8 reduced the sodium/flux addition to 2.6 percent, which produced a low viscosity (V-3) melt that cooled to a good quality glass. Leach testing of this glass indicated that leaching was occurring for gross alpha (15,800 wt/wt), gross beta (4460 wt/wt), and uranium (1.4 ppm) in the MTCLP, and cadmium (45 ppm), silicon (23 ppm), fluoride (31 ppm), and sulfate (8 ppm) in the MPCT. It appears that increased leachability may parallel reduced sodium/flux content and because of this the higher sodium/flux formulation (5.2 percent; P6-7) was chosen for use in the advanced phase testing.

Two waste/flyash tests were designed to increase the flyash loading of the range-finding formulation and test the effect of lower sodium/flux loading. P6-11 raised the flyash to waste loading to 2:1 and kept the flux addition at 5.2 percent. It produced a pourable viscosity (V-2/V-3) melt that cooled to a nonglossy, porous, near-vitreous monolith. Leach testing of this product indicated that leaching of uranium (1.8 ppm) and chromium (0.1 ppm) was occurring in the MTCLP, and aluminum (5 ppm), silicon (11 ppm), and fluoride (3.5 ppm) in the MPCT. Gross alpha/beta were at LLD in both tests.

P6-9 maintained the flyash to waste loading at 2:1 but reduced the flux loading to 2.6 percent and produced a good viscosity (V-3) melt that cooled to a glossy black, vitreous mass. Leach testing of this product indicated some leachability, uranium (2.7 ppm) in the MTCLP, and silicon (11 ppm) and aluminum, cadmium, magnesium, and fluoride (all <5 ppm) in the MPCT. Gross alpha/beta were LLD in both tests.

The low flux addition formulation (P6-9) produced a better appearing glass with acceptable leachability performance and was therefore chosen for use in the advanced phase testing.

Remedy Selection Tests

The advanced phase formulations are given in Table 4-70. Table 4-71 gives the bulking factors. The soil formulation, Formulation 1, produced a high viscosity melt that cooled to a nonporous, dark amber glass with heavy streaking of incompletely vitrified material. This streaking was not observed during remedy screening. The bulking factor for this glass was 73 percent.

The flyash formulation, Formulation 2, produced a low viscosity melt that cooled to a porous, crystalline product. The same material was produced during the Remedy Screening tests. The bulking factor for this material was -50 percent.

Results for Waste Pit 6 TCLP radionuclides for the two formulations are shown in Table 4-72. The metals in the TCLP leachates for the waste treated with the two vitrification formulations and the TC criteria for metals are shown in Table 4-73. Both formulations pass the TC regulatory criteria. Formula 1 performs slightly better than Formula 2 for inorganic compounds.

The mean dilution adjusted concentrations for Formula 2 were lower for most of the radiological CPCs than Formula 1. Of particular interest is the uranium concentrations which are an order of magnitude lower for Formula 2. Formula 1 had better results for Pu-238, Ra-226, and Th-230.

The results of the PCT expressed as NLRs are presented in Table 4-74. The waste/soil glass NLRs were less than 1 percent of the SRHLWC except for the Na and K at 45 percent and 29 percent of the

VITRIFICATION--PIT 6
ADVANCED PHASE FORMULATIONS

Table 4-70

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	175	0	14
2	100	0	200	20

VITRIFICATION--ADVANCED PHASE PIT 6
BULKING FACTOR, AVERAGE BULKING FACTOR

Table 4-71

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
Composite	1	-73	-62
Composite	2	-50	

TABLE 4-72

WASTE PIT 6 VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	20.000	ND
Neptunium-237	NA	5.000	0.648
Plutonium-238	NA	1.933	
Plutonium-239/240	NA	ND	ND
Radium-226	NA	ND	0.626
Radium-228	NA	ND	ND
Strontium-90	NA	8.060	ND
Technetium-99	NA	236.000	ND
Thorium-228	NA	2.060	1.750
Thorium-230	NA	4.850	5.119
Thorium-232	NA	ND	ND
Uranium-234	NA	1010.000	111.240
Uranium-235/236	NA	104.000	9.428
Uranium-238	NA	5500.000	533.520
	Raw Waste Characterization (mg/l)	**Formula 1 (mg/l)**	**Formula 2 (mg/l)**
Thoruim (Total)	NA	ND	ND
Uranium (Total)	NA	16.400	1.588

* See Table 4-6

\+ See Table 4-6

0381

TABLE 4-73

WASTE PIT 6 VITRIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS
Antimony	ND	ND	ND	
Arsenic	0.550	0.004	0.012	5.000
Barium	1.731	ND	0.145	100.000
Beryllium	0.009	ND	0.002	
Cadmium	ND	ND	ND	1.000
Chromium	ND	ND	ND	5.000
Cobalt	ND	ND	ND	
Copper	ND	ND	0.029	
Cyanide	ND	ND	ND	
Lead	0.596	ND	ND	5.000
Manganese	1.255	1.530	0.103	
Mercury	ND	ND	ND	0.200
Molybdenum	ND	ND	ND	
Nickel	0.095	0.035	0.028	
Selenium	ND	ND	ND	1.000
Silver	0.047	ND	ND	5.000
Thallium	0.660	ND	ND	
Vanadium	ND	ND	ND	
Zinc	1.551	0.070	0.080	

* See Table 4-6

\+ See Table 4-6

PIT 6 - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Table 4-74

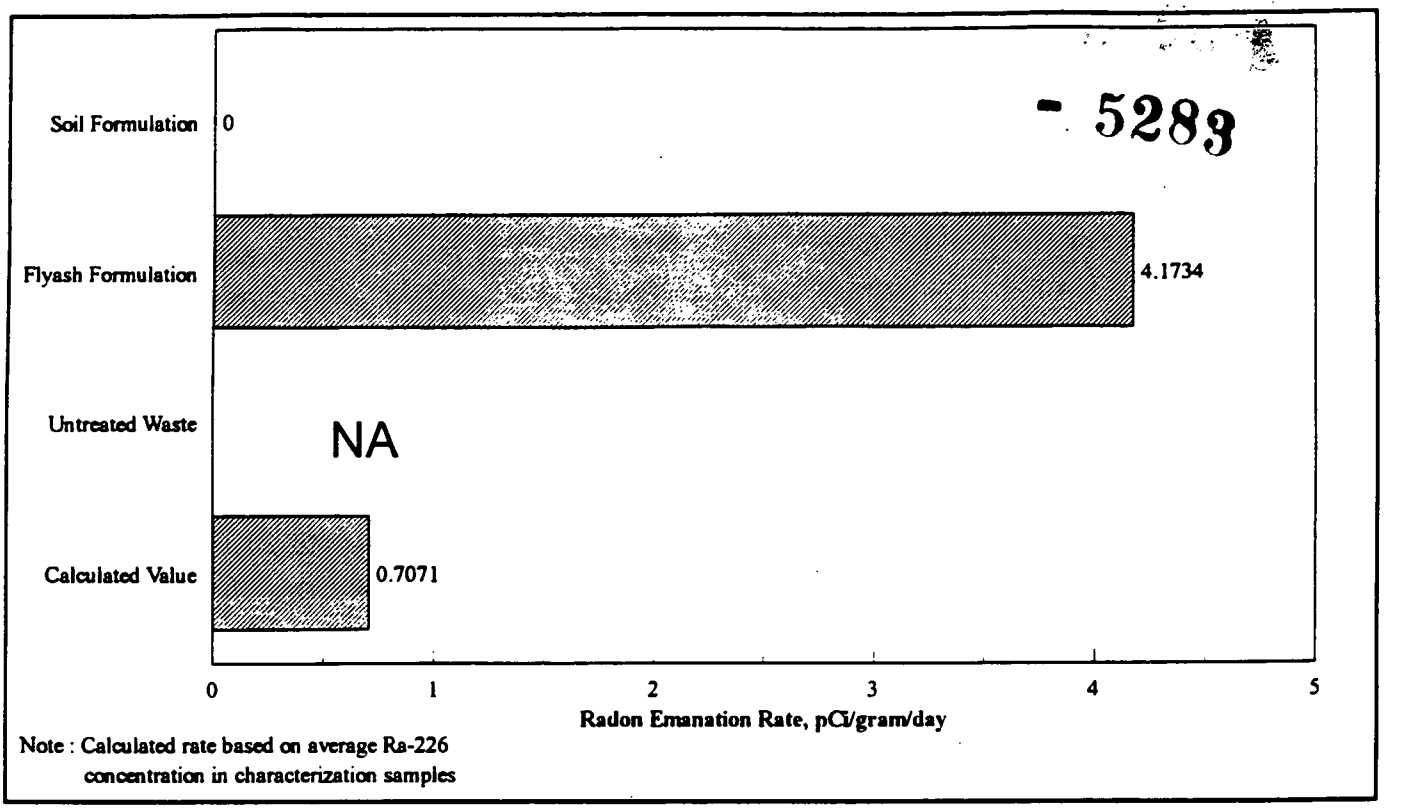
Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	Composite	0.3	0.009	45	1	0.01	Not Calc'd	29	Not Calc'd
2	Composite	0.3	0.1	59	0.5	Not Calc'd	Not Calc'd	4	271

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

SRHLWC, respectively. Boron exceeded the SRHLWC for the waste/flyash product. Excluding sodium at 59 percent, the remaining metals were less than 4 percent of the SRHLWC.

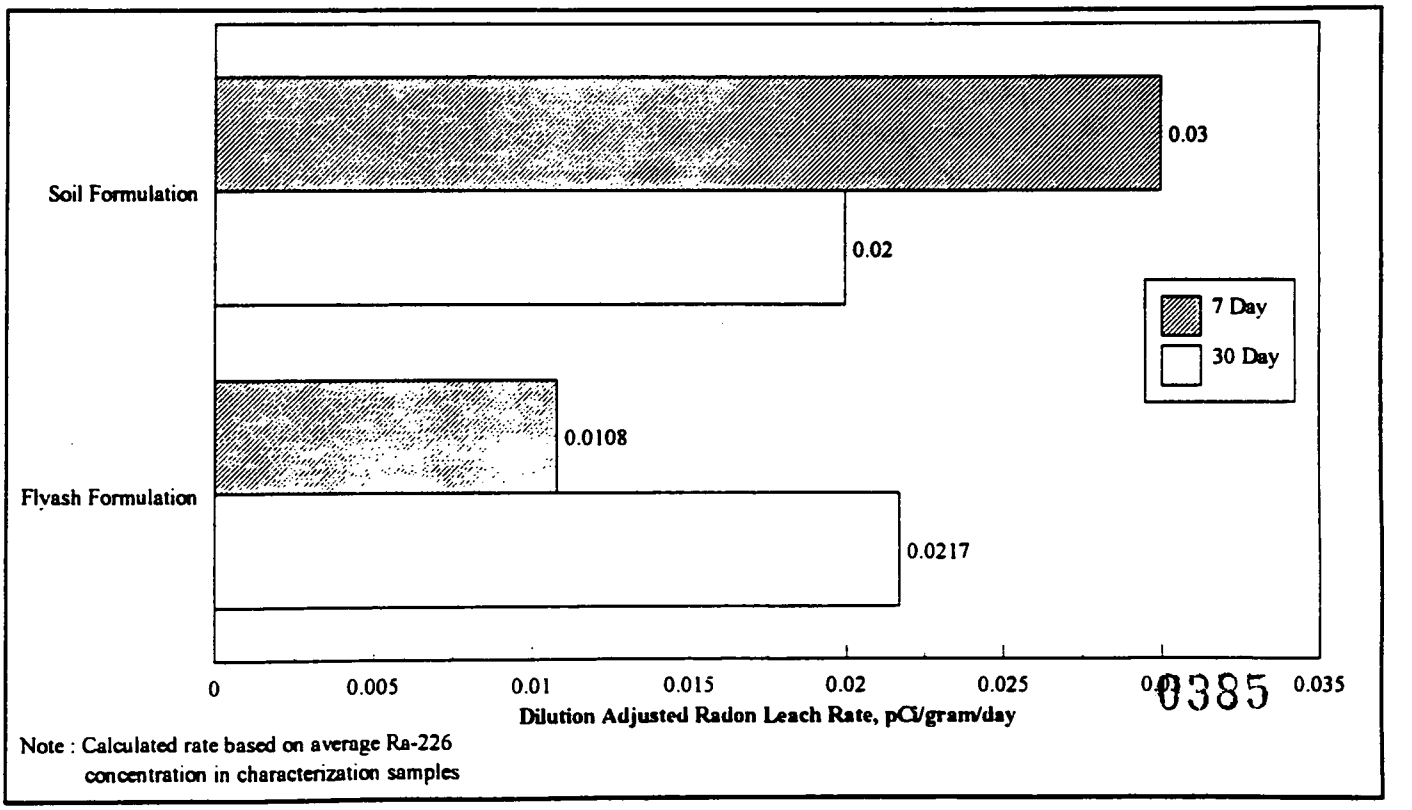
Waste Pit 6 Vitrification - Radon Emissions

Figure 4-20 and 4-21 shows radon leach rates lower than the calculated rate.



FL/FEMP/OU1TR/4.6-7A

FIGURE 4-20 - PIT 6 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES



FL/FEMP/OU1TR/4.6-7B

FIGURE 4-21 - PIT 6 VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

BURN PIT

Compositional Analysis

As vitrification feed material, the Burn Pit waste contains 70.58 mole percent glass formers and 29.41 mole percent flux. The former/flux ratio is 2.40, the highest of all the pits. In addition, it contains the lowest combined concentration of cadmium and magnesium.

Range-Finding Tests

The as-is waste formulation was tested first and found to be very successful; therefore, waste/soil and waste/flyash formulations tests were unnecessary. Instead, during Remedy Screening waste/soil and waste/flyash formulations were designed on the basis of past experience with the other waste pits.

The as-is formulation (P7-1) produced a low viscosity (V-4) melt that cooled to an excellent black glass. Although not strictly necessary, during Remedy Screening the effect of sodium/flux addition was evaluated.

Remedy Screening Tests

This second round of testing generated eight samples that further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-75 presents these formulations. For P7-2, the as-is formulation was supplemented with 7.4 percent sodium/flux and found to produce a good viscosity (V-3) melt and an excellent brownish-black glass. Leach testing of this glass indicated minor leaching of uranium (1.3 ppm) in the MTCLP and silicon (20 ppm) in the MPCT.

Two waste/soil formulations were designed at 0.5:1 soil to waste loading and at two levels of sodium/flux addition: 2.6 percent (P7-2) and 5.2 percent (P7-3). The higher flux formulation produced a fairly low viscosity (V-3/V-4) melt that cooled to a translucent, glossy black glass. Leach testing of this glass indicated leaching of uranium (3.7 ppm) and chromium (0.2 ppm) in the MTCLP, and cadmium (24 ppm) and silicon (24 ppm) in the MPCT. Gross alpha/beta were LLD for both tests. The lower flux formulation produced a medium viscosity melt (V-2/V-3) that cooled to a glossy, dark black glass with a second phase of undissolved specks. These specks appeared to be

Table 4-75

BURN PIT
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P7-1 10500701	100	0	0	0	V-4	Excellent vitreous product
(Soil) No range finding samples were prepared.						
(Flyash) No range finding samples were prepared.						

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

BURN PIT
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P7-2 10502908	100	0	0	7.4	V-3	Excellent vitreous product	1.3 U (MTCLP); 20 Si (PCT)
(Soil) P7-3 10502607	100	50	0	5.2	V-3/V-4	Translucent vitreous product	3.7 U, 0.2 Cr (MTCLP); 24 Ca, 24 Si (MPCT)
(Soil) P7-4 10502707	100	50	0	2.6	V-2/V-3	Vitrous with crystal inclusions	0.3 U (MTCLP); 12 Ca, 21 Si (MPCT)
(Flyash) P7-5 10502808	100	0	100	4.6	V-1	Slag-like with entrapped gas	NA[d]
(Flyash) P7-6 10503017	100	0	100	7.0	V-1	Slag-like with crystal inclusions	NA
(Flyash) P7-7 10502818	100	0	100	8.3	V-1	Dark amber vitreous product	0.2 U (MTCLP)
(Flyash) P7-8 10503205	100	0	100	7.7	V-2/V-3	Dark amber viteous product	0.6 U (MTCLP); 7 Al, 14 Si, (MPCT)
(Flyash) P7-9 10503206	100	0	100	9.6	V-3/V-4	Excellent viteous product	0.4 U (MTCLP); 8 Al, 17 Si, 30 Na (MPCT)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d]Not analyzed.

crystalline in nature and may have been an artifact of too slow a cooling rate or indicative of minor attack or intrusion of the firebrick crucible. Leach testing of this glass indicated minor leaching of uranium (0.3 ppm) in the MTCLP, and cadmium (12 ppm) and silicon (21 ppm) in the MPCT. Gross alpha/beta were LLD for both tests.

Considering the quality of glass produced (e.g., appearance and leachability performance) as compared to sodium/flux addition, it was decided that no significant advantage was gained from a sodium/flux addition beyond 2.6 percent. Therefore the lower flux level formulation (P7-4) was chosen for use in advanced phase testing.

Five waste/flyash formulations were tested, maintaining a 1:1 flyash to waste loading ratio and adjusting the sodium/flux addition from 4.6 percent up through 9.6 percent. The 4.6 percent formulation (P7-5) produced a very high viscosity melt (V-1) and a slag-like monolith with entrapped gas bubbles. The 7 percent formulation (P7-6) produced an equally unpourable monolith with undissolved crystalline inclusions. Due to the very poor quality of these products no leach testing was performed on them. The 7.7 percent formulation (P7-6) was designed after seeing the results of the other four runs. It produced a pourable (V-2/V-3) melt that cooled into a glossy amber-black glass. Leach testing of this glass indicated slight leaching of uranium (0.6 ppm) in the MTCLP, and aluminum (7 ppm) and silicon (14 ppm) in the MPCT. Gross alpha and beta were at LLD for both tests.

Continuing with the higher flux formulations, the 8.3 percent formulation (P7-7) produced a very high viscosity (V-1) melt that cooled to a glossy, dark amber glass. When broken into thin fragments, it was very homogeneous and completely vitreous. Leach testing of this glass indicated minor leaching of uranium (0.2 ppm) in the MTCLP, and all metals and anions at <3 ppm in the MPCT. Gross alpha/ beta were at LLD for these tests. The highest flux formulation was 9.6 percent and it produced a low viscosity (V-3/V-4) melt and cooled to an excellent amber-black glass. Leachability results indicated trace leaching of uranium (0.4 ppm) in the MTCLP, and aluminum (8 ppm), silicon (17 ppm), and sodium (30 ppm) in the MPCT.

Although some of the waste/flyash formulations produced very good quality glasses with acceptable leachability performance, it was decided that at least one of the FEMP waste pits should be taken into the advanced phase in the as-is formulation. Because the Burn Pit produced such a visually good quality glass, the as-is formulation was carried forward into the advanced phase where individual Burn Pit zone differences might be highlighted.

Remedy Selection Tests

The advanced phase Burn Pit zone samples used the formulations listed in Table 4-76. The soil formulation, Formulation 1, produced pourable viscosity melts that cooled in two of the three zones, into black, nonporous glasses. The Zone 1 material became very porous, with a granite-like appearance. The remedy screening tests produced glasses like those resulting for Zones 2 and 3. The Zone 1 granite-like product was atypical and suggests that Zone 1 may have higher levels of alumina than the other two. Bulking factors are given in Table 4-77. The bulking factors for these glasses were from -31 percent to -57 percent.

No waste/flyash formulations were prepared for the Burn Pit in the advanced phase testing. Instead, an as-is formulation, Formulation 2, including 7.4 percent sodium/flux addition was tested. The flux-supplemented Zones 1 and 2 material produced low viscosity melts that cooled to slightly different products. Zone 1 product was porous and crystalline, while the Zone 2 material was nonporous and vitreous. The Zone 2 product is consistent with what was observed during remedy screening. The Zone 1 product appears to be incompletely processed and may be due to insufficient flux being present. The bulking factor for both these glasses was -62 percent.

Results for the Burn Pit TCLP radionuclides for the two formulations are shown in Table 4-78. The metals in the TCLP leachates for the waste treated with the two vitrification formulations and the TC criteria for metals are shown in Table 4-79. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds.

The PCT results expressed as NLRs are presented in Table 4-80. The waste/soil glass NLRs were all less than 6 percent of the SRHLWC. Uranium leached variably, but at very low levels, from 0.005

VITRIFICATION-BURN PIT
ADVANCED PHASE FORMULATIONS

Table 4-76

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	50	0	4
2	100	0	0	8

VITRIFICATION--ADVANCED PHASE BURN PIT BULKING FACTOR, AVERAGE BULKING FACTOR

Table 4-77

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
1	1	-50	-52
2	1	-31	
3	1	-57	
1	2	-62	
2	2	-62	

TABLE 4-78

BURN PIT VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	ND	0.585	0.410
Plutonium-238	ND	0.633	0.620
Plutonium-239/240	ND	0.227	ND
Radium-226	23.600	2.377	2.140
Radium-228	4.500	ND	ND
Strontium-90	ND	4.030	ND
Technetium-99	25.000	ND	ND
Thorium-228	2.010	4.936	2.260
Thorium-230	2.160	22.073	8.450
Thorium-232	ND	2.904	1.090
Uranium-234	10200.000	240.570	96.400
Uranium-235/236	643.000	11.771	4.870
Uranium-238	11000.000	465.590	112.000
	Raw Waste Characterization (mg/l)	**Formula 1 (mg/l)**	**Formula 2 (mg/l)**
Thoruim (Total)	ND	0.019	0.010
Uranium (Total)	23.920	1.389	0.336

* See Table 4-6

\+ See Table 4-6

TABLE 4-79

BURN PIT VITRIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.095	0.008	ND	
Arsenic	0.078	0.012	0.003	5.000
Barium	1.395	0.173	0.147	100.000
Beryllium	0.005	0.018	ND	
Boron	0.368	ND	ND	
Cadmium	0.017	ND	ND	1.000
Chromium	0.176	0.043	0.055	5.000
Cobalt	0.050	0.038	ND	
Copper	0.053	0.033	0.044	
Cyanide	ND	ND	ND	
Lead	0.065	0.010	0.056	5.000
Manganese	3.820	0.940	0.173	
Mercury	ND	ND	ND	0.200
Milybdenum	0.025	0.033	ND	
Nickel	0.081	0.051	0.040	
Selenium	0.190	ND	ND	1.000
Silicon	4.760	44.950	16.900	
Silver	0.121	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.070	0.012	ND	
Zinc	0.513	0.201	0.127	

* See Table 4-6

\+ See Table 4-6

BURN PIT - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	B
		Percentages							
1	1	0.3	0.01	4	2	0.005	Not Calc'd	0.1	Not Calc'd
1	2	0.1	1.2	4	0.9	0.01	Not Calc'd	2	6
1	3	0.3	0.01	5	0.9	0.07	Not Calc'd	0.6	Not Calc'd
2	Composite	0.4	0.6	26	0.4	Not Calc'd	Not Calc'd	0.7	8

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

to 0.1 percent of the SRHLWC. An as-is waste glass formulation was produced instead of a waste/flyash formulation and its NLRs were less than 8 percent of the SRHLWC except for sodium at 26 percent of the SRHLWC. The waste/soil product had the lowest overall NLR for the Burn Pit waste.

Burn Pit Vitrification - Radon Emissions

Figures 4-22 and 4-23 show radon leach rates much lower than the untreated waste or the calculated rate. The unusually high emanation rates for the treated waste (in comparison to raw and calculated rates) may be due to changes in the background. A background measurement was made every day before measurements were started. Any changes occurring during the day would have gone undetected.

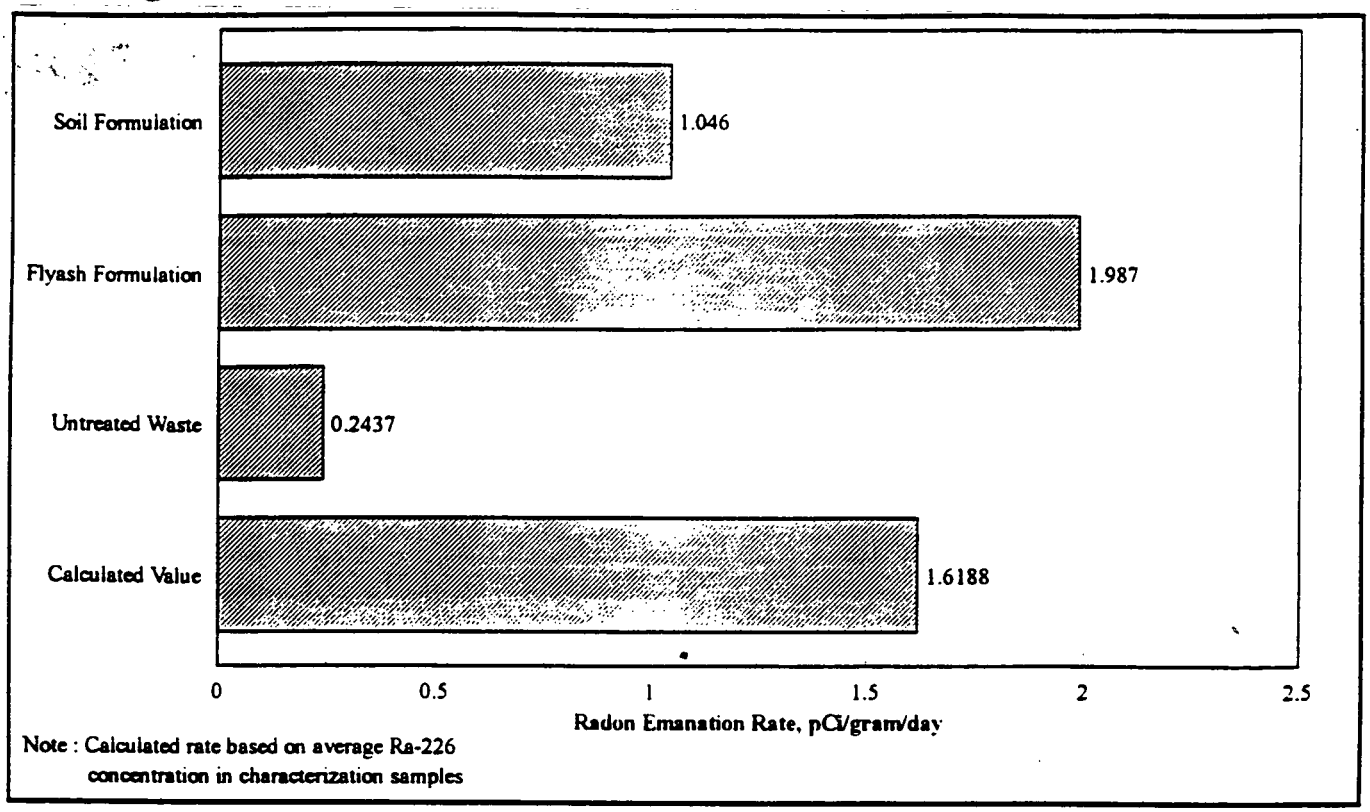


FIGURE 4-22 - BURN PIT VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

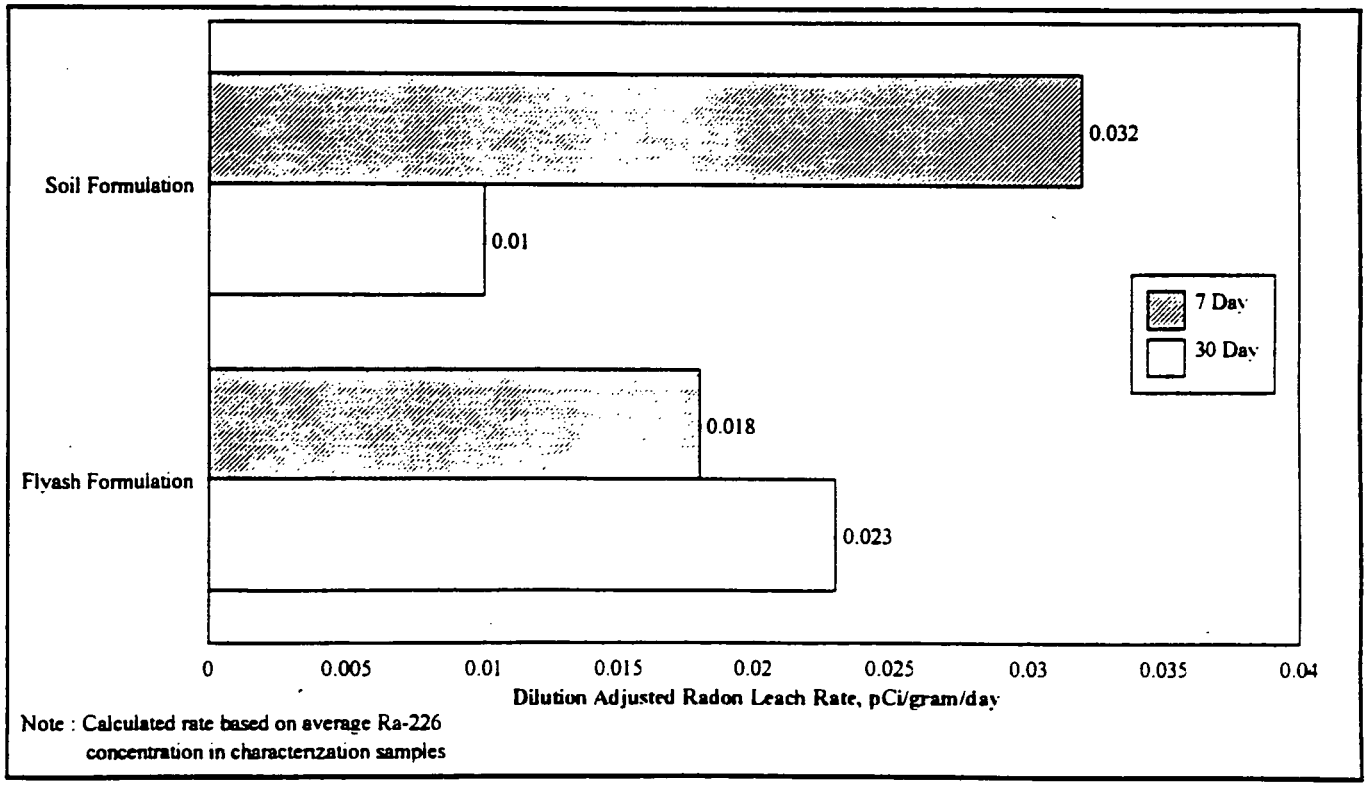


FIGURE 4-23 - BURN PIT VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

CLEARWELL

Compositional Analysis

As vitrification feed material, the Clearwell waste contains 38.49 mole percent glass formers and 61.51 mole percent flux. The former/flux ratio is 0.626 which satisfies the desired 0.5 or greater target. Additionally, compositional data reveals the presence of barium, chromium, and uranium at levels that might result in significant leaching in poor glass formulations.

Range-Finding Tests

Initial testing generated two samples that evaluated the performance of Clearwell composite material to vitrify as-is and with soil. No waste/flyash formulation was evaluated prior to Remedy Screening. The formulations are presented in Table 4-81.

The as-is formulation (P8-1) produced a medium viscosity (V-2/V-3) melt, which cooled to a homogeneous, nonporous vitreous mass with a very slight slag-like film on surfaces, which contacted the crucible walls. During Remedy Screening, this formulation was adjusted by sodium/flux addition to decrease viscosity and perhaps further process the slag-like material into a completely vitreous formulation.

Because the as-is pit waste performed so well, only one waste/soil formulation (P8-2) was tested. At a 1:1 waste to soil ratio and 5 percent flux addition the melt viscosity was good (V-3) and an excellent glass resulted. During Remedy Screening, testing focused on reducing the soil loading and adjusting the sodium/flux addition to produce a good quality, higher waste loading glass.

Remedy Screening Tests

This second round of testing generated 6 samples that further refined the evaluation of soil, flyash, and sodium/flux additives. Table 4-81 presents these formulations.

The as-is formulation (P8-1) was modified with 8.2 percent sodium/flux addition to produce a lower viscosity formulation (P8-3). This formulation produced a good viscosity (V-3) melt that cooled to an excellent amber, vitreous material. However, slight corrosive attack of the crucible was observed.

Table 4-81

CLEARWELL
REMEDY SCREENING RANGE FINDING TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	% Na_2O	Viscosity[b]	Description of Glass
(As-Is) P8-1 10501907	100	100	0	5.0	V-2/V-3	Vitreous with slag-like skin
(Soil) P8-2 10501507	100	0	0	0	V-3	Excellent vitreous product
(Flyash) No range finding samples were prepared.						

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.

Table 4-81
(Continued)

CLEARWELL
REMEDY SCREENING PRELIMINARY PHASE TESTS

Formulation	Waste (g)	Soil (g)	Flyash (g)	%Na_2O	Viscosity[b]	Description of Glass	Leachate Analysis[c]
(As-Is) P8-3 10502907	100	0	0	8.2	V-3	Excellent vitreous product	2.0 U (MTCLP); 23 Ca, 23 Si (PCT)
(Soil) P8-4 10502608	100	50	0	5.2	V-1	Vitreous but non-pourable	NA[d]
(Soil) P8-5 10502708	100	50	0	9.8	V-3/V-4	Good vitreous product	1.9 U, 0.1 Cr (MTCLP); 23 Ca, 27 Na, 27 Si (MPCT)
(Soil) P8-6 10503015	100	50	0	11.0	V-3	Good vitreous product	28 Ca, 23 Si, 30 Na (PCT)
(Flyash) P8-7 10502807	100	0	100	8.8	V-3	Good vitreous product	0.14 U (MTCLP); 5 Al, 44 Ca, 14 Si, 4.5 Na (MPCT)
(Flyash) P8-8 10503016	100	0	100	12.0	V-3	Good vitreous product	0.8 U (MTCLP); 6 Al, 13 Ca, 16 Si, 25 Na (MPCT)

[a]Formulations are dry weights given as "parts waste"/"parts soil or fly ash"/ % Na_2O addition.
[b]Viscosity designations used here are defined in Section A.1.0 of Appendix B.
[c]Results are given for MTCLP and PCT leach tests and are reported in ppm (w/w). Analytes not reported were not detected.
[d]Not analyzed.

Leach testing of this glass indicated some leaching of uranium (2.0 ppm) in the MTCLP, and cadmium (23 ppm) and silicon (23 ppm) in the MPCT.

Three waste/soil formulations were designed to test the effect of varying sodium/flux levels with a reduced soil to waste loading ratio (0.5:1). P8-4 (5.2 percent flux) produced a very high viscosity (V-1) melt that cooled to a glossy black, nonporous monolith. This sample had an asphaltic character to it that suggested homogeneity but incomplete vitrification. No leach testing was performed on this sample. P8-5 (9.8 percent flux) produced a low viscosity (V-3/V-4) melt that cooled to a semi-transparent amber black mass with good vitreous character. Leach testing of this glass indicated leaching of some uranium (1.9 ppm) and chromium (0.1 ppm) in the MTCLP, and cadmium (23 ppm), sodium (27 ppm), and silicon (27 ppm) in the MPCT. Gross alpha/beta were at LLD. The highest flux addition formulation (11 percent; P8-6) produced a pourable viscosity (V-3) melt and cooled to a fully vitreous monolith, but darker and less translucent than P8-5. Leach testing of this glass indicated some leaching in the MPCT of cadmium (28 ppm), silicon (23 ppm), and sodium (30 ppm). Gross alpha/beta were at LLD in the MPCT and MTCLP.

Comparison of these formulations with respect to their appearance and leaching performance led to the conclusion that the mid-level flux formulation (9.8 percent; P8-5) produces a superior glass to P8-4 and justifies the additional sodium/flux. The high level flux (11 percent; P8-6) produces a glass that is not as high quality in appearance as P8-5 and whose leaching performance is not significantly better to warrant the extra flux addition. Therefore, it was decided that the 9.8 percent flux addition formulation (P8-5) would be developed in the advanced phase testing.

As with the waste/soil tests, the fact that the waste vitrifies on its own was relied on to require a minimum of testing waste/flyash formulations. Based on previous experience with the FEMP waste pits, a 1:1 waste to flyash loading ratio was chosen for testing. Two formulations were tested, one at 8.8 percent flux addition (P8-7) and one at 12 percent flux addition (P8-8). The lower flux formulation produced a pourable (V-3) melt that cooled to a black glassy monolith of better than

average quality. Leach testing of this glass indicated minor leaching of uranium (0.14 ppm) in the MTCLP, and aluminum (5 ppm), cadmium (4.4 ppm), silicon (14 ppm), and sodium (4.5 ppm) in the MPCT. Gross alpha/beta were at LLD in both tests.

The vitrified product of the higher flux formulation (P8-8) was nearly identical to P8-7. Its leaching performance also paralleled closely that of the lower flux formulation indicating no advantage from the additional sodium/flux; therefore, the lower flux formulation (P8-7) was developed in the advanced phase.

Remedy Selection Tests

The advanced phase Clearwell composite samples used the soil and flyash formulations listed in Table 4-82. The soil formulation, Formulation 1, produced a pourable viscosity melt that cooled to a fairly homogeneous black glass, which upon remelt in an inconel 601 crucible became crystalline to near-vitreous. This change in product character is no doubt due to interaction of the melt with the inconel crucible resulting in a modified glass formulation. The bulking factor for this glass was -58 percent (Refer to Table 4-83). The flyash formulation, Formulation 2, produced a low viscosity melt that cooled to a dark amber, homogeneous glass. Its bulking factor was -15 percent.

Clearwell Vitrification - TCLP

Results for Clearwell TCLP radionuclides for the two formulations are shown in Table 4-84. The TCLP metals in the TCLP leachate are shown in Table 4-85. Both formulations pass the TC regulatory criteria. Formula 2 performs better than Formula 1 for inorganic compounds.
The mean dilution adjusted concentrations for Formula 2 were lower for most of the radiological CPCs. Of particular interest is the uranium concentrations which are an order of magnitude lower for Formula 2. Formula 1 had better results for Pu-238, Ra-226, Tc-99 and Th-230.

The results of the PCT expressed as NLRs are presented in Table 4-86. The waste/soil composite glass NLRs did not exceed 3 percent of the SRHLWC, while none of the calculated waste/flyash NLRs exceeded 35 percent of the SRHLWC. Except for the 35 percent for sodium, the waste/flyash product had the lowest overall NLR for the Clearwell waste.

Table 4-82

VITRIFICATION--PIT--CLEARWELL ADVANCED PHASE FORMULATIONS

Formulation	Normalized Waste	Normalized Soil	Normalized Flyash	Normalized Sodium Oxide
1	100	50	0	16
2	100	0	100	20

Table 4-83

VITRIFICATION--ADVANCED PHASE PIT--CLEARWELL BULKING FACTOR, AVERAGE BULKING FACTOR

Zone	Formulation	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)
Composite	1	-58	-36
Composite	2	-15	

TABLE 4-84

CLEARWELL VITRIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	ND	ND
Neptunium-237	NA	1.650	0.408
Plutonium-238	NA	0.820	1.356
Plutonium-239/240	NA	ND	ND
Radium-226	NA	ND	0.360
Radium-228	NA	ND	ND
Strontium-90	NA	4.270	ND
Technetium-99	NA	ND	97.080
Thorium-228	NA	1.840	1.788
Thorium-230	NA	3.310	7.644
Thorium-232	NA	0.150	ND
Uranium-234	NA	64.200	4.032
Uranium-235/236	NA	3.190	ND
Uranium-238	NA	163.000	17.160
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thoruim (Total)	NA	0.001	ND
Uranium (Total)	NA	0.485	0.052

* See Table 4-6

\+ See Table

TABLE 4-85

CLEARWELL VITRIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.101	ND	ND	
Arsenic	ND	0.007	0.004	5.000
Barium	2.001	1.080	0.136	100.000
Beryllium	ND	ND	ND	
Cadmium	0.010	ND	ND	1.000
Chromium	0.010	2.170	0.103	5.000
Cobalt	0.095	0.019	ND	
Copper	0.822	0.138	0.052	
Cyanide	ND	ND	ND	
Lead	0.123	0.059	0.008	5.000
Manganese	66.986	3.470	0.073	
Mercury	ND	ND	ND	0.200
Molybdenum	0.037	0.092	ND	
Nickel	0.886	0.121	ND	
Selenium	ND	ND	ND	1.000
Silver	0.049	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.040	0.075	0.013	
Zinc	0.609	0.198	0.020	

* See Table 4-6

\+ See Table 4-6

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TABLE 4-86

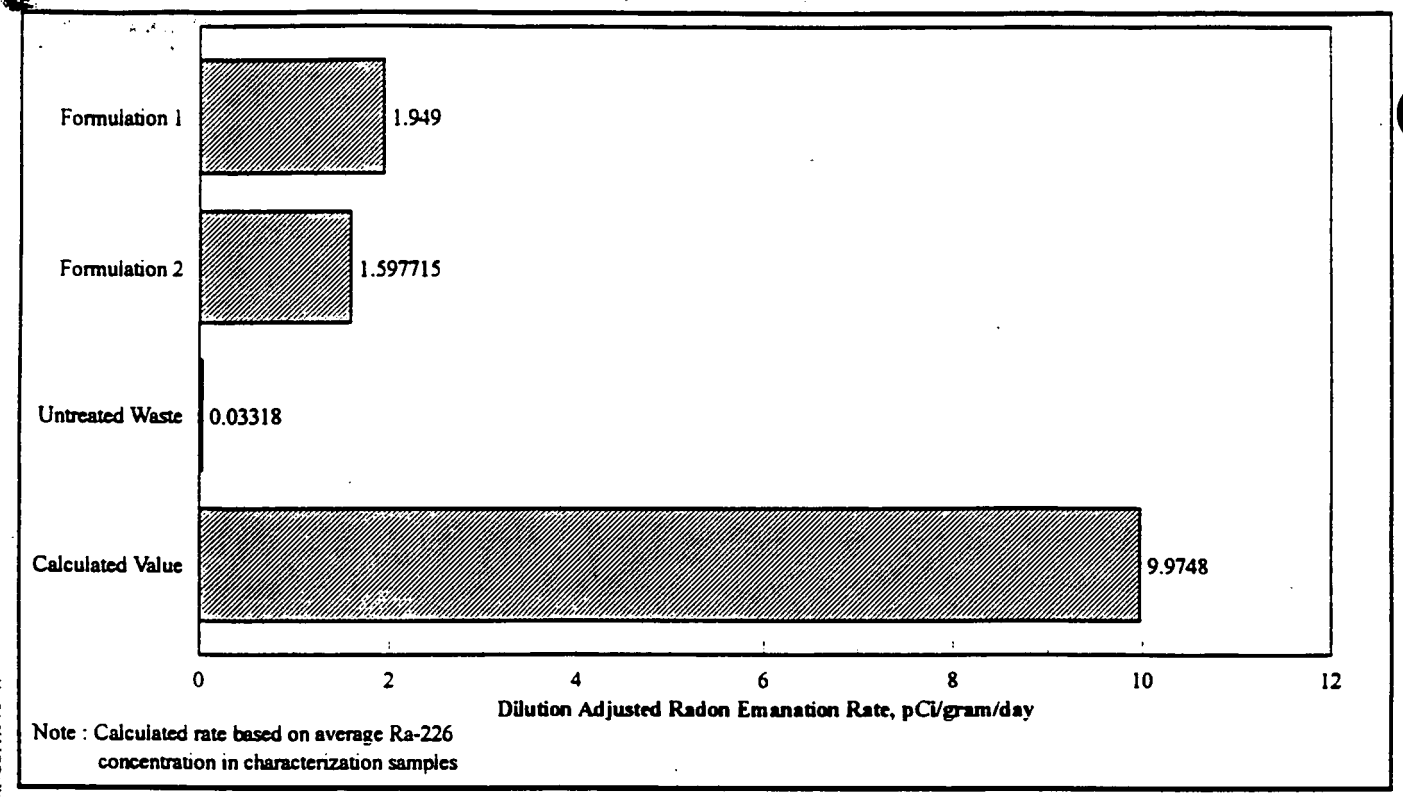
CLEARWELL - NORMALIZED LEACHATE RATES EXPRESSED AS A PERCENTAGE OF SAVANNAH RIVER HIGH LEVEL WASTE CRITERIA

Formulation	Zone	Al	Mg	Na	Si	U	Li	K	
		Percentages							
1	Composite	1	0.007	3	1	0.05	Not Calc'd	2	Not Calc'd
2	Composite	0.4	0	35	0.4	Not Calc'd	Not Calc'd	1	14

NOTE: Not Calc'd indicates a normalized leach rate was not calculated because the metal was not found in the glass.

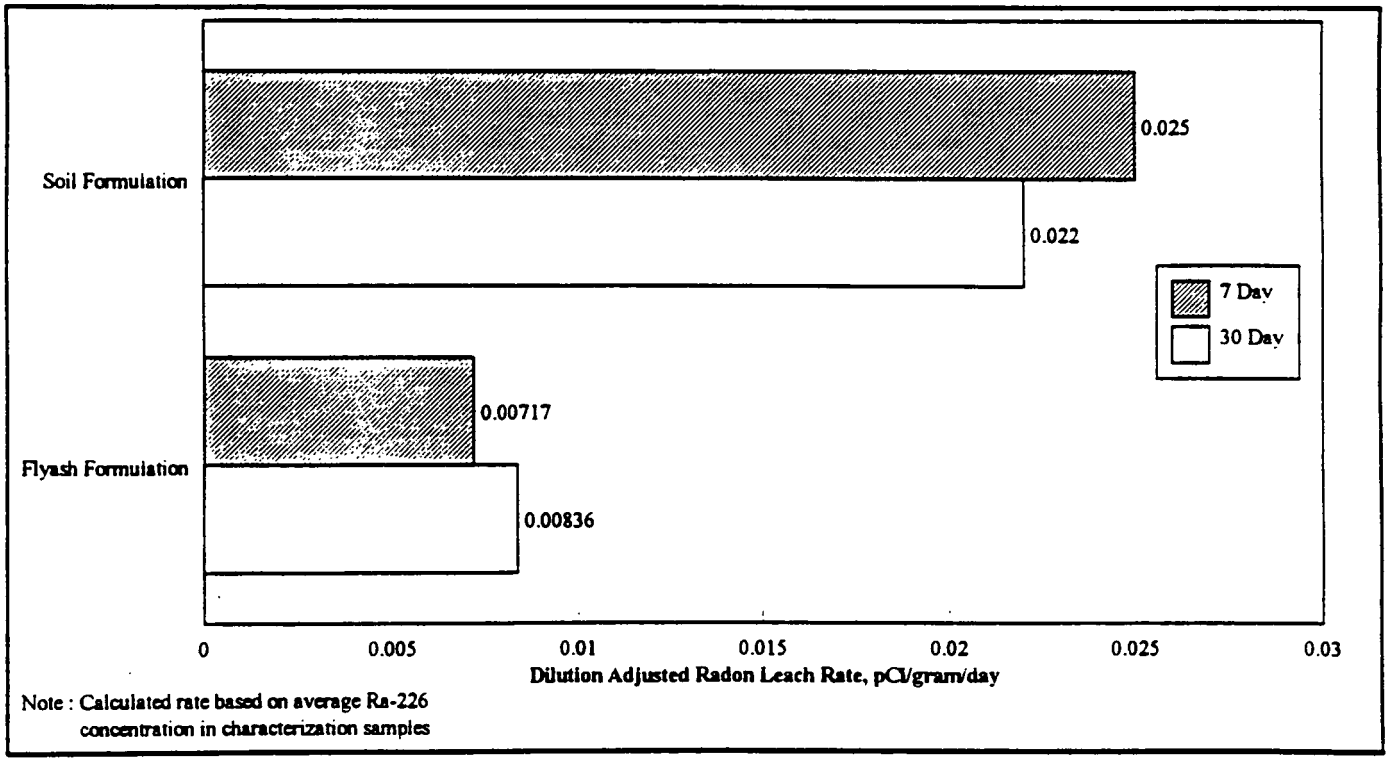
Clearwell Vitrification - Radon Emissions

Figures 4-24a and 4-24b show radon leach rates much lower than the calculated rate. The unusually high emanation rates for the treated waste (in comparison to raw and calculated rates) may be due to changes in the background. A background measurement was made every day before measurements were started. Any changes occurring during the day would have gone undetected. Also, the relatively low emanation rates from the untreated waste were probably due to the wet, clay-like nature of the waste that was tested. Such material would be expected to have extremely low porosity, reducing the ability of radon to diffuse through it.



FL/FEMP/OU1TR/48-7A

FIGURE 4-24a -CLEARWELL VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES



FL/FEMP/OU1TR/48-7B

FIGURE 4-24b -CLEARWELL VITRIFICATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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Comparison to Test Objectives

Performance objectives were established to demonstrate the technology was an effective solution for the treatment of the waste (proof of process), to develop data for various aspects of the FS, to develop preliminary process parameters for use in later treatability studies, and to develop a database between treatment variables and process results. All of the performance objectives established in the treatability study work plan were met through the course of the testing program.

Summary

A glass product was formed for each waste pit which was reduced in volume. All formulations passed the TC regulatory criteria in the TCLP leachate. Although not all waste samples passed the PCT, the results indicated further testing could develop an acceptable formulation.

In the CTS Duratek/CVA studies the glass formulas are designed to have process viscosities at 1200 °C or lower. Vitrification equipment can be made of less costly materials with significantly less maintenance cost if the melt temperature is 1200 °C or lower. The Remedy Screening/Remedy Treatability Selection Studies crucible melts were performed between 1250 °C and 1400 °C. These higher temperatures resulted in the erosion of even platinum crucibles. No erosion problems have been noticed during the GTS Duratek/CVA and the ongoing Minimum Additive Waste Stabilization (MAWS) studies. No noticeable erosion was noticed in the GTS Dunatek melter even after 1000+ hours of operation with actual and simulated high-fluoride Pit 5 wastes.

The Pit Wastes contain high percentages of fluoride as magnesium fluoride. Historically, commercial glasses have been made with fluoride concentrations up to three or five percent. The MAWS studies have found a new level of fluoride stability in making fluoride glass with concentrations between 18 and 22 percent. These glasses are durable and meet the TCLP and PCT tests. They approach the durability of Savannah River highly-radioactive glasses.

To provide a fluoride glass process, some design obstacles had to be overcome. These were:

- Fluoride Off-Gasing. During the initial mini-melter runs, it was discovered that the glass melts emit hydrogen fluoride. This was important for two reasons:

  - The glass formulas depends on the fluoride as a flux. If too much fluoride evaporates from the melt the glass becomes too viscous (thick) and the conductivity decreases. The amount of fluoride that evaporates can be significant. The amount lost is a function of time and temperature. The loss increased with time and higher temperatures. Up to 1/3 of the fluoride in the melt was lost. The mechanism for losing the fluoride is thought to be that the fluoride chemically combines with silica to form silicon tetrafluoride (SiF_4), which is a gas. Then this gas immediately reacts with moisture to form hydrogen fluoride, another gas.

  - The fluoride needs to be recovered. A fluoride recovery system was designed and installed with the MAWS melters. The recovery system uses sodium hydroxide which reacts with the hydrogen fluoride to produce sodium fluoride in a stainless steel reaction vessel. The hot air dries the sodium fluoride to a powder that falls to the bottom or collects on the sides of the vessel. A rotating blade scraps the remaining fluoride loss from the wall. The fluoride is pumped, as a slurry, back to the tanks that feed the melter.

- Fluoride Effect On Glass Viscosity and Conductivity. The once thought disadvantages of fluoride were turned into advantages. Fluoride significantly reduces the viscosity of glass. This has positive and negative aspects to it. The positive aspect is the lower viscosity means the glasses can be easily made at lower temperatures. The negative aspect is that the glass will leak in a conventual melter. This resulted in a special design of the MAWS melters to prevent leaks.

- Fluoride Effect on Glass Conductance. The fluoride also makes the glass more conductive. Adjustments to the standard melter design need to be made to melt highly conductive glasses efficiently.

Adjustments were made in the MAWS melter design to handle lower viscous and higher conductive glasses. Additions to the off-gas system made the vitrification process more robust and capable of processing a wider range of wastes besides fluoride.

Additives used in the MAWS glass development include sodium oxide (from sodium carbonate), calcium oxide (from calcium carbonate), boron oxide (from borax and/or boric acid), and sodium fluoride. The sodium fluoride comes from the reaction of hydrogen fluoride in the off-gas with

sodium hydroxide (see the above paragraphs). Fluoride was added to crucible melts and surrogate melter runs to maintain correct glass viscosity, conductance, and liquidus temperature[1]. The use of boron oxide, as a glass additive, helps to stabilize the glass, reduce the liquidus temperature (reduce crystallization), and increase waste loading.

Fernald site soils are not as good a source of silica (a glass former) as quartz sand. This is because the soils contain high concentrations of calcium (approximately 1/4 to 1/3 of the total dry weight as calcium carbonate). The calcium concentration forces the silica concentration to be lower. Also, the calcium in the soil is not needed because the Pit Wastes themselves generally have high concentrations of calcium. The calcium concentration usually ranges between 1/4 to 1/3 of the total dry weight.

Site soils could be used as a glass former for treatment of the Wastes Pits if the soils themselves need to be remediated. The best situation, if the site soils need to be treated, is to use soil washing. The soil washing in the MAWS program physically separates the contaminated soil into three size fractions -- fine, middle, and course. The middle fraction is high in silica, and therefore, can be sent to the melter without further treatment. The fines and course fractions may be leached to remove the contamination. Clean soils and contaminated residues are produced. The contaminated residues may be sent to the melter and the clean soils are released. The middle fraction and the contaminated residues are called the "soil concentrates." The soil concentrates were used in determining the glass formulas in the MAWS program. The soil concentrates give higher waste loadings than the site soils themselves.

Cooling glass quickly through the liquidus temperature was found to increase the waste loading in some cases. Cooling glass slowly, like letting a crucible cool naturally in the lab, can cause the glass to devitrify. Such glass melts can (1) take on a granite, powdery, crystalline, fractured appearance; (2) change color; and/or (3) form particulate or crystals in the glass. These may or may not affect the leachability of the glass. Forming the glass into frit (formed by pouring molten glass into water), marbles, or gems, can quickly cool the glass below the liquidus temperature. This can increase waste

[1]The liquidus temperature is the temperature at which the glass will crystalize if maintained at this temperature for prolonged periods of time.

loading above solid pours even when factoring in the void space between the glass pieces. Frit has a void fraction of about 50 percent; marbles have a void fraction of about 65 percent; and gems have a void fraction of about 20 percent. The MAWS program is using gems as its waste form. The MAWS program is developing methods and equipment for efficient production of gems.

Some crucible melts and melter runs by GTS Duratek /CVA characterized the melt viscosity and electrical conductivity as functions of temperature, leach resistance (by the TCLP and PCT procedures), crystallization behavior and liquidus temperature, chemical composition, waste loadings, and volume reduction.

Most large-scale development activities were done on Pit 5, but crucible studies also show that the glass formulations for the other pit sludges exhibit:

- High Leach Resistance, Treatment Effectiveness - the glasses pass the TCLP test and show very good performance in comparison with high-level waste glasses on the PCT test.

- Acceptable melt viscosity and electrical conductivity - the behavior of these properties with temperature makes these wastes suitable for processing in joule-heated melter vitrification system operating at temperatures around 1150 °C.

- Acceptable liquidus temperatures - overall phase stability imposed a major constraint on the formulation of high-waste loading compositions. However, a composition range was identified with sufficiently low liquidus temperature for processing at 1150 °C.

- Contaminants are contained by the process - Approximately 99.9 wt percent of the uranium and thorium was contained within the glass before recycle of the off-gas system's scrubber sludge (i.e., volatilization of UF_6 is not a problem). Heavy metals and radionuclides are efficiently retained within the glass melt. The process off-gas passed/met air emission requirements/standards.

- Fluoride problems were overcome - Fluoride was captured in the off-gas system and recycled into the feed batch. Fluoride emissions were below regulatory levels.

- High waste loading - Pit 5 sludges were processed between 77 to 88 wt percent continuously in melters.

- High volume reduction - Overall volume reduction calculations for Waste Pit 5 samples (counting all materials added to produce a vitrified blend, including soil and fly ash) yielded a volume reduction of about 80 percent. Volume reductions for GTS Dunatek/CVA studies with Waste Pit 3 and 4 were lower.

- Implementability - At the time of this report, the process has been successfully proven on the 100-kg/day system at The Catholic University of America in Washington D.C. The process performed better and produced a better glass with actual Pit 5 wastes than it did with surrogate wastes. The 300-kg/day system has produced surrogate glass gems, but the system has not yet operated at full capacity with actual FEMP wastes.

One of the tasks of the MAWS program is to determine the economics of vitrification as is applicable to processing/treating low-level and hazardous wastes on a large scale. Vitrification of large vilumes of low-level radiactive waste has never been demonstrated before. Life-cycle cost studies will be done after operating the MAWS facilities continuously, mass and energy balances are made, and operational and personnel costs are determined. These costs will be calculated for the actual operation of the MAWS and system extrapolated to a full-scale facility to determine the economic viability of large-scale waste vitrification.

4.1.2.2 Cement Solidification

Remedy Screening and Remedy Selection Studies

The overall objective of this portion of the treatability testing program was to develop data to assess the performance of cement solidification/stabilization (CSS) of Operable Unit 1 wastes. For cement solidification, the Operable Unit 1 Work Plan (DOE 1991) identified four response variables -- leachability, UCS, permeability, and bulking factor -- as the primary criteria for evaluating the performance of the various cement solidification mixtures. These response variables for the various formulations were compared to performance objectives to determine if a particular reagent mixture produced an acceptable waste form.

The cement solidification program consisted of Remedy Screening (preliminary phase), and Remedy Selection (advanced phase) tests of waste from Waste Pits 1 through 6, Burn Pit, and Clearwell. The overall approach is described by Figure 4-25. The Remedy Screening study used composite samples. In the Remedy Selection phase, zone (top, middle, and bottom) samples were used for Waste Pits 1 through 4 and Burn Pit, and composite samples for Waste Pits 5, 6 and Clearwell. The work plan specified this approach so the advanced phase formulations would be based on preliminary phase results, giving a much higher probability of success. This section of the treatability study report describes the Remedy Screening and the Remedy Selection phase results for cement stabilization. The technical approach for the study is presented in Section 3.0. Results for each pit material are presented separately. The presentation is ordered from Waste Pits 1 through 6, Burn Pit, and Clearwell. Within each waste area, the effect of stabilization reagents on the UCS, leachability (as defined by the MTCLP results), and general processability is addressed.

Remedy Screening Approach

Remedy Screening was a range-finding phase that had lower quality assurance/quality control (QA/QC) requirements on the analysis of the treated waste. This enabled screening of a wider range of variables than was practical with the advanced phase analytical requirements. The effects various formulations had on the performance criteria (leachability and UCS) were determined in this phase. The objective of this phase was to develop effective formulations for testing in the advanced or

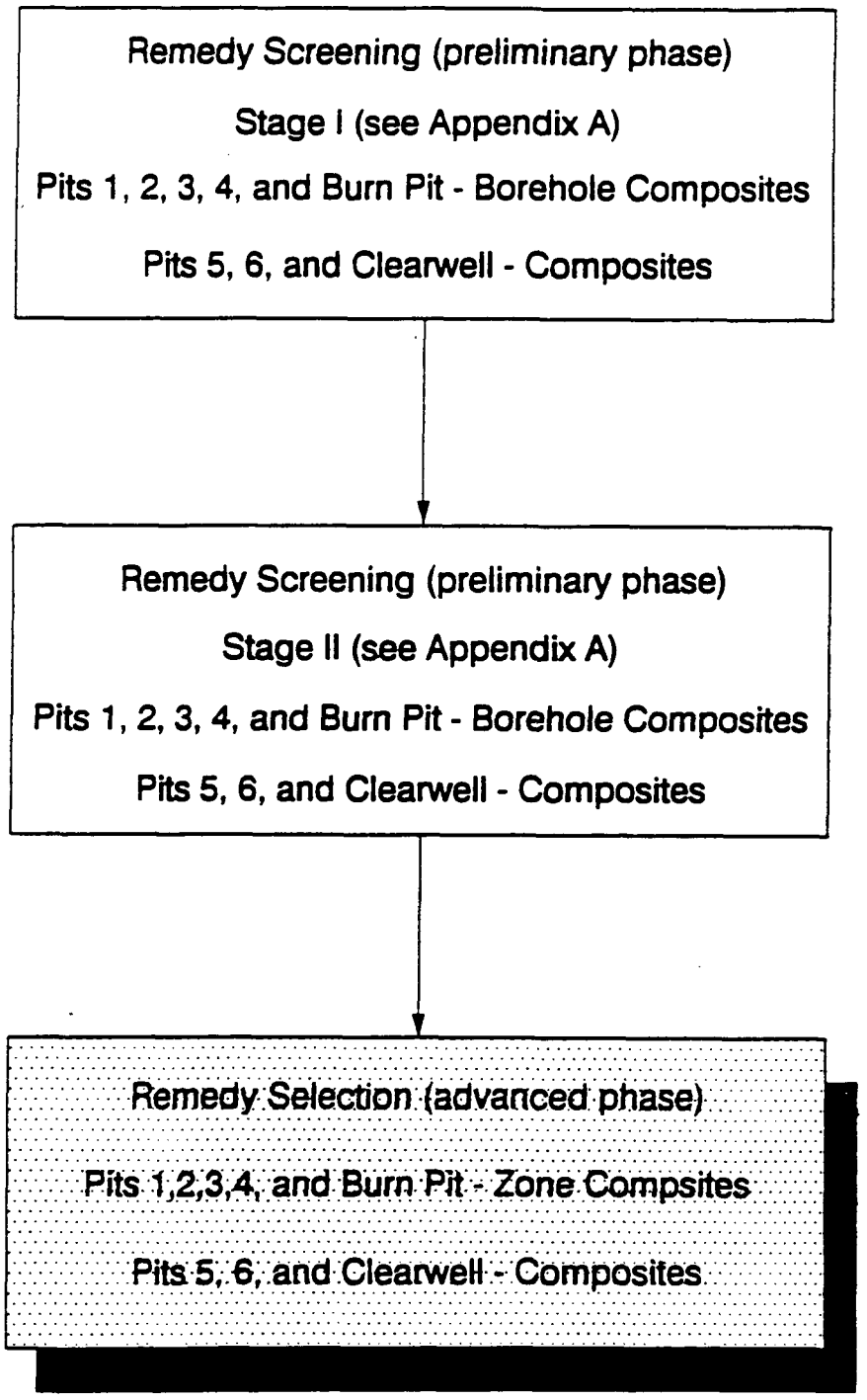

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FIGURE 4-25 STABILIZATION OF UNTREATED MATERIAL

confirmation phase. Binding agents considered were portland cement, flyash, blast furnace slag (BFS), and sodium silicate. Adsorbents (attapulgite and clinoptilolite) were added to reduce the leachability of metals in the waste. Various ratios of waste to reagents were tested to minimize the amount of reagents required to produce an acceptable stabilized waste form.

Remedy Screening experiments were statistically designed to yield trends of response variables (e.g., UCS values) as a function of the reagent loadings and to determine the envelope of reagents that would meet the performance criteria. The performance criteria for this preliminary phase study was for the 28-day cured treated sample to develop a UCS of at least 500 pounds per square inch (psi) and pass the toxicity characteristics (TC) regulatory requirements for metals in the modified Toxicity Characteristic Leaching Procedure (MTCLP) test. The initial stabilization reagent/wet paste needed a consistency that was readily mixable and which did not exhibit a significant temperature rise. This was accomplished by including a wide range of reagent loadings. The range of cement and flyash loadings varied from 26 to 68 percent expressed as weight of reagent divided by wet weight of waste (w/w). The adsorbents (attapulgite and clinoptilolite) and set/strength accelerator (sodium silicate) percentages ranged from 0 to 12 and 0 to 7 (w/w) percent, respectively. The Remedy Screening phase was performed in two stages. BFS was used in Stage II experiments to enhance strength potential, lower permeability, provide silicates for metal retention, increase resistance to sulfate and chlorides, improve workability, and lower the rate of set.

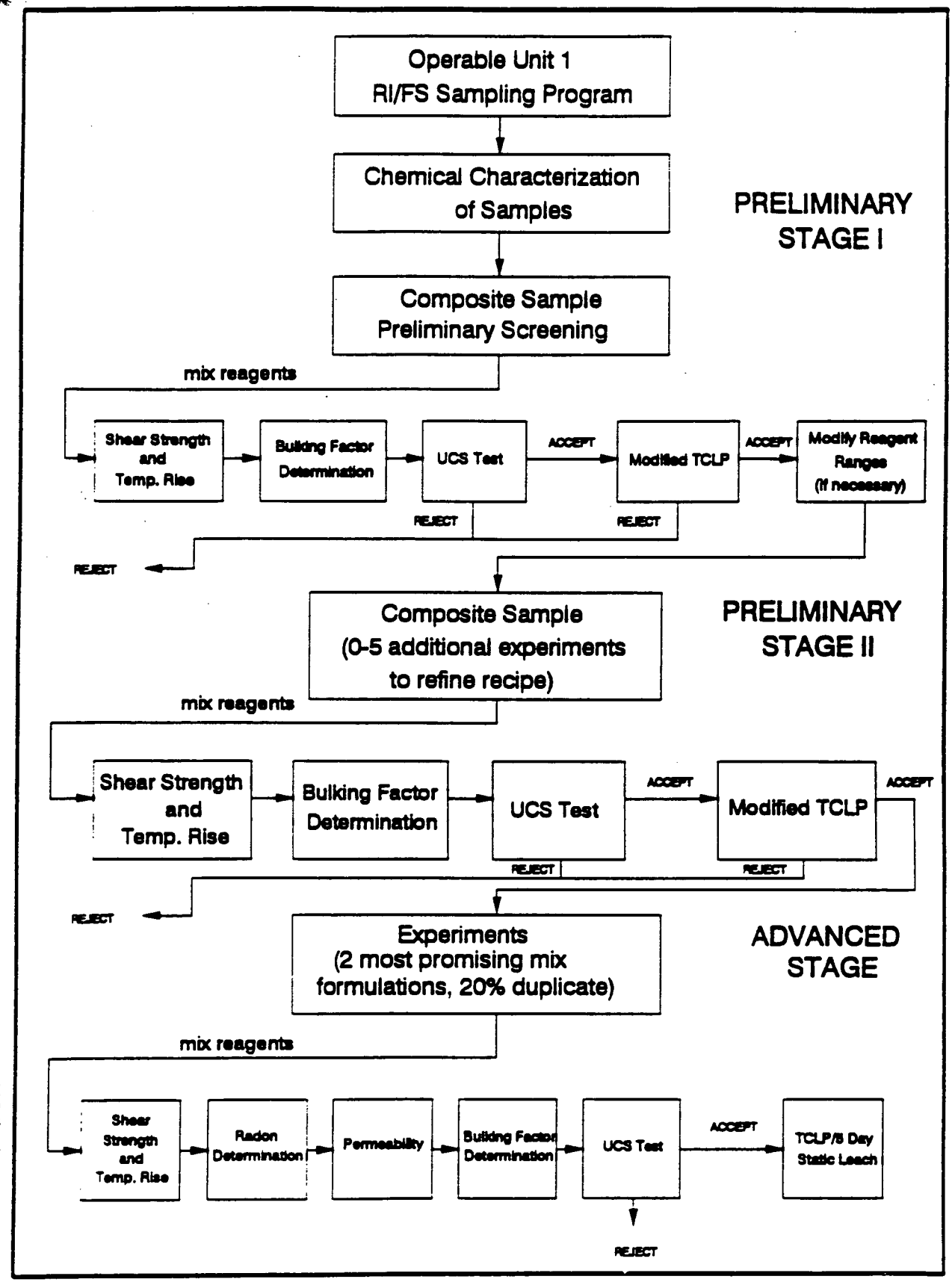
The solidification additives, water, and Operable Unit 1 waste were mixed and set in plastic molds. Small plastic molds, 1.38 inches in diameter by 2.75 inches long, were used during this phase to minimize waste generation and sample usage. Portions of the mix were also set in plastic specimen cups. The penetration resistance (PR) of this material, as measured with a pocket penetrometer, was used to monitor the curing of the sample and the relative rate of set. If the treated material did not achieve at least 3.0 tons per square foot (tsf) within a 24-hour cure time, the formulation was considered not easily processable. After the samples cured, the molds were cut from the samples and UCS was measured. The samples were then ground and extracted to determine the leachable metal concentrations by using the MTCLP procedure. The MTCLP procedure was identical to the Toxicity Characteristic Leaching Procedure (TCLP) extraction except that only 2.5 to 10 g of sample was

extracted. This screening analysis required less labor and sample than the TCLP. Bulk density and BF were determined and indicated the increase or reduction in volume due to the addition of stabilization additives.

Figure 4-26 is a flow diagram for the test procedure. A summary of the cement stabilization procedures follows:

- For the preliminary phase tests, transfer approximately a 100-g aliquot of OU1 waste to a beaker. For the advanced phase, transfer a 300-g aliquot to a planetary mixer.
- Add the correct proportions of stabilization additives and water to the beaker and mix with a spatula until a consistent paste is produced. The mixing time is typically 2 to 5 minutes. Add sufficient water to form a stiff but plastic paste.
- Transfer approximately 50 g of the paste to a 120 ml specimen cup and qualitatively determine the shear strength, using a Torvane shear device, and temperature rise of the mixture in the cup. Tap the paste down to a flat surface and determine the PR of the freshly produced paste using a pocket penetrometer. Cap the specimen cup for latter PR measurements.
- Transfer enough material to fill the mold to a third of its volume. Using a vibrating table, vibrate the paste in the mold for about 2 minutes. Repeat the transfer to mold and vibrating step two more times to fill the mold. Cap the mold.
- Using the sample in the specimen cup, determine the PR after curing times of 3, 7, 14, and 28 days. If the PR exceeded 4.5 tsf on a given day, the subsequent measurements would be omitted.
- After the 28-day cure time, cut the plastic mold from the sample and determine the UCS of the samples. Calculate the bulk density and BF for the molded sample.
- Crush the material from the UCS test and submit for MTCLP or TCLP analysis.

In addition to leachability of metals, UCS, and rate of set, several measurements of preliminary stabilization process parameters were obtained. The temperature rise, shear strength, and pH of the stabilization mix were measured as the molds were set. A temperature rise of over 5 to 10° Celsius (C) during mixing of small batches indicated a reactive system that could potentially cause problems in a larger scale. These could include the potential for safety hazards from flashing of steam and



CEMENT STABILIZATION LABORATORY SCREENING FLOWCHART

exposure to hot waste. Excessive shear strength indicated a mixture may be difficult to handle in the mixing equipment of the full scale system. The desired consistency of the stabilization reagent/waste paste varies from that of "split pea soup" to "well-cooked oatmeal" (shear strength less than 1 tsf). Initial pH was a parameter that was monitored as a measure of the relative alkalinity of the initial mix.

The formulations used and the results from UCS, bulking factor (BF), and MTCLP are presented in tabular form in their respective sections. In these tables, the reagent loadings are normalized to grams of reagent added to each 100 g of wet weight of waste. The first column in each table is the formulation number assigned to each test. The formulation number was also used in subsequent tables and graphs as an identification of the formula. The data in these tables are sorted by ascending order of cement loading, flyash loading, and UCS values. Also included in the tables are the Stage I group numbers.

- Group 1 samples were statistically designed experiments that had attapulgite and clinoptilolite at 6 normalized percent.
- Group 2 samples were similar to Group 1 samples except site flyash was used instead of commercial flyash.
- Group 3 samples used attapulgite and clinoptilolite loadings at 0 or 12 normalized percent.
- Group 4 samples were also similar to Group 1 samples except that portland cement Type 1 was substituted for portland cement Type 2.
- Group 5 samples used only portland cement Type 2 at loadings of 60 and 80 normalized percent.

Remedy Screening Results

The Remedy Screening tests identified cement-based reagent mixtures, which (during the advanced phase program) produced UCSs of approximately 500 psi, minimal volume increases, and TCLP leachates meeting the TC regulatory limits. Summaries of results for the UCS, permeability, bulking factor, TCLP, 5-day static leach tests, and radon analysis of the treated waste, as well as a summary

comparison of test results with test objectives, are presented in this section for each waste pit. The TCLP results are compared with the characterization TCLP analyses of similar untreated waste.

The relative difficulty of solidifying each pit material and reducing the leachability of uranium from the treated material is illustrated by the data in Table 4-87. The table lists the percentage of formulations passing the UCS criteria and the maximum uranium concentration in the MTCLP extracts for the 20 formulations investigated in Stage I. Waste Pits 4, 5, 6, and the Clearwell had at least 50 percent of the formulations meet or exceed the UCS criteria. The materials from the remaining pits (Pits 1, 2, 3, and the Burn Pit) had less than 50 percent success rate. Materials from Waste Pit 2 and the Burn Pit were significantly more difficult to solidify than material from the other Operable Unit 1 waste areas. UCS results were a criteria for the selection of formulations for the Remedy Selection (advanced) phase.

The leachability, defined as the concentration measured in the MTCLP of uranium from the treated material, could be categorized into five general groups. The first group consisted of the Waste Pit 4 material, which contained lumps of yellow and green uranium salts and had 452 parts per million (ppm) leachable uranium in the MTCLP. The second group contained Waste Pit 6 material, with 18 ppm leachable uranium. The Burn Pit and Clearwell materials made up the third group, with leachable uranium concentrations of 6 and 3 ppm, respectively. The fourth group had leachable uranium concentrations from 0.9 to 1.0 ppm uranium. This group consisted of Waste Pits 1, 2, and 3. The final group was Pit 5, with a nondetectable level of uranium in the MTCLP. Uranium leachability results were a criteria for the selection of formulations for the remedy selection phase.

The concentration of Resource Conservation and Recovery Act (RCRA) metals in the MTCLP tests were all less than one-half the TC regulatory level. Therefore, in this study, the concentration of RCRA metals in MTCLP was not a selection criteria for determining formulations to investigate in the Remedy Selection phase of the project.

TABLE 4-87

GENERAL COMPARISON
AT COMPLETION OF STAGE I

Area	Formulations Passing UCS (%)	Uranium Maximum (ppm)
Pit 1	40	1.0
Pit 2	15	1.0
Pit 3	35	0.9
Pit 4	50	452
Pit 5	60	ND
Pit 6	75	18
Burn Pit	0	6
Clearwell	80	3

Remedy Selection Approach

The Remedy Selection study was a confirmation phase where the UCS analysis was conducted in duplicate (at a frequency of one to five) and the TCLP analyses were conducted at a certified analytical laboratory. In this advanced phase, the stabilized waste was set in larger molds (2 inch diameter by 4 inch long) than the preliminary phase. Duplicate molds for each sample were set at a frequency of one in five formulations. The optimum formulations identified in the preliminary phase were used in the advanced phase. The advanced phase treated samples were sent to IT Analytical Services (ITAS) for TCLP analysis after the 28-day cure. ITAS used the Contract Laboratory Program (CLP) protocol during the TCLP analyses. The operating procedures for stabilization testing are provided in Appendices B and C of the Operable Unit 1 Treatability Test Work Plan (DOE 1991) and in Appendix A. The principal steps in this procedure are similar for the preliminary and advanced phases.

The formulations used for the Remedy Selection are presented in Table 4-88. The amount of reagent added to each 100 g of combined wet weight of waste are in grams. Portland cement, blast furnace slag, flyash, and clinoptilolite were added to solidify the waste.

Leachability

The data from these analyses are presented in the tables in this section, for dilution adjusted formulation leachate concentrations, leach rates for specific analytes or as leachate concentrations relative to regulatory limits.

Bulking Factor

Bulking factor is the percent increase in volume due to treatment.

Permeability Testing

There was no defined goal for permeability in the Work Plan. However, EPA's document, *Handbook for Cement Stabilization/Solidification of Hazardous Waste*, states that "Permeabilities measured in solidified waste typically range from around 10^{-4} to 10^{-8} cm/s. Such low permeabilities indicate decreased mobility in the treated waste and a slower transfer of contaminants from the solid mass to

TABLE 4-88

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
FOR FERNALD OPERABLE UNIT 1

Pit	Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	1	100	50	15	25	-	30-43
1	2	100	51	31	-	-	29-40
2	1	100	53	15	25	-	24-42
2	2	100	51	31	-	-	15-41
3	1	100	51	15	25	-	22-31
3	2	100	51	31	-	4	18-32
4	1	100	51	31	-	4	34-59
4	2	100	80	-	-	6	33-61
5	1	100	51	15	25	-	-
5	2	100	51	30	25	-	0-4
6	1	100	53	15	25	-	64
6	2	100	43	43	-	-	2
Burn	1	100	51	15	31	-	44-69
Burn	2	100	54	33	-	4-6	42-63
Clearwell	1	100	15	-	15	-	20
Clearwell	2	100	26	-	-	-	20-22

Note: All quantities are normalized to express quantities of reagent used per 100 grams of waste. Waste was not dried before mixing.

leaching waters" (EPA 1990b). Given these low permeabilities, the dominant flow of water should be around the treated material instead of through the material.

Radon Emissions

All radon results were multiplied by the reagent dilution factor so all results were expresses relative to the amount of pit waste in the stabilized sample. The results were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. The calculated radon emission rate given for comparison was based on the average radium (Ra)-226 concentration found in characterization samples. Each pCi of RA-226 generates radon (Rn)-222 at a rate of 0.1813 pCi per day.

Durability Testing

Preliminary studies produced CSS formulations capable of satisfying preliminary test requirements. Subsequently, specimens were produced using two different formulations for each of the seven waste pits (Pits 1-6, Burn Pit, and the Clearwell). As an indicator of durability of these mix designs, the specimens were tested according to the requirements of ASTM 4842-90, "Standard Test Method for Determining the Resistance of Solid Wastes to Freezing and Thawing", and ASTM 4843-88, "Standard Test Method for Wetting and Drying Test of Solid Waste". All waste pit durability results are presented at the end of this section.

Summaries of the initial waste and TCLP characterization data for each pit are located in their respective appendices (C-J). A complete summary report on the preliminary phase of the cement stabilization testing (formulations, UCSs, leachability, and mixing information) is included in Appendix A. All data in Appendix A is stored in Clipper® database files, which are included in Appendices C through J. Waste Pits 1 through 6, Burn Pit, and Clearwell are in individual appendices. Each of the respective appendices includes a list of CPCs, cement stabilization and vitrification TCLP data (characterization and treatability) in laboratory format with qualifiers and in reduced form (SAS format), TCLP percent reduction tables, 5-day static leach test results, and respective Clipper files.

WASTE PIT 1

Remedy Screening Tests

The formulations investigated, UCS, BF, and MTCLP radiological results from the preliminary phase are presented in Tables 4-89 and 4-90. The formulation numbers in the tables are in order of increasing cement loading, fly ash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and in Appendix A are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 150 psi to greater than 650 psi; the values are graphically presented in Figure 4-27. The formulation numbers in the figure correspond to Table 4-89. A horizontal line is added to Figure 4-27 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbents, attapulgite and clinoptilolite, and formulations with activated BFS addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 13 (43 percent cement), 3 (29 percent cement), and 14 (50 percent cement), respectively.

General observation and trends noted for UCS follow:

- Analysis of statistical trends shows that with adsorbents added to the waste, the UCS generally increases with cement loading and that at least 43 percent cement was necessary to meet the UCS requirement.
- Addition of adsorbents lowered the UCS for a given cement loading.
- Addition of BFS increased the UCS and slightly increased the temperature rise of the wet paste for a given cement loading.
- Portland Type 1 and 2 cements had similar results.
- Commercial and site flyash had similar results.

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Table 4-89

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 1 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	6	6	50	0	1	1	164	180
2	100	27	20	7	6	6	50	0	1	1	223	191
3	100	29	29	0	0	0	34	0	3	1	547	137
4	100	33	54	7	6	6	65	0	1	1	205	275
5	100	33	54	0	6	6	58	0	1	1	309	245
6	100	43	43	4	12	0	68	0	3	1	304	272
7	100	43	43	4	0	12	68	0	3	1	334	255
8	100	43	43	4	6	6	64	0	4	1	396	252
9	100	43	43	0	6	6	63	0	4	1	485	244
10	100	43	43	4	6	6	55	0	1	1	395	238
11	100	43	43[c]	4	6	6	54	0	2	1	425	246
12	100	43	42[c]	0	6	6	54	0	2	1	386	226
13	100	43	43	0	0	0	50	0	4	1	580	196
14	100	50	15	0	0	0	47	25	_	2	580	195
15	100	50	40	0	0	0	52	0	_	2	509	217
16	100	51	31	0	6	6	53	0	1	1	520	220
17	100	51	31	0	0	0	44	0	_	2	580	185
18	100	54	33	8	6	6	66	0	1	1	580	266
19	100	60	0	0	0	0	37	0	5	1	580	140

0426

Table 4-89
(Continued)

PIT 1 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
20	100	60	60	0	6	6	70	0	1	1	580	300
21	100	64	64	0	0	0	65	0	3	1	580	264
22	100	69	68	7	6	6	76	0	1	1	580	337
23	100	80	0	0	0	0	47	0	5	1	580	168

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

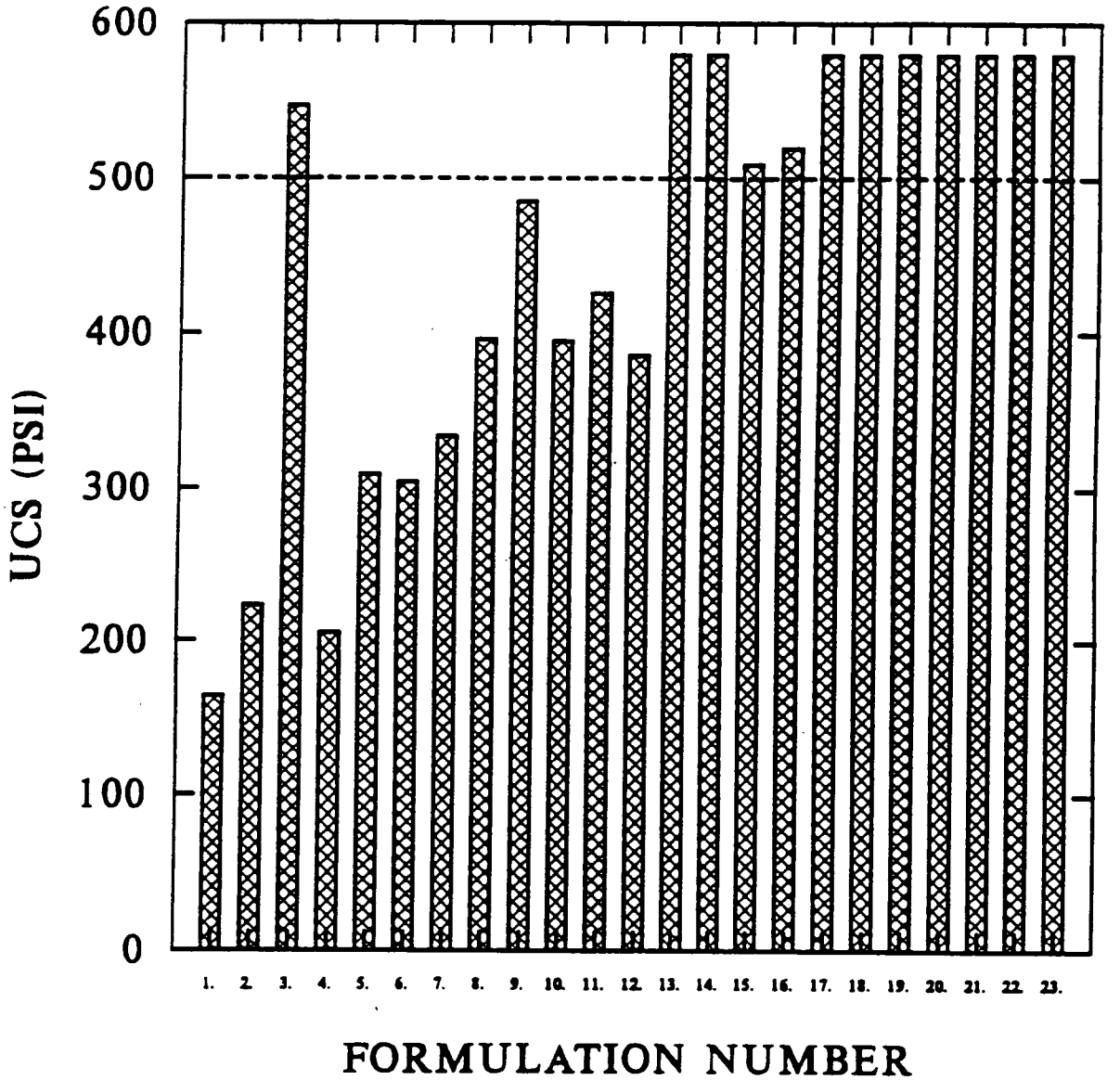
TABLE 4-90

FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 1 - REMEDY SCREENING (PRELIMINARY PHASE) CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	LLD	LLD	ND	9.5
2	LLD	LLD	0.21	9.1
3	LLD	LLD	ND	9.7
4	LLD	LLD	ND	11.4
5	LLD	LLD	ND	9.2
6	LLD	LLD	ND	10.3
7	LLD	LLD	ND	9.8
8	LLD	LLD	0.9761	5.7
9	LLD	LLD	ND	9.5
10	LLD	LLD	ND	9.6
11	LLD	LLD	ND	11.4
12	LLD	LLD	ND	11.7
13	LLD	LLD	ND	11.1
14	LLD	LLD	ND	10.12
15	LLD	LLD	ND	11.07
16	LLD	LLD	ND	9.7
17	LLD	LLD	ND	11.42
18	LLD	LLD	ND	10.5
19	LLD	LLD	ND	11.9
20	LLD	LLD	ND	10.2
21	LLD	LLD	ND	11.5
22	LLD	LLD	0.0265	10.2
23	LLD	LLD	ND	12.1

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level



BAR GRAPH
UCS VS. FORMULATION NUMBER
PIT 1. STAGES I & II

0429

Figure 4-27

- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash were investigated. Sixty percent cement loading without addition of other reagents successfully stabilized the waste.

Bulking Factor (BF)

The BFs for Waste Pit 1 samples are listed in Table 4-89 and graphically presented (bar graph) in Figure 4-28. The data are ordered by formulation number. The BFs range from approximately 140 to 340 percent for the formulations investigated.

The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Pit 1 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the Remedy Selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclide leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-90 for these values. The gross alpha and beta numbers were all below the limits of detection. The uranium concentration was below .1 ppm (w/w) for all treated samples. In most cases, its concentration was below the detection limit.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.5, all uranium values were below detection limits.

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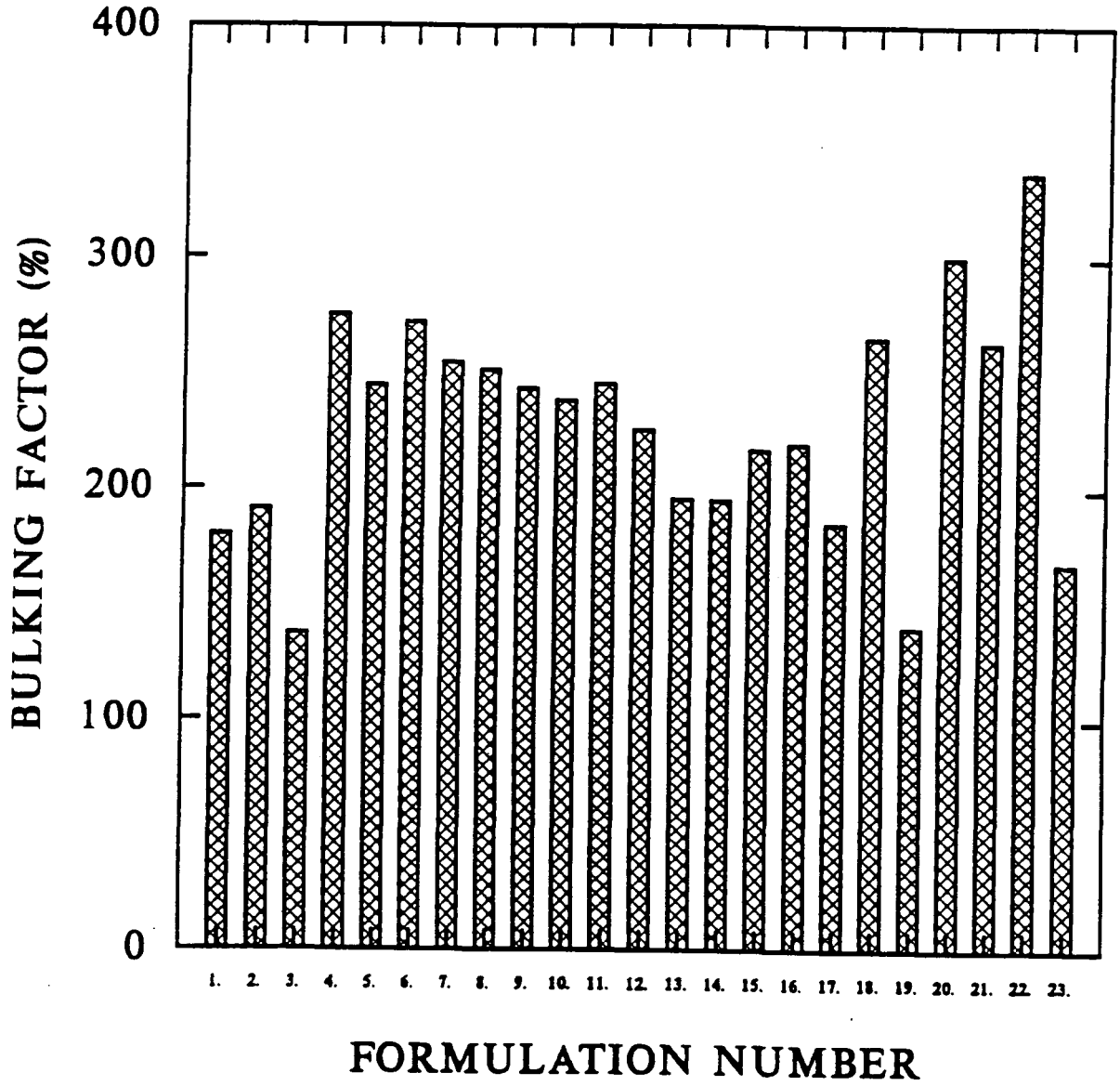

BAR GRAPH

B.F. VS. FORMULATION NUMBER

PIT 1, STAGES I & II

0431

Figure 4-28

The uranium concentration in the MTCLP of similar untreated waste was 27 ppm. Therefore, the treatment would appear to significantly reduce the leachability of uranium.

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As noted above, the site and commercial flyash also had similar effects on the UCS results. Thus, site flyash could be considered for stabilizing the waste in Waste Pit 1 instead of buying commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). The formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, lowered the UCS, and had minimal effect on leachability. The effects of sodium silicate additions were ambiguous. Since the addition of these three reagents had minimal positive effects, it is recommended that the three additives not be used with Waste Pit 1 material.

Recommended Formulations for Remedy Selection (ADVANCED PHASE)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Table 4-89 and 4-90. Analysis of the results indicates that stabilization of the Waste Pit 1 waste can readily achieve the desired UCS and leachability values. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within a 24-hour cure time.

The UCS values, uranium leachability, and BFs were the deciding criteria for selecting the formulations for the Remedy Selection (advanced phase) studies. The formulations had to exceed the

500 psi UCS criteria, have uranium concentrations in the MTCLP at nondetectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without adsorbent addition, which met the above requirements, were selected. Formulation numbers 14 (cement, flyash, and BFS) and 17 (cement and flyash) were chosen from the formulations presented in Table 4-89.

Remedy Selection Tests

The formulations used on each zone in the advanced phase experiments are given in Tables 4-91. Table 4-92 summarizes the UCSs, bulking factors, and permeabilities. All of the UCS results were well above the minimum desired value of 500 psi. The UCS values ranged from 1458 to greater than 3100 psi. The bulking factors (percent volume increase due to treatment) for both formulations were very close, ranging from 152 to 168 percent. Permeabilities were very low, ranging from 2.0×10^{-11} to 3.8×10^{-9} centimeters per second (cm/s). With one exception Formulation 1 had lower permeabilities than Formulation 2.

Dilution adjusted TCLP results for Waste Pit 1 TCLP radionuclides for the two formulations are shown in Table 4-93. Results for metals are shown in Table 4-94. Formulations 1 and 2 had similar leaching results for inorganic compounds.

The leachability of radionuclides for both Formula 1 and Formula 2 were nearly identical. U-235/236 had an ND for the Formula 2 dilution adjusted concentration, Ra-226, Ra-228, Sr-90, and Tc-99 had NDs as dilution adjusted concentrations for both formulations.

Waste Pit 1 Cement Solidification - Radon Emissions

All radon results in Figures 4-29 and 4-30 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in these figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. Figures 4-29 shows that Formulation 1 was more effective in reducing the rate at which radon diffuses from the treatability sample into water. The emanation in air (Figure 4-30) also showed Formulation 1 to have a lower radon emission rate than Formulation 2, although

TABLE 4-91

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 1
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	50	15	25	0	30-43
2	100	51	31	0	0	29-40

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

TABLE 4-92

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY - PIT 1
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
1	1	>3107	168	159	2.0×10^{-11}
1	1	>3150	168		
2	1	>3154	158		$<4.0 \times 10^{-11}$
2	1	3151	159		
2	1	>3133	164		$<6.2 \times 10^{-11}$
2	1	>3141	162		
3	1	>3167	158		1.0×10^{-9}
3	1	>3173	159		
1	2	1458	164		3.8×10^{-9}
1	2	1599	158		
2	2	2203	153		1.2×10^{-9}
2	2	2604	154		
3	2	3131	155		8.8×10^{-10}
3	2	2756	152		

TABLE 4-93

WASTE PIT 1 SOLIDIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	ND	ND	ND
Radium-226	83.500	ND	ND
Radium-228	27.300	ND	ND
Strontium-90	7.290	ND	ND
Technetium-99	35.350	ND	ND
Thorium-228	ND	ND	ND
Thorium-230	ND	ND	ND
Thorium-232	ND	ND	ND
Uranium-234	3990.000	11.230	14.030
Uranium-235/236	247.000	24.440	ND
Uranium-238	4910.000	32.660	8.810
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	ND	ND	ND
Uranium (Total)	7.380	0.110	0.030

* Dilution Adjusted Concentration -
The results for treatability samples were multiplied by a dilution factor, defined as the weight of a treated sample divided by the weight of the raw waste that went into the treated sample.

\+ TCLP results on similar raw waste samples provided for relative comparison purposes only. Results are from samples taken form the same borehole and same zone as treatability samples but are not identical.

TABLE 4-94

WASTE PIT 1 SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.055	ND	ND	
Arsenic	0.003	ND	ND	5.000
Barium	1.562	3.309	3.803	100.000
Beryllium	0.007	ND	ND	
Boron	ND	0.670	0.397	
Cadmium	0.008	ND	ND	1.000
Chromium	0.100	ND	0.164	5.000
Cobalt	0.022	ND	ND	
Copper	0.048	ND	0.022	
Cyanide	ND	ND	ND	
Lead	0.005	ND	ND	5.000
Manganese	0.213	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	0.027	ND	ND	
Nickel	0.121	ND	ND	
Selenium	0.002	ND	ND	1.000
Silver	0.080	ND	ND	5.000
Thallium	ND	ND	0.042	
Vanadium	0.048	ND	ND	
Zinc	0.086	0.103	0.096	

* See Table 4-93

\+ See Table 4-93

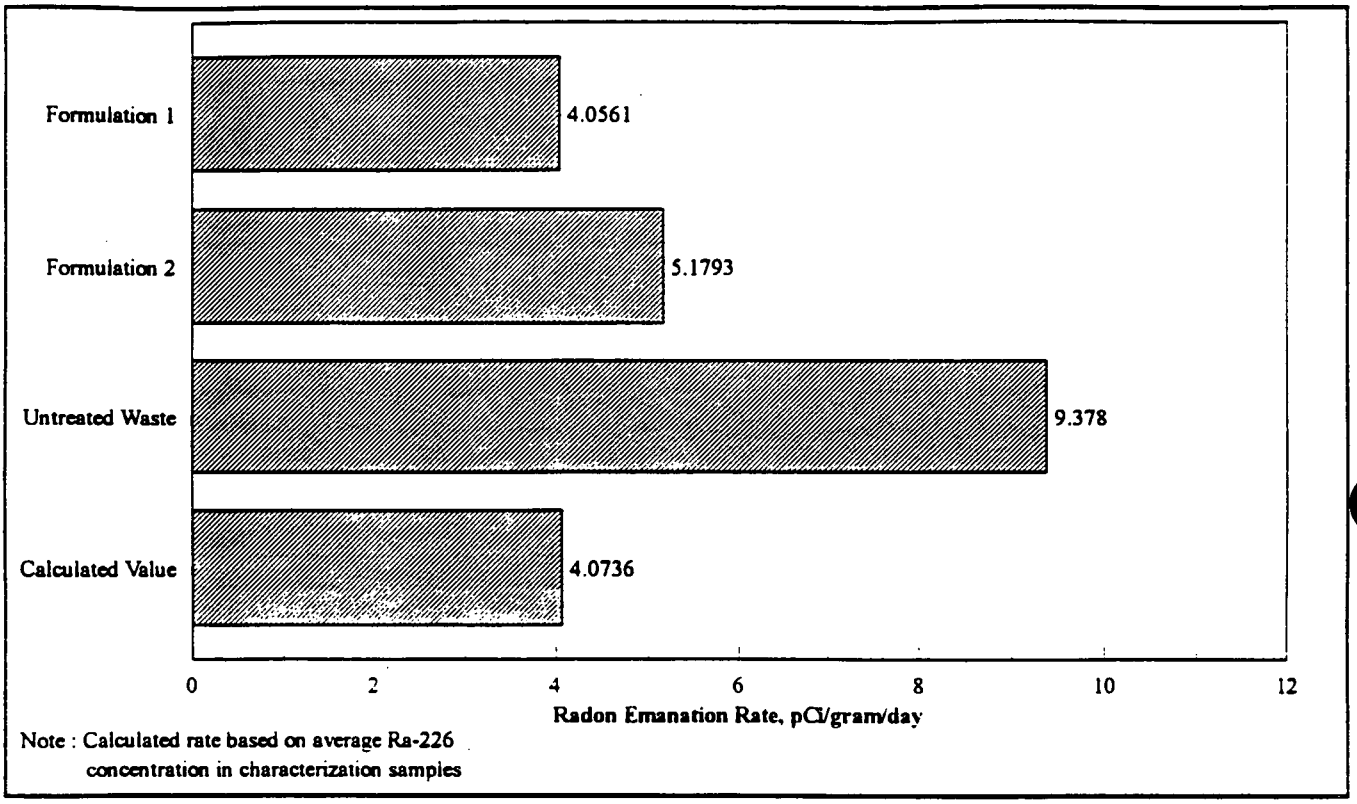

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FIGURE 4-29 -PIT 1 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

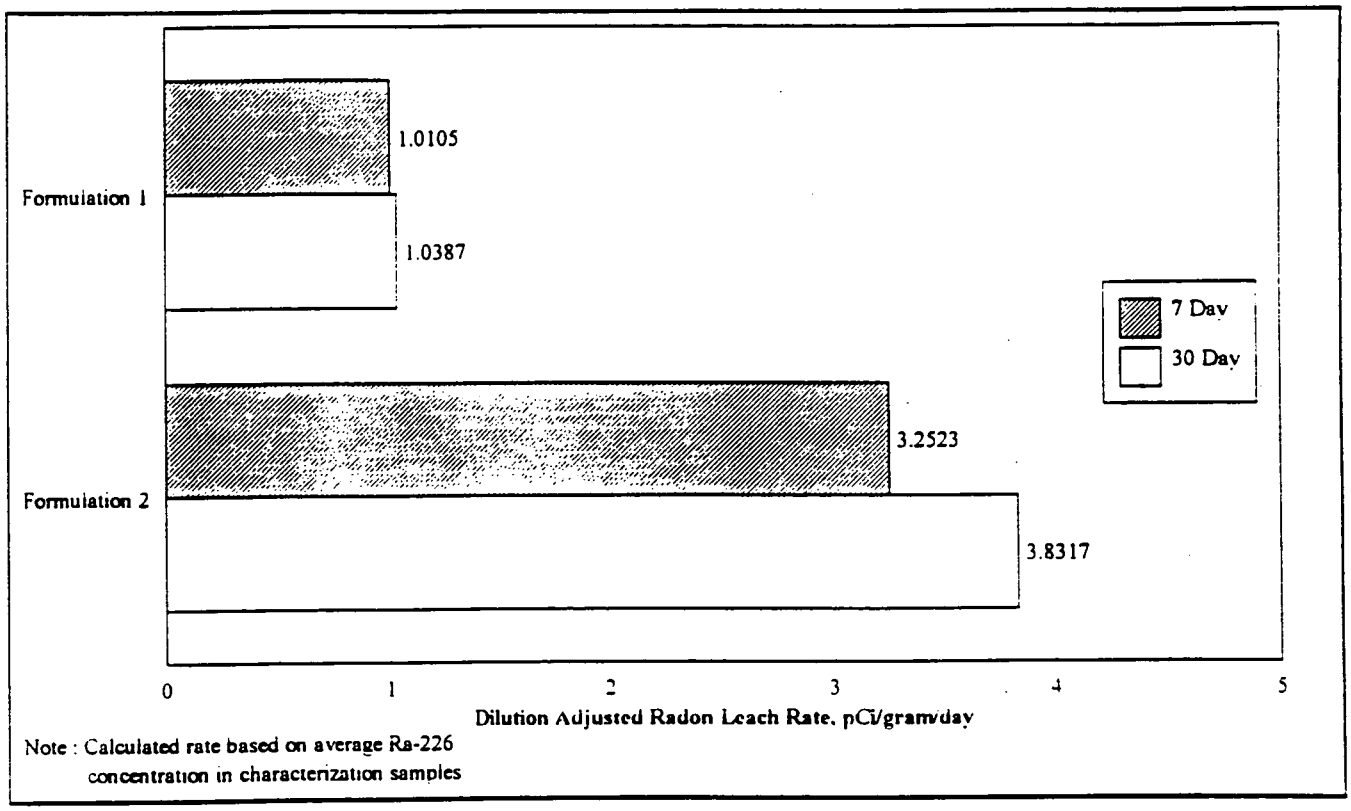

FIGURE 4-30 -PIT 1 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

the difference in rates did not appear to be significant. The emanation rate for untreated waste was approximately double that of the treated waste.

The calculated radon emission rate given for comparison in both figures was based on the average radium (Ra)-226 concentration found in characterization samples. Each pCi of Ra-226 generates radon (Rn)-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 22.47 pCi/g, with the concentrations ranging from 13.4 to 99.6 pCi/g. The relatively high emanation rates measured compared to the calculated rate probably indicate that the Ra-226 concentration in the treatability samples is higher than in the characterization samples.

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WASTE PIT 2

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are depicted in Tables 4-95 and 4-96. The formulation numbers in the tables are in order of increasing cement loading, fly ash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and in Appendix A are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 150 psi to greater than 710 psi; the values are graphically presented in Figure 4-31. The formulation numbers in the figure correspond to Table 4-95. A horizontal line is added to Figure A-10 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbent, attapulgite and clinoptilolite, and formulations with activated BFS addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 19 (54 percent cement), 14 (51 percent cement), and 16 (53 percent cement), respectively.

General observations and trends noted for UCS are listed below.

- Analyses of statistical trends show that with adsorbents added to waste, the UCS generally increases with cement loading and that at least 50 percent cement was necessary to meet the UCS requirement.
- Addition of adsorbents lowered the UCS for a given cement loading.
- Addition of BFS increased the UCS and slightly increased the temperature rise of the wet paste for a given cement loading.
- Portland Type 1 and 2 cements had similar results.
- Commercial and site flyash had similar results.

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 2 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	6	6	40	0	1	1	148	118
2	100	26	26	0	0	0	31	0	3	1	175	91
3	100	28	20	7	6	6	44	0	1	1	151	129
4	100	31	31	0	6	7	53	0	1	1	106	163
5	100	33	54	7	6	6	53	0	1	1	209	176
6	100	42	42	4	12	0	58	0	3	1	291	180
7	100	43	43	0	6	6	62	0	4	1	134	176
8	100	43	43[c]	4	6	6	53	0	2	1	210	179
9	100	43	43	4	0	12	52	0	3	1	399	166
10	100	44	43	0	0	0	49	0	4	1	210	147
11	100	44	43	5	7	6	55	0	1	1	218	173
12	100	44	43	5	6	6	60	0	4	1	246	183
13	100	44	43[c]	0	6	6	53	0	2	1	315	173
14	100	51	31	0	0	0	45	0	_	2	586	138
15	100	51	32	0	6	6	53	0	1	1	312	160
16	100	53	0	0	0	0	53	53	_	2	710	167
17	100	53	15	0	0	0	44	25	_	2	710	143
18	100	53	53	0	0	0	53	0	_	2	600	171
19	100	54	33	7	6	6	56	0	1	1	516	177
20	100	60	0	0	0	0	31	0	5	1	251	96

Table 4-95

Table 4-95 (Continued)

PIT 2 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
21	100	64	64	0	6	6	77	0	1	1	308	234
22	100	65	64	0	0	0	58	0	3	1	574	197
23	100	68	68	7	6	6	80	0	1	1	476	255
24	100	80	0	0	0	0	47	0	5	1	710	124

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

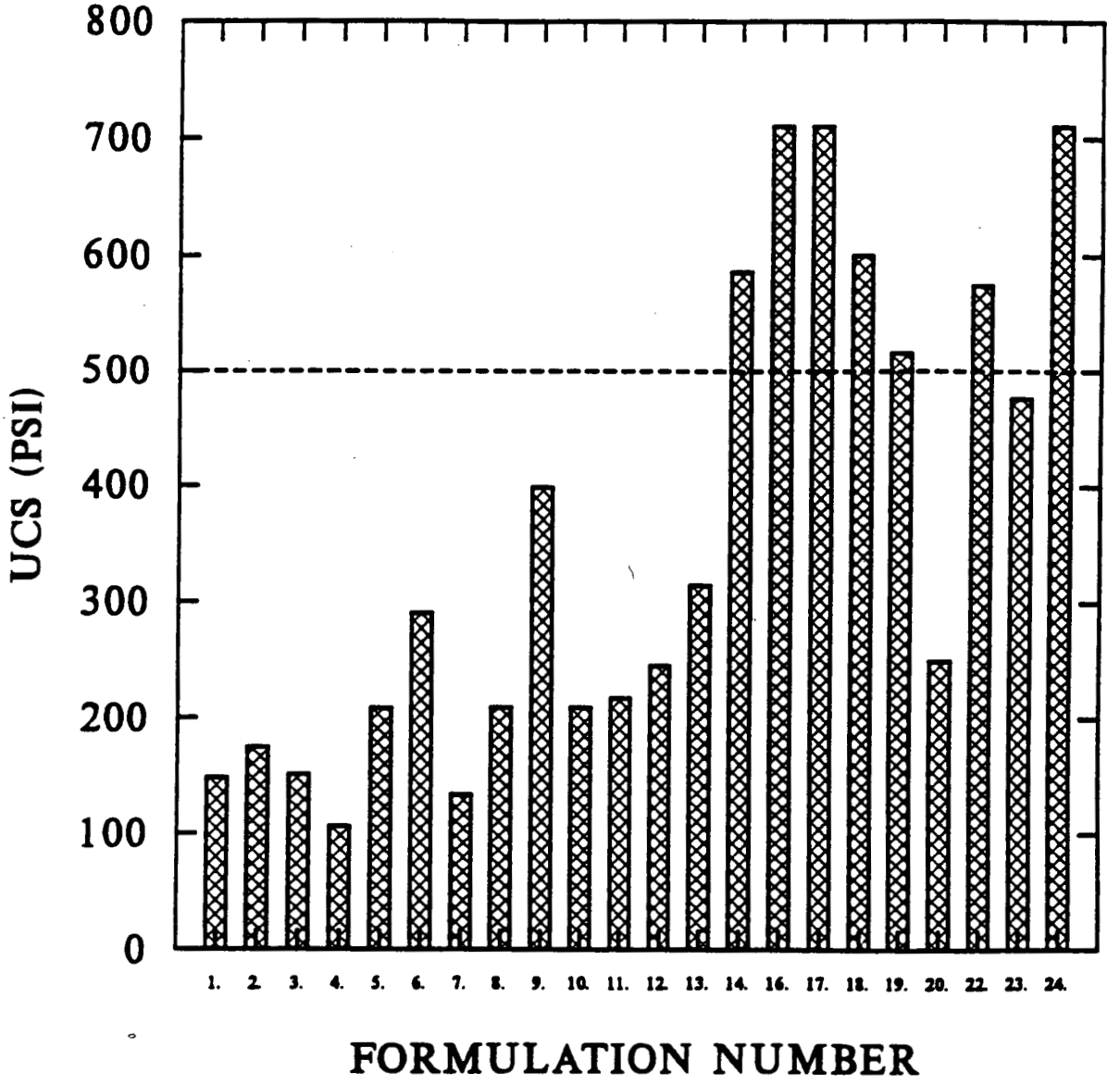
Table 4-96

FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 2 - REMEDY SCREENING (PRELIMINARY PHASE)
CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction (std. units)
1	LLD	LLD	0.3903	8.45
2	LLD	LLD	0.133	9.05
3	LLD	LLD	0.3505	8.15
4	LLD	LLD	0.3256	8.55
5	LLD	LLD	0.8803	7.65
6	LLD	LLD	ND	9.7
7	LLD	LLD	0.7016	7.45
8	LLD	LLD	ND	10.35
9	LLD	LLD	ND	9.75
10	LLD	LLD	1.0247	7.75
11	LLD	LLD	ND	9.95
12	LLD	LLD	ND	9.75
13	LLD	LLD	ND	10.35
14	LLD	LLD	ND	11.5
15	LLD	LLD	ND	11.35
16	LLD	LLD	ND	11.58
17	LLD	LLD	ND	11.57
18	LLD	LLD	ND	11.22
19	LLD	LLD	ND	10.82
20	LLD	LLD	0.0124	11.45
21	LLD	LLD	ND	11.25
22	LLD	LLD	0.0126	11.5
23	LLD	LLD	ND	10.85
24	LLD	LLD	ND	11.75

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected (detection limit ranged from 0.005 to 0.1 ppm (w/w)).
LLD - Under the lower limit detection level which ranged from 5 to 25 dpm/4cc.



BAR GRAPH
UCS VS. FORMULATION NUMBER
PIT 2, STAGES I & II

0446

Figure 4-31

- Without addition of adsorbents, BFS, or flyash, 80 percent cement loading was required to successfully stabilize the waste.

Bulking Factor(BF)

The BFs for Pit 2 samples are listed in Table 4-95 and graphically presented (bar graph) in Figure 4-32. The data are ordered by formulation number. The BFs range from approximately 90 to 250 percent for the formulations investigated.

The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

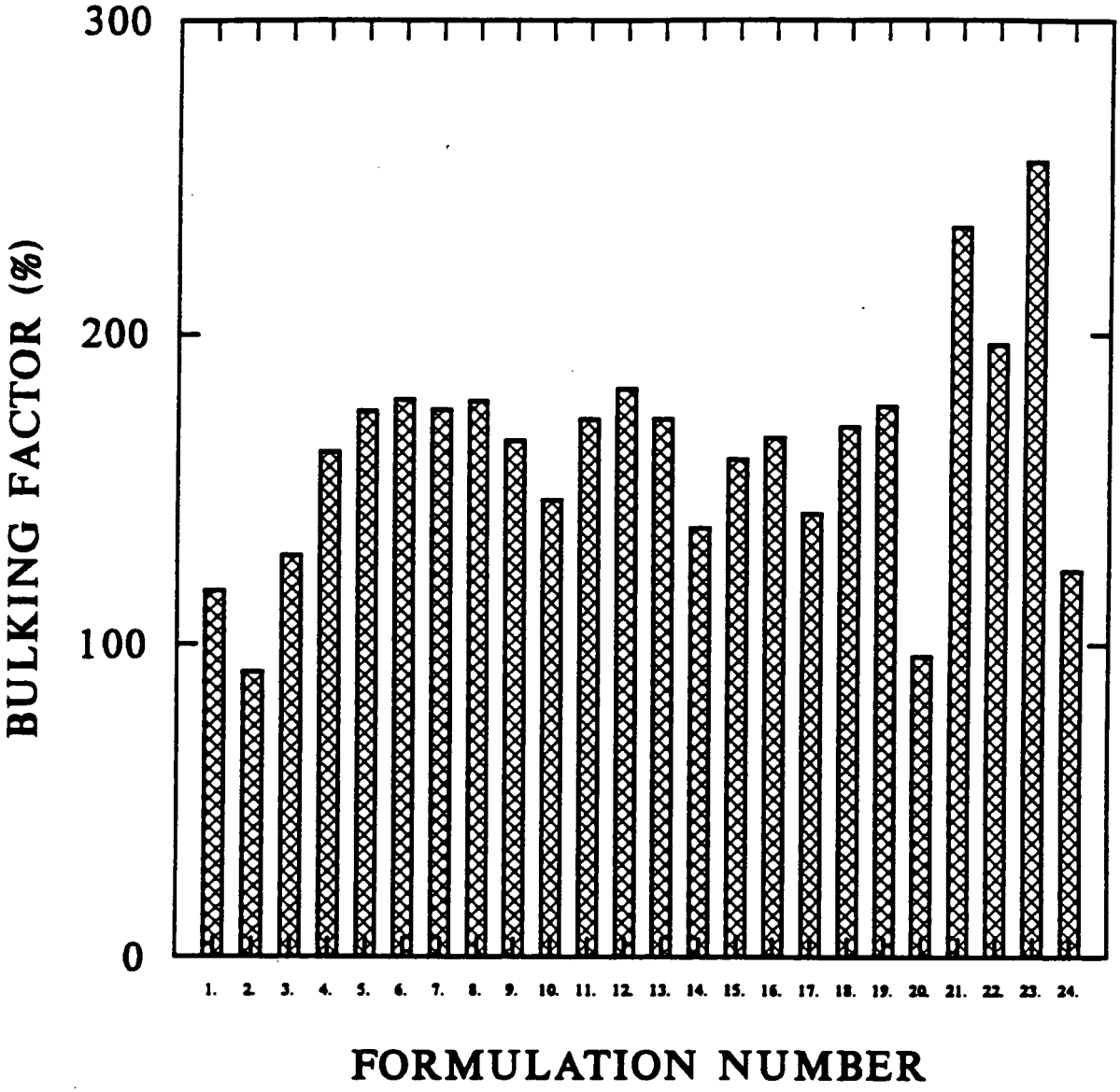
MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Pit 2 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the Remedy Selection (advanced phase).

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test included gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-96 for those values. The gross alpha and beta numbers were all below the lower limit of detection. The uranium concentration was below 1.03 ppm (w/w) for all treated samples. Cement loading greater than or equal to 43 percent was necessary to consistently minimize the uranium concentration in the MTCLP.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 9.7, all uranium values were below detection limits.



BAR GRAPH
B.F. VS. FORMULATION NUMBER
PIT 2, STAGES I & II

Figure 4-32

0448

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As previously noted, the site and commercial flyash also had similar effect on the UCS results. Thus site flyash could be considered for stabilizing the Pit 2 waste instead of buying commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). The formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, lowered the UCS, and had minimal effect on leachability. The effects of sodium silicate additions were ambiguous. Since the addition of these three reagents had minimal positive effects, it is recommended that the three additives not be used with Waste Pit 2 material.

Recommended Formulations for Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Table 4-95 and 4-96. Analysis of the results indicates that stabilization of the Pit 2 waste can achieve the desired UCS and leachability values with at least 50 percent cement added to the waste. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 45 tsf. within the 24-hour cure time.

The UCS values, uranium leachability, and BFs were the deciding criteria for selecting the formulations for the Remedy Selection (advanced phase) studies. The formulations had to exceed the 500 psi UCS criteria, have uranium concentrations in the MTCLP at nondetectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without

adsorbents additions which met the above requirements were selected. Formulation numbers 14 (cement and flyash) and 17 (cement, flyash, and BFS) were chosen from the formulations presented in Tables 4-95 and 4-96.

Remedy Selection Tests

The Advanced Phase formulations are presented in Tables 4-97 and 4-98. Zone 1, Formulation 1 exhibited the highest UCS, while Zone 2, Formulation 2 had the lowest UCS, close to the stated desired goal of >500 psi. Overall UCSs ranged from >3162 psi for Zone 1, Formulation 1 to 554 psi for Zone 2, Formulation 2. The average UCS for all the samples is 1480 psi. Bulking factors were very close in magnitude, ranging from a high of 131 percent for the Zone 1, Formulation 1 sample to a low of 102 percent for the single Zone 3, Formulation 2 sample. The average bulking factor was 123 percent. Again, permeabilities were considered to be low in the acceptable range of 1.0×10^{-8} to 2.0×10^{-10} cm/s.

Dilution adjusted TCLP Results for Waste Pit 2 TCLP radionuclides for the two formulations are shown in Table 4-99. The results for metals are shown in Table 4-100 and for organics in Table 4-101. Both formulations pass the TC regulatory criteria. Formulation 2 performed slightly better than Formulation 1 for inorganic compounds.

The leachability of radionuclides for Formula 1 was on the average slightly better than for Formula 2. There was not much difference for any of the uranium species and Tc-99. Formula 1 results were better than Formula 2. Formula 2 also had a better leachability for Ra-228. Formula 2 did perform better than Formula 1 with respect to Th-230.

Waste Pit 2 Cement Solidification - Radon Emissions

Formulations 1 and 2 radon results given in Figures 4-33 and 4-34 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. The leaching results show little difference in rates between the 7-day and 30-day rates for the same formulation. Formulation 1 had lower radon

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 2
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	53	15	25	0	24-42
2	100	51	31	0	0	15-41

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

Table 4-98

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY - PIT 2
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
1	1	>3149	131	123	5.2×10^{-8}
1	1	>3162	131		
2	1	1443	127		1.0×10^{-8}
2	1	1233	126		
1	2	1582	126		2.0×10^{-10}
1	2	835	125		
2	2	599	118		1.2×10^{-8}
2	2	554	119		
3	2	762	102		--

TABLE 4-99

PIT 2 SOLIDIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	ND	ND	ND
Plutonium-238	ND	1.290	0.669
Plutonium-239/240	ND	ND	0.424
Radium-226	13.180	726.000	1517.000
Radium-228	3.510	ND	335.000
Ruthenium-106	ND	ND	ND
Strontium-90	ND	5.100	23.700
Technetium-99	67.600	ND	ND
Thorium-228	1.690	8.600	11.400
Thorium-230	1.780	2.770	1.570
Thorium-232	ND	ND	ND
Uranium-234	61.710	1.030	1.530
Uranium-235/236	13.500	ND	ND
Uranium-238	112.170	1.600	2.440
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	0.010	ND	ND
Uranium (Total)	0.050	0.005	0.007

* See Table 4-93

\+ See Table 4-93

TABLE 4-100

PIT 2 SOLIDIFICATION TCLP METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.156	ND	ND	
Arsenic	0.600	0.007	0.007	5.000
Barium	0.048	1.851	2.738	100.000
Beryllium	0.004	ND	ND	
Boron	0.569	0.357	0.277	
Cadmium	0.028	ND	ND	1.000
Chromium	0.077	0.400	0.281	5.000
Cobalt	1.913	ND	ND	
Copper	0.244	0.038	0.059	
Cyanide	ND	0.014	ND	
Lead	0.006	ND	ND	5.000
Manganese	5.215	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	0.235	0.402	0.451	
Nickel	2.181	ND	ND	
Selenium	0.025	0.012	0.007	1.000
Silicon	29.650	12.784	8.976	
Silver	0.052	ND	ND	5.000
Thallium	0.008	ND	ND	
Vanadium	0.429	ND	ND	
Zinc	0.134	ND	ND	

* See Table 4-93

\+ See Table 4-93

TABLE 4-101

PIT 2 SOLIDIFICATION TCLP ORGANICS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
2-Methylnaphthalene		0.016	0.011	
4.4-DDT	ND	ND	ND	
4-Nitroaniline	ND	ND	ND	
4-Nitrophenol	ND	ND	ND	
Acenaphthene	0.055	0.064	0.021	
Acenaphthyine	ND	ND	ND	
Anthracene	0.012	0.026	0.025	
Aroclor-1248	ND	ND	ND	
Aroclor-1254	ND	ND	ND	
Benzene	ND	ND	ND	0.500
Benzo(a)anthracene	ND	ND	ND	
Benzo(a)pyrene	ND	ND	ND	
Benzo(b)fluoranthene	ND	ND	ND	
Benzo(g.h.i.)perylene	ND	ND	ND	
Benzo(k)fluoranthene	ND	ND	ND	
Chrysene	ND	ND	ND	
Dibenzo(a.h.)anthracene	ND	ND	ND	
Dibenzofuran	0.030	ND	ND	
Fluoranthene	0.011	0.042	0.034	
Fluorene	0.038	ND	ND	
Indeno(1.2.3-cd)prene	ND	ND	ND	

* See Table 4-93

\+ See Table 4-93

0455

TABLE 4-101
(Continued)

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Naphthalene	0.130	0.059	0.038	
Phenanthrene	0.084	0.209	0.134	
Pyrene	0.007	0.031	0.020	
Tetrachloroethene	ND	ND	ND	0.700
Tributyl phosphate		0.300		0.036
Vinyl chloride	ND	ND	ND	0.200

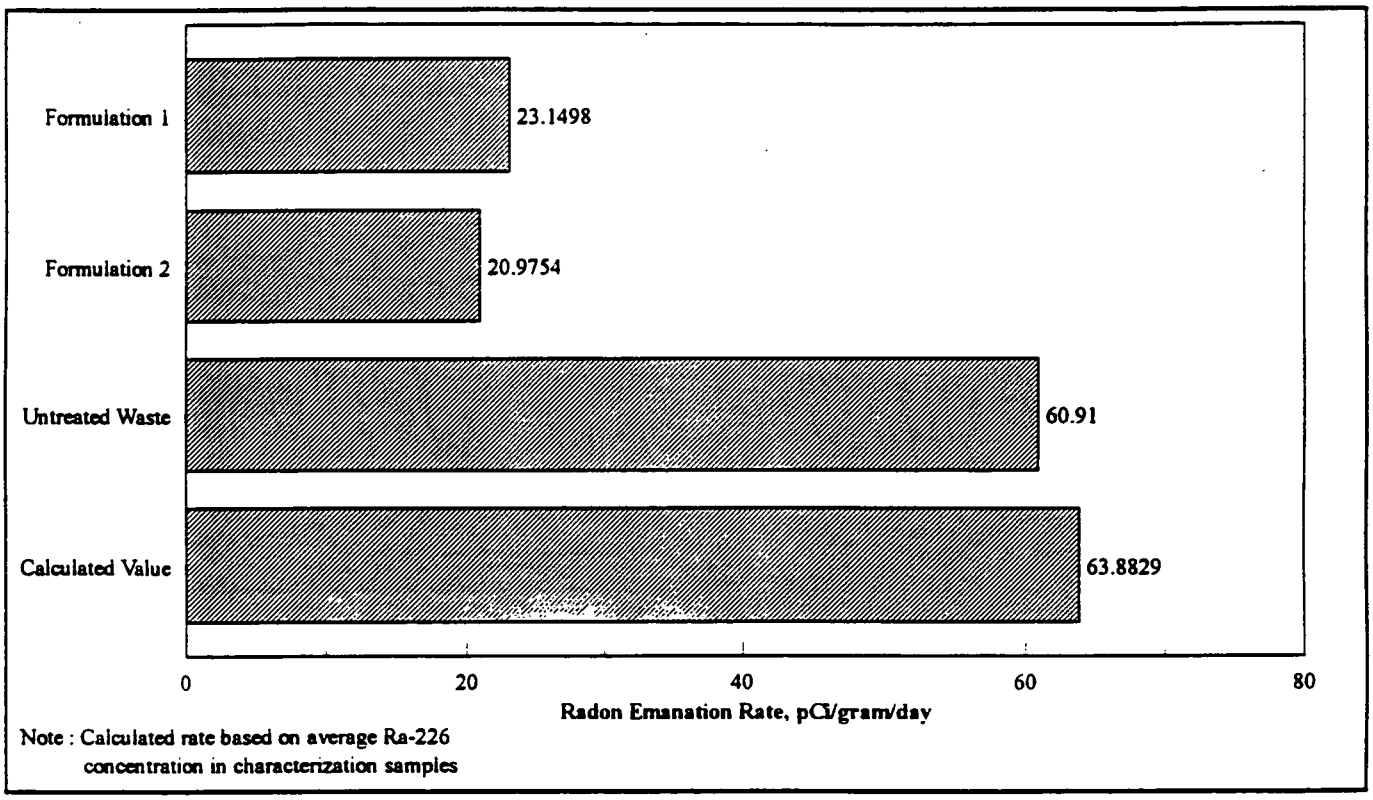


FIGURE 4-33 -PIT 2 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

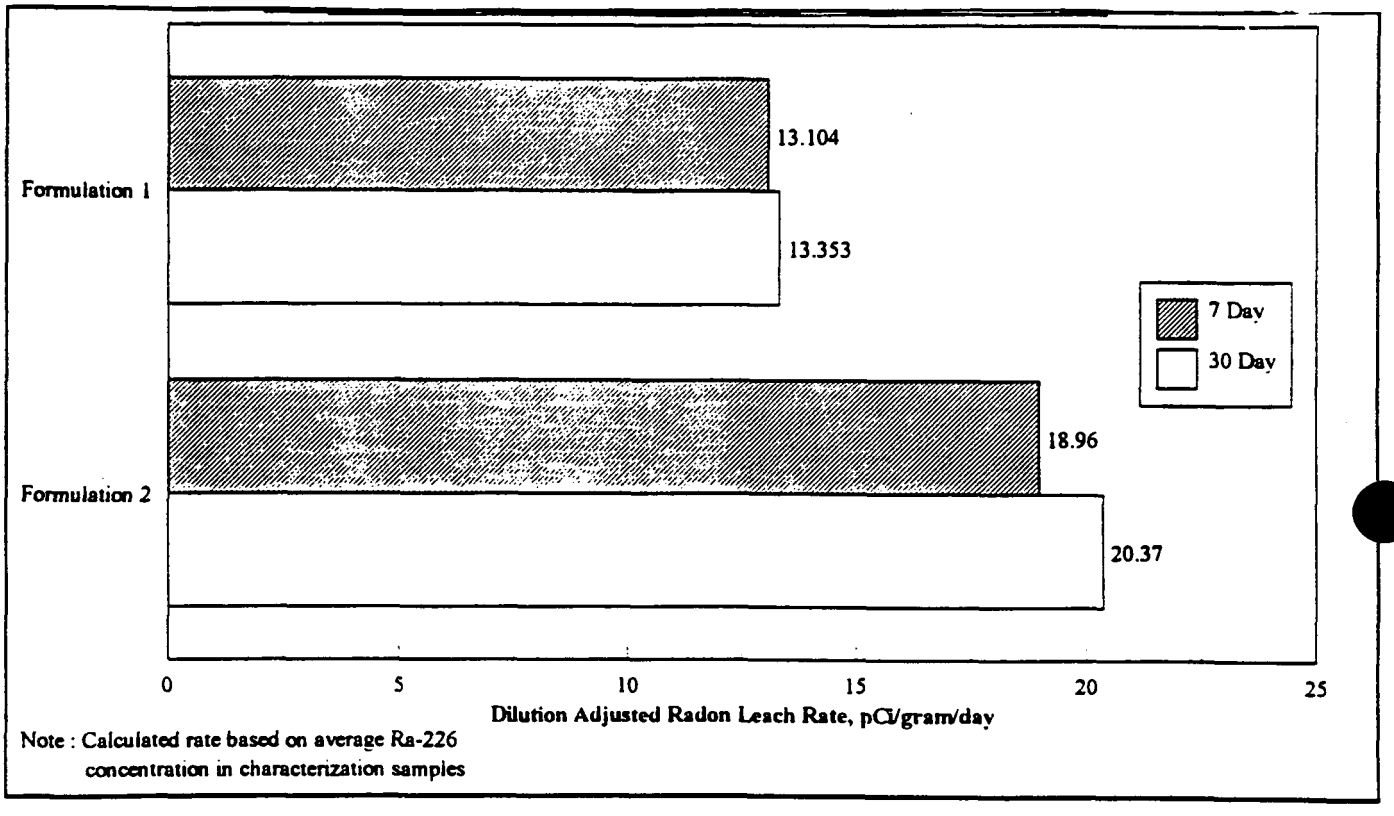


FIGURE 4-34 -PIT 2 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

leaching rates. For radon emanation, the difference in the radon rates between Formulations 1 and 2 was not significant. The results of the treated samples show that the radon emission rates were reduced to approximately one-third of the pretreated values.

The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 352.4 pCi/g.

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WASTE PIT 3

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are depicted in Tables 4-102 and 4-103. The formulation numbers in the table are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and in Appendix A are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 190 psi to greater than 650 psi; the values are graphically presented in Figure 4-36. The formulation numbers in the figure correspond to Table 4-102. A horizontal line is added to Figure 4-36 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The average UCS value was approximately 455 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbent, attapulgite and clinoptilolite, and formulations with activated BFS addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 11 (43 percent cement), 17 (51 percent cement), and 14 (51 percent cement), respectively.

General observations and trends noted for UCS follow:

- Analyses of statistical trends show that with adsorbents added to waste, the UCS generally increases with cement loading and that at least 43 percent cement was necessary to meet the UCS requirement.
- Addition of adsorbents lowered the UCS for a given cement loading.
- The UCS for samples substituting BFS for flyash were similar to cement/flyash formulation.
- Waste treated with portland Type 1 cement had larger UCS values than samples treated with portland Type 2 cement.
- Commercial and site flyash had similar results.

Table 4-102

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 3 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	6	6	27	0	1	1	293	87
2	100	26	26	0	0	0	19	0	3	1	375	64
3	100	27	20	7	6	6	33	0	1	1	311	100
4	100	31	51	0	6	6	47	0	1	1	255	132
5	100	33	54	7	6	6	49	0	1	1	190	152
6	100	43	43	4	12	0	53	0	3	1	262	152
7	100	43	43	0	6	6	43	0	4	1	277	131
8	100	43	43	4	0	12	40	0	3	1	383	129
9	100	43	43	0	0	0	27	0	4	1	396	108
10	100	43	43	4	6	6	40	0	1	1	422	131
11	100	43	43[c]	4	6	6	34	0	2	1	593	128
12	100	43	43[c]	0	6	6	24	0	2	1	616	107
13	100	43	43	4	6	6	47	0	4	1	638	134
14	100	51	0	0	0	4	29	31	_	2	650	98
15	100	51	15	0	0	0	32	25	_	2	650	101
16	100	51	31	0	6	6	47	0	1	1	566	128
17	100	51	31	0	0	0	25	0	_	2	650	95
18	100	54	33	7	6	6	47	0	1	1	370	144

Table 4-102
(Continued)

PIT 3 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
19	100	60	0	0	0	0	20	0	5	1	650	65
20	100	64	64	0	6	6	67	0	1	1	340	190
21	100	64	64	0	0	0	43	0	3	1	650	148
22	100	68	68	7	6	6	75	0	1	1	650	217
23	100	81	0	0	0	0	28	0	5	1	372	89

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

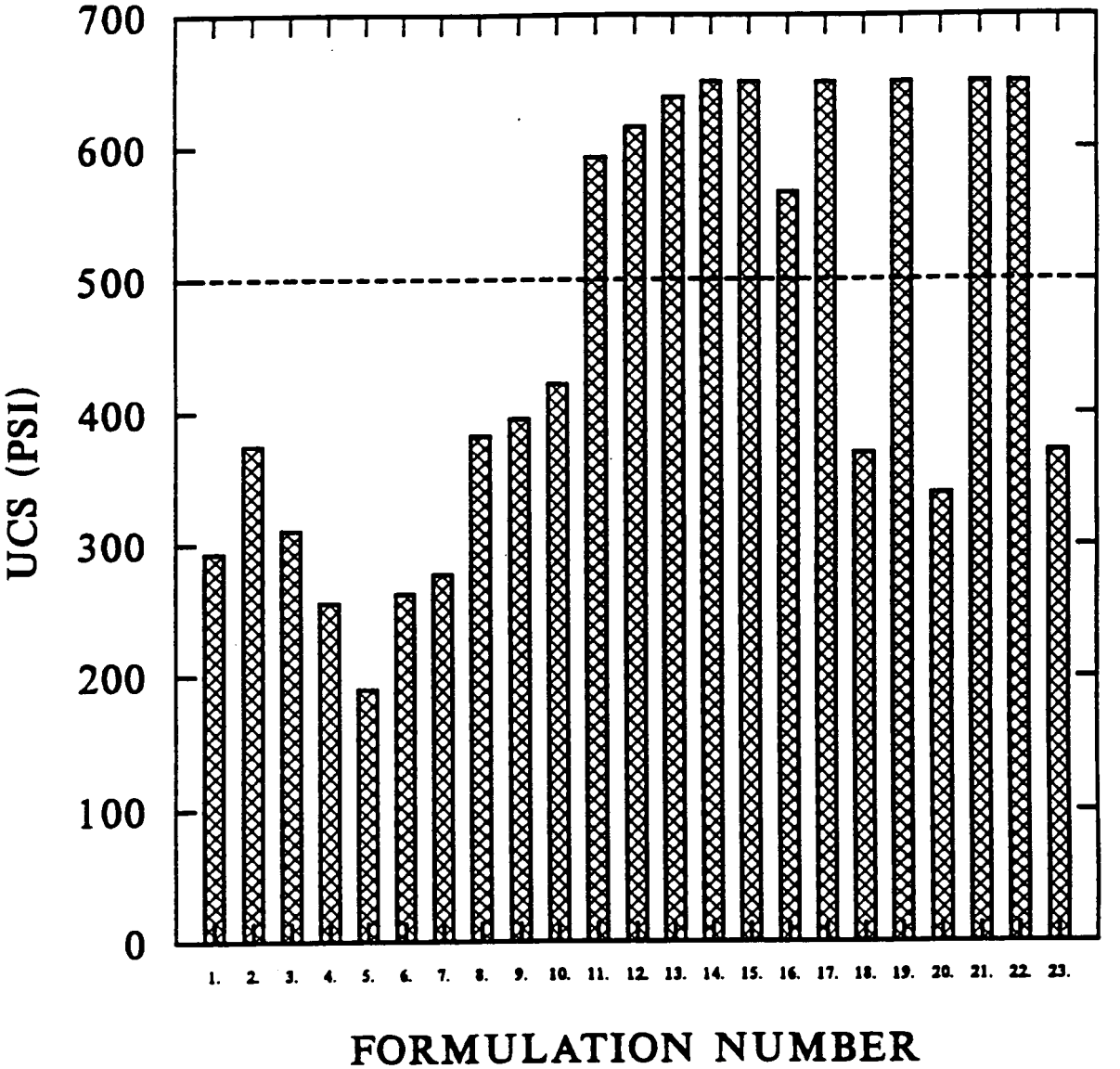
Table 4-103

FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 3 - REMEDY SCREENING (PRELIMINARY PHASE) CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	LLD	LLD	0.2723	8.35
2	LLD	9.3	0.9434	8.05
3	LLD	LLD	0.1709	8.1
4	LLD	LLD	ND	9.15
5	LLD	LLD	ND	8.4
6	LLD	LLD	0.2206	8.6
7	LLD	LLD	ND	10.15
8	LLD	LLD	0.3152	8.9
9	LLD	LLD	ND	10.65
10	LLD	LLD	0.0221	10.05
11	LLD	LLD	ND	10.85
12	LLD	LLD	ND	11
13	LLD	LLD	0.0189	9.15
14	LLD	LLD	ND	10.61
15	LLD	LLD	ND	11.79
16	LLD	LLD	ND	11.2
17	LLD	LLD	ND	11.31
18	LLD	LLD	ND	11.05
19	LLD	LLD	0.0177	11.7
20	LLD	LLD	ND	11.1
21	LLD	LLD	0.5971	9.2
22	LLD	LLD	ND	11.15
23	LLD	LLD	ND	11.8

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level



BAR GRAPH

UCS VS. FORMULATION NUMBER

PIT 3, STAGES I & II

Figure 4-36

0465

- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash was investigated. Sixty percent cement loading without addition of other reagents successfully stabilized the waste.

Bulking Factor (BF)

The BFs for Waste Pit 3 samples are listed in Table 4-102 and graphically presented (bar graph) in Figure 4-37. The data are ordered by formulation number. The BFs range from approximately 60 to 220 percent for the formulations investigated. The average BF was about 113 percent.

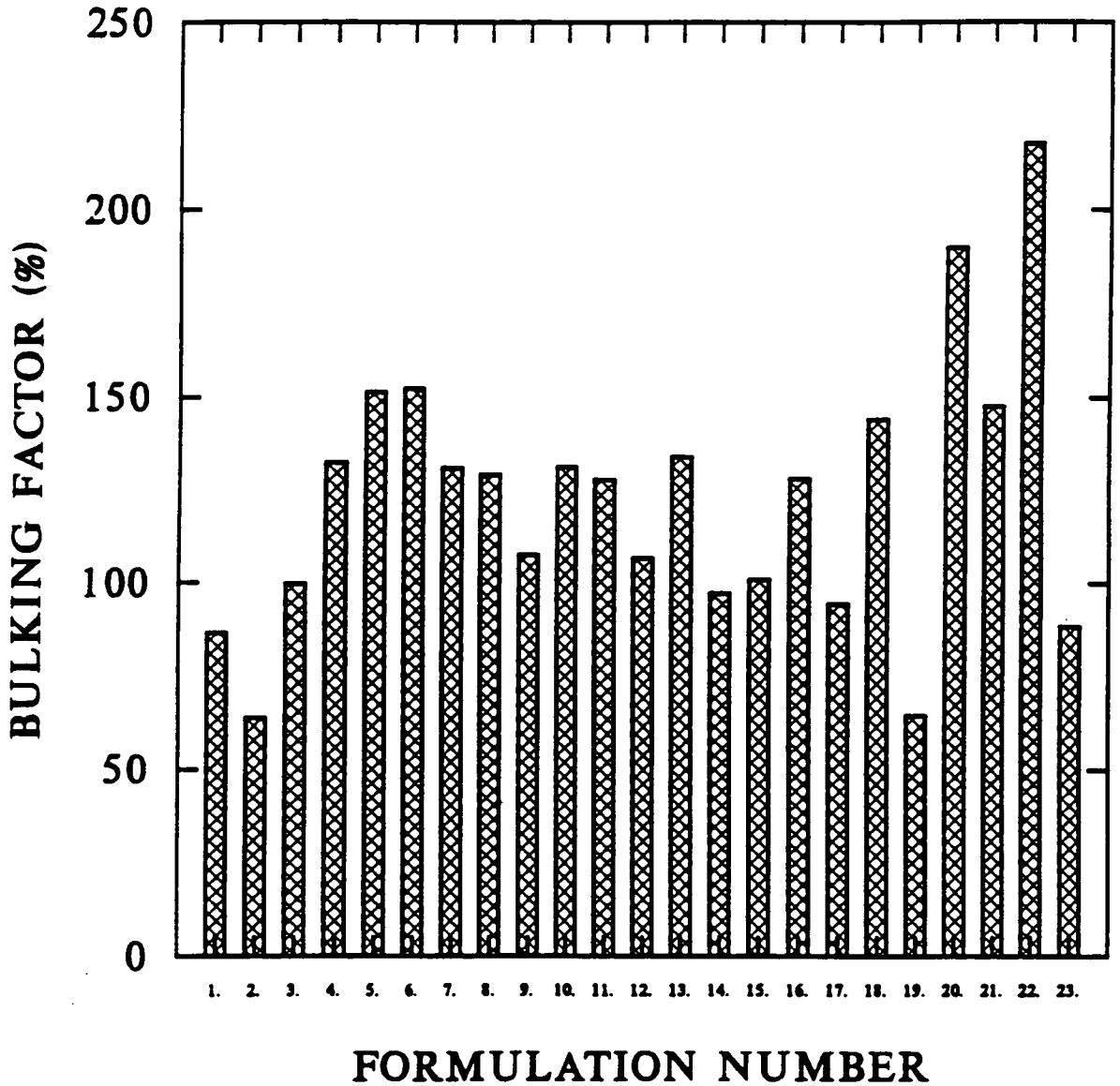
The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Waste Pit 1 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the remedy selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-103 for those values. All except one of the gross alpha and beta values were at the lower limit of detection. The one gross beta value had a low value at 9 disintegrations per minute (dpm) of 4 cubic centimeters (cc) of MTCLP extract. The uranium concentration was below 1.0 ppm (w/w) for all treated samples. Of the 9 samples out of 24 that had uranium concentrations above the detection limit, the average uranium value was 0.63 ppm. Cement loading greater than or equal to 43 percent were necessary to consistently minimize the



BAR GRAPH

B.F. VS. FORMULATION NUMBER

PIT 3, STAGES I & II

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Figure 4-37

uranium concentration in the MTCLP. The concentration of uranium in the MTCLP decreased as the cement and/or flyash loadings were increased.

The uranium concentration in the MTCLP of the sample of untreated waste was 0.3 ppm. The cement-based stabilization treatment would appear to reduce the leachability of uranium.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.1, all uranium values were below detection limit except for one sample at 11.7 pH with 0.018 ppm uranium in it.

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As previously noted, the site and commercial flyash also had similar effects on the UCS results. Thus, site flyash could be considered for stabilizing the waste in Waste Pit 3 instead of buying commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed (was easily mixed), had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). Generally, the samples which set quickly, as measured with a pocket penetrometer, had poor UCS values. The formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF and lowered the UCS. In experiments with 12 normalized percent attapulgite or clinoptilolite, concentrations of uranium in the MTCLP extractants were decreased. The addition of sodium silicate may increase the UCS values. The effect is greater at lower cement loadings.

Recommended Formulations For Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-102 and 4-103. Analysis of the results indicates that stabilization of the Pit 2 waste can achieve the desired UCS and leachability values. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within the 24-hour cure time.

The UCS values, uranium leachability, and BFs were the deciding criteria for determining the formulations for the Remedy Selection (Advanced Phase) studies. The formulations had to exceed the 500 psi UCS criteria, have uranium concentrations in the MTCLP at nondetectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without adsorbent addition which met the above requirements were selected. The cement/flyash formulation chosen for the Advanced Phase was not listed in Tables 4-102 and 4-103. Several of the 43 percent cement/43 percent flyash formulations from the preliminary phase had MTCLP uranium concentration above the detection level. Therefore, the cement and flyash loadings were increased from 43 percent of each reagent to 51 and 31 percent, respectively. In addition, 4 percent clinoptilolite was added because clinoptilolite addition lowered the MTCLP uranium concentration. The BFS formulation number 15 was selected from formulations presented in Tables 4-102 and 4-103.

Remedy Selection Tests

The Advanced Phase formulations are presented in Tables 4-104 and 4-105. The overall UCSs were very high, exceeding the stated desired goal of >500 psi. The highest (3156 psi) was developed for the Zone 1, Formulation 1 and 2 samples, while the lowest (1520 psi) was found in the Zone 3, Formulation 1 sample. The average UCS was 2393 psi. Bulking factors were considered low, with the highest +97 percent for the Zone 3, Formulation 1 sample, and the lowest 81 percent found in the Zone 2, Formulation 1 sample. The average bulking factor was 87 percent.

Permeabilities were also very low, with the highest for the Zone 2, Formulation 2 sample (1.0×10^{-7} cm/s) and the lowest for the Zone 1, Formulation 2 sample (5.1×10^{-9} cm/s).

Table 4-104

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 3
FOR FERNALD OPERABLE UNIT 1

Formulanon	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	51	15	25	0	22-32
2	100	51	31	0	4	18-32

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

Table 4-105

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY - PIT 3
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
1	1	>3148	90	87	2.1×10^{-9}
1	1	>3156	89		
2	1	>3156	81		4.7×10^{-9}
2	1	1642	81		
2	1	2289	84		3.3×10^{-9}
2	1	3138	86		
3	1	1520	91		5.1×10^{-9}
3	1	1591	97		
1	2	2878	89		1.0×10^{-7}
1	2	2868	88		
1	2	2166	87		3.0×10^{-9}
1	2	2848	88		
2	2	1590	88		2.1×10^{-7}
2	2	1821	88		
3	2	2240	86		1.4×10^{-9}
3	2	2243	86		

Dilution adjusted TCLP results for Waste Pit 3 TCLP radionuclides for the two formulations are shown in Table 4-106. Results for metals are shown in Table 4-107. Both formulations pass the TC regulatory criteria. Formulation 1 performed slightly better than Formulation 2 for the metals. Formula 1 had better results for Ra-226, and Th-230. Formula 2 shows better results for Ra-228, Th-228, and U-238.

Waste Pit 3 Cement Solidification - Radon Emissions

All radon results in Figures 4-38 and 4-39 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. Figure 4-38 shows that Formulation 1 was more effective in reducing the rate at which radon was released from the sample. This result is also reflected in Figure 4-39. Figure 4-39 shows a raw waste emanation rate much lower than the calculated rate. This effect might be explained by the wet nature of the untreated sample. Water will absorb some radon, and will also lower the rate of diffusion from the material. The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average concentration of Ra-226 in the characterization samples was 70.3 pCi/g.

TABLE 4-106

WASTE PIT 3 SOLIDIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	ND	0.036	0.490
Plutonium-238	ND	0.290	0.360
Plutonium-239/240	ND	0.270	0.520
Radium-226	9.620	70.560	587.520
Radium-228	13.030	49.950	ND
Strontium-90	ND	2.880	ND
Technetium-99	867.000	20.140	24.620
Thorium-228	6.440	4.380	2.990
Thorium-230	1.070	0.600	1.850
Thorium-232	ND	0.090	ND
Uranium-234	74.900	0.690	1.430
Uranium-235/236	7.240	ND	ND
Uranium-238	181.250	ND	1.170
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	ND	ND	ND
Uranium (Total)	0.390	ND	0.002

* See Table 4-93

\+ See Table 4-93

TABLE 4-107

WASTE PIT 3 SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Aluminum	3.432	3.084	0.788	
Antimony	0.184	ND	ND	
Arsenic	0.298	0.011	0.024	5.000
Barium	0.312	2.800	2.011	100.000
Beryllium	0.007	ND	0.004	
Boron	0.998	0.381	0.588	
Cadmium	0.054	ND	ND	1.000
Chromium	0.124	ND	0.095	5.000
Cobalt	0.120	ND	ND	
Copper	0.475	0.036	0.054	
Cyanide	ND	ND	ND	
Lead	0.007	0.025	0.009	5.000
Manganese	49.812	ND	ND	
Mercury	0.001	ND	ND	0.200
Molybdenum	0.370	0.952	2.382	
Nickel	0.709	ND	ND	
Selenium	0.218	0.013	0.006	1.000
Silver	0.092	ND	ND	5.000
Thallium	0.013	0.004	ND	
Vanadium	0.729	0.060	0.495	
Zinc	0.397	0.074	ND	

* See Table 4-93

\+ See Table 4-93

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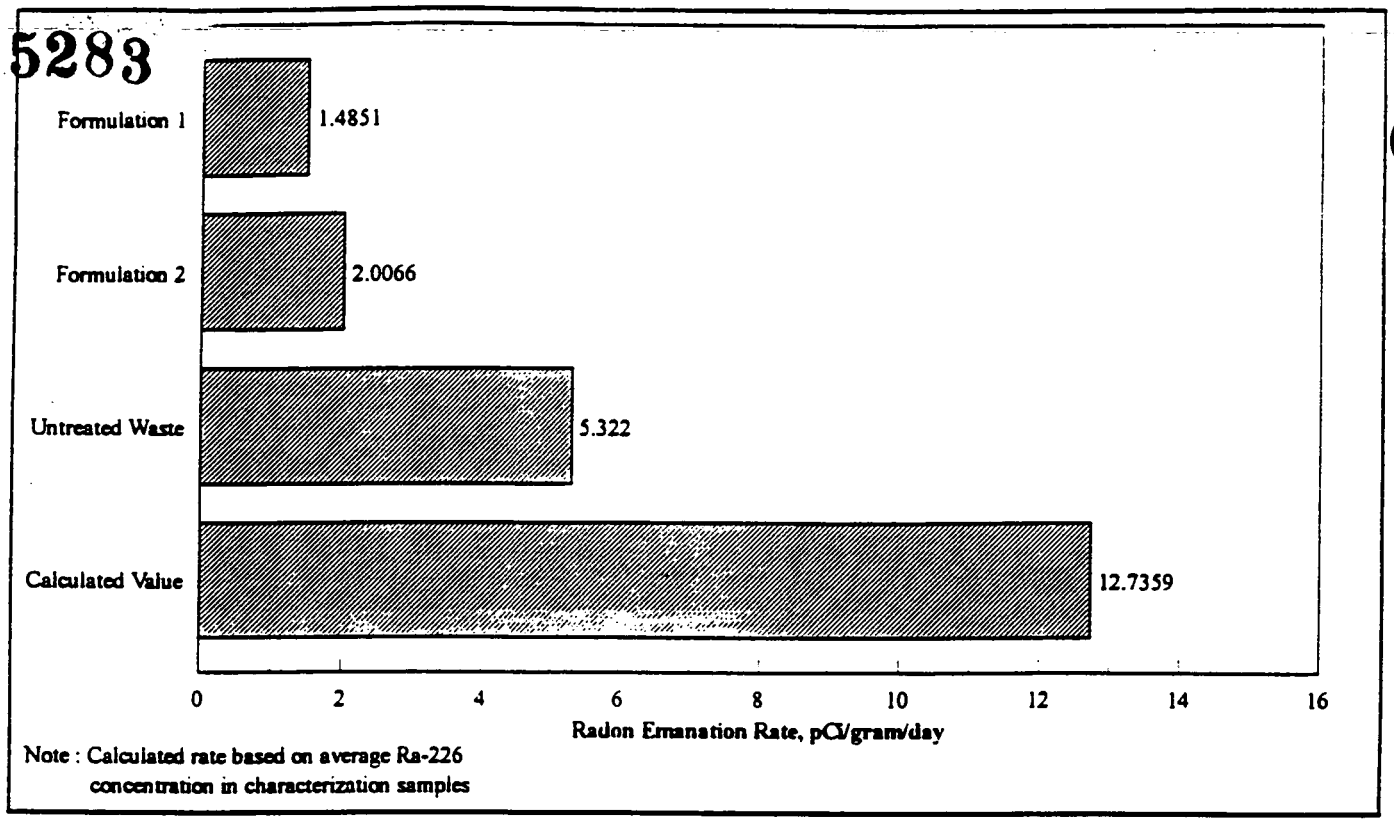

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FIGURE 4-38 - PIT 3 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

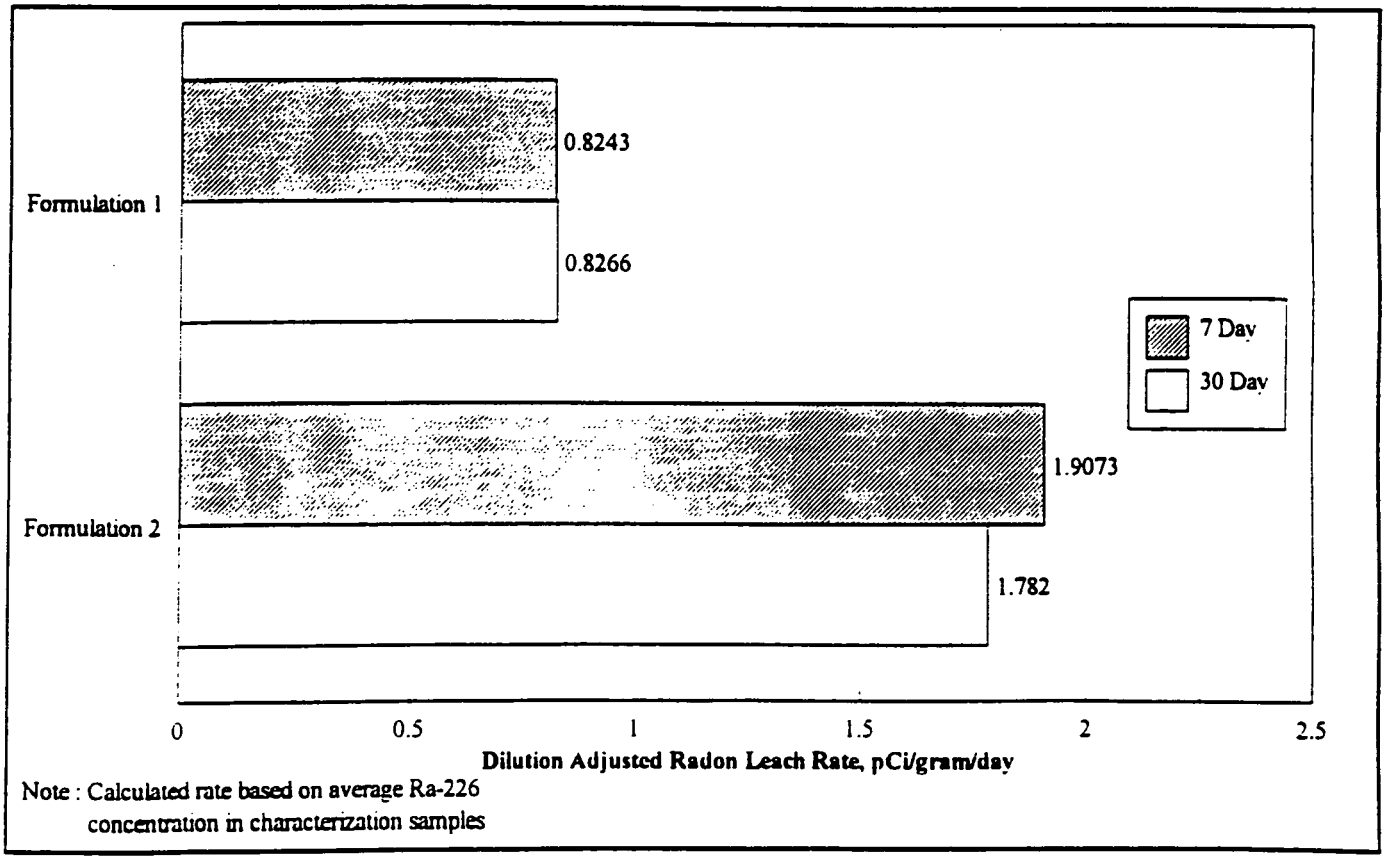

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FIGURE 4-39 - PIT 3 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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WASTE PIT 4

Remedy Screening Tests

The preliminary phase formulations investigated, UCSs, BFs, and MTCLP radiological results are depicted in Tables 4-108 and 4-109. The formulation numbers in the tables are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and Appendix A, are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 120 psi to greater than 600 psi; the values are graphically presented in Figure 4-40. The formulation numbers in the figure correspond to Table 4-108. A horizontal line is added to Figure 4-40 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbents, attapulgite and clinoptilolite, and formulations with activated BFS addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 12 (43 percent cement), 2 (26 percent cement), and 14 (51 percent cement), respectively.

General observations and trends noted for UCS follow:

- Analyses of statistical trends show that when adsorbents and flyash were added to the waste, the UCS generally increased with cement loading and at least 38 to 45 percent cement was necessary to meet the UCS requirement.
- Addition of adsorbents lowered the UCS for a given cement loading.
- Addition of BFS had similar UCS results to cement and flyash additions.
- No obvious trend was observed when comparing the UCS results for samples made with portland Type 1 and 2 cements.
- Commercial and site flyash had similar results.

Table 4-108

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 4 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	6	6	54	0	1	1	179	156
2	100	26	26	0	0	0	32	0	3	1	540	92
3	100	27	20	7	6	6	55	0	1	1	273	162
4	100	31	51	0	6	6	77	0	1	1	118	221
5	100	33	54	7	6	6	75	0	1	1	201	231
6	100	43	43	4	12	0	71	0	3	1	317	217
7	100	43	43	0	6	6	40	0	4	1	376	165
8	100	43	43[c]	4	6	6	53	0	2	1	413	198
9	100	43	43	4	6	6	67	0	1	1	463	213
10	100	43	43	4	0	12	63	0	3	1	593	199
11	100	43	43	0	0	0	40	0	4	1	600	141
12	100	43	43	4	6	6	61	0	4	1	600	199
13	100	43	43[c]	0	6	6	53	0	2	1	600	192
14	100	51	15	0	0	0	48	25	-	2	600	156
15	100	51	31	0	6	6	57	0	1	1	474	177
16	100	51	31	0	0	0	39	0	-	2	600	139
17	100	51	31	0	0	4	47	0	-	2	600	154
18	100	54	33	7	6	6	67	0	1	1	557	212
19	100	60	0	0	0	0	33	0	5	1	600	93
20	100	64	64	0	6	6	80	0	1	1	524	265

Table 4-108
(Continued)

PIT 4 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
21	100	64	64	0	0	0	60	0	3	1	600	217
22	100	68	68	7	6	6	93	0	1	1	459	303
23	100	80	0	0	0	0	35	0	5	1	600	113

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

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Table 4-109

FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 4 - REMEDY SCREENING (PRELIMINARY PHASE)
CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	1278.7	128	407.1	7
2	431	133	175.5	7.2
3	1003.4	88.3	452.1	7
4	424.5	114	223.6	6.45
5	331.2	91.5	162.1	6.25
6	96.8	21.5	24.83	8.05
7	LLD	9.9	7.255	9.75
8	297.5	18.2	118.3	7
9	516.8	42.2	5.4108	7
10	127.9	43.9	63.64	8.05
11	LLD	LLD	0.0469	10.35
12	208.3	52.6	50	7.35
13	705.1	57.9	243.8	7
14	265.5	83.1	181.93	7.39
15	LLD	LLD	7.222	9.6
16	280.6	64.1	83.29	7.55
17	LLD	LLD	0.2	10.21
18	LLD	LLD	0.2829	9.25
19	LLD	LLD	0.0532	11.5
20	77.1	27	39.43	9.05
21	117	84.4	94.32	7.75
22	120.8	20.4	44.3	9
23	LLD	LLD	0.1281	11.75

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level

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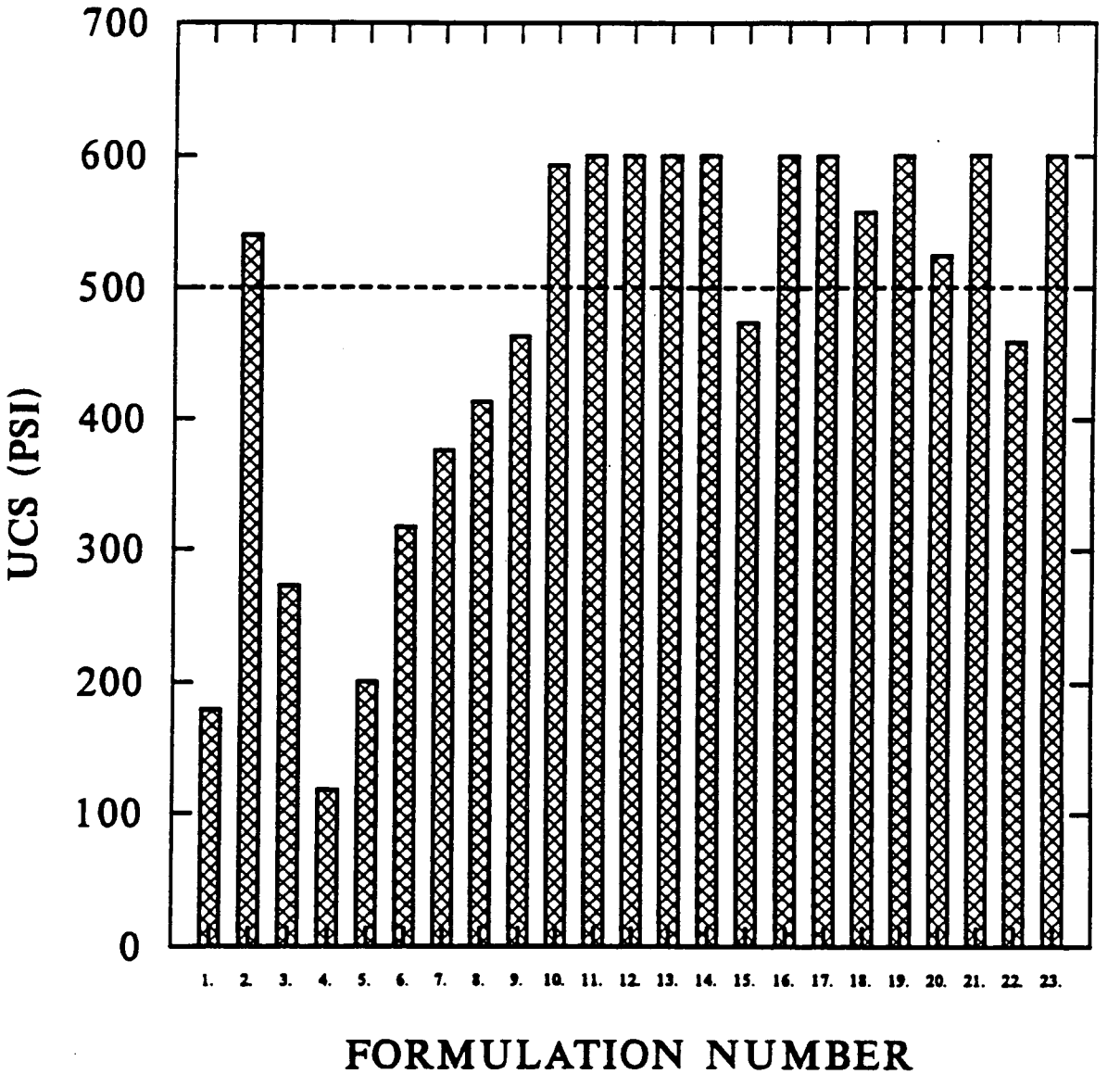


BAR GRAPH
UCS VS. FORMULATION NUMBER
PIT 4, STAGES I & II

0479

Figure 4-40

- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash was investigated. Sixty percent cement loading without addition of other reagents successfully solidified the waste.

- The addition of sodium silicate may have a negative impact on the UCS.

Bulking Factor (BF)

The BFs for Waste Pit 4 samples are listed in Table 4-108 and graphically presented (bar graph) in Figure 4-41. The data are ordered by formulation number. The BFs range from approximately 90 to 300 percent for the formulations investigated.

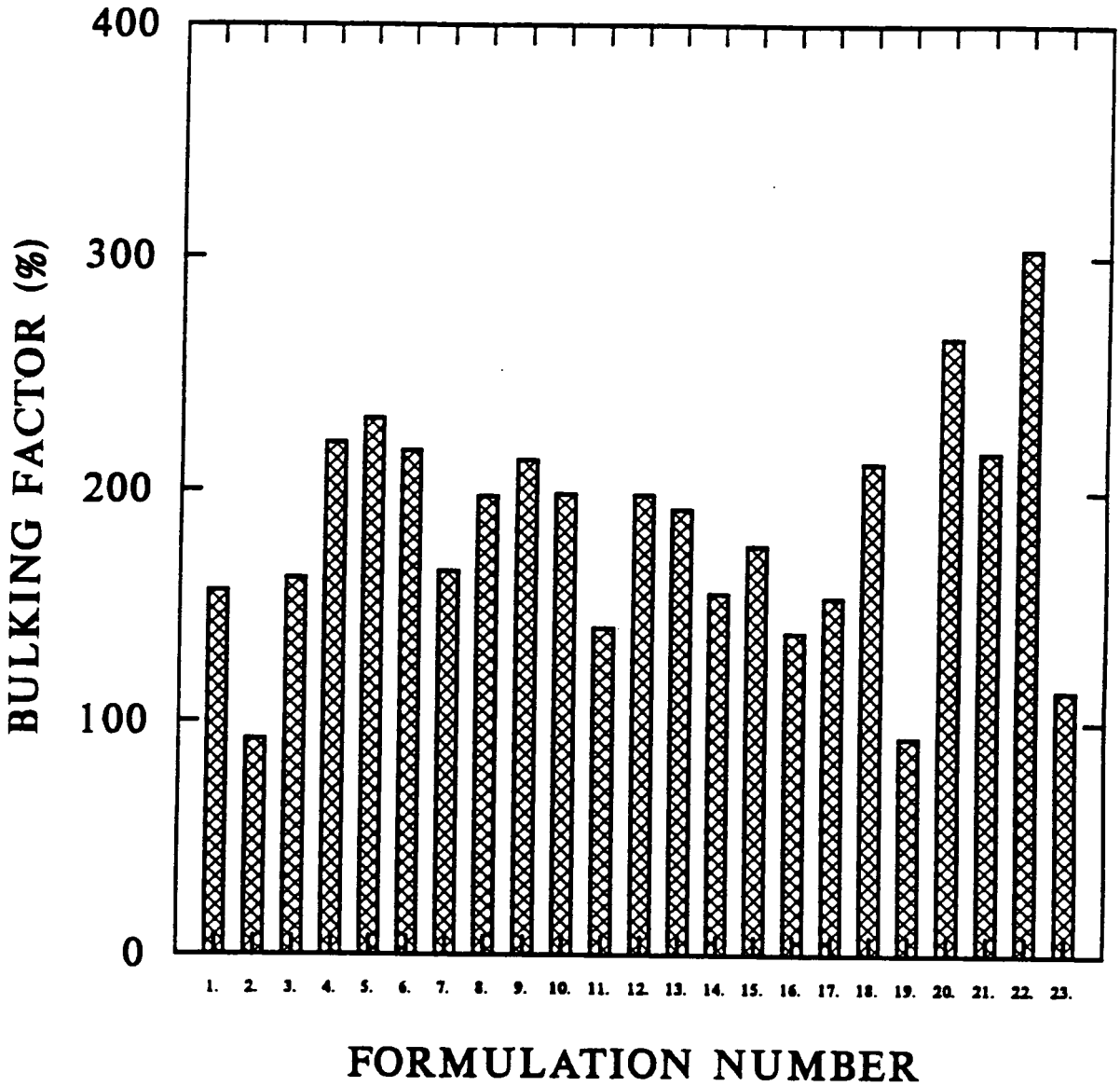
The BF was increased by the addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase the cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Pit 4 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the remedy selection (advanced) phase.

MTCLP - Radionuclides

From the compositional analyses of the pit waste (see Appendix B), it was determined that the uranium concentration in Waste Pit 4 was greater than 15 percent (w/w). This high concentration of uranium in the waste corresponds to the higher concentration of uranium in the MTCLP. The MTCLP uranium concentration from the untreated material was 948 ppm (w/w). In addition, the Pit 4 waste had relatively hard green or yellow chunks in it. Those colored chunks had more radiological activity, when measured on a pancake meter, than the bulk of the waste. It is believed that those chunks contained high concentrations of uranium. These chunks were not evenly dispersed throughout the waste nor were they always completely dispersed or dissolved during the stabilization



BAR GRAPH
B.F. VS. FORMULATION NUMBER
PIT 4, STAGES I & II

Figure 4-41

0481

process. Since the waste stream was heterogenous, in reference to uranium concentration, the variability of the MTCLP uranium concentration was not surprising.

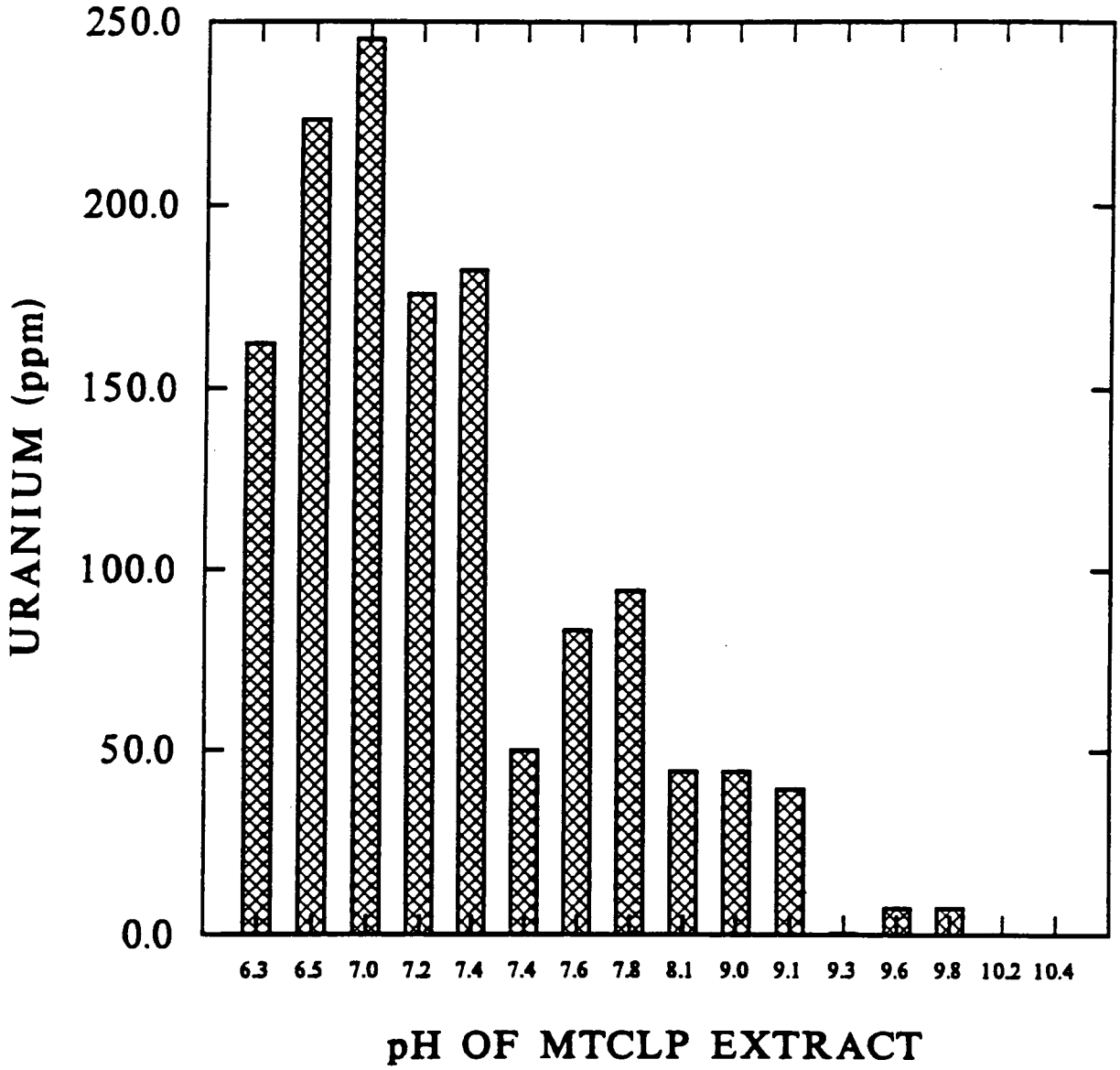
Indicators of radionuclides leachability for the MTCLP leach test included gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-109 for those values. The gross alpha and beta numbers ranged from lower limits of detection to more than 1000 dpm/4 cc (alpha) and 133 dpm/4 cc (beta). The uranium concentration ranged from 0.13 ppm (w/w) to greater than 400 ppm. The average uranium concentration was approximately 104 ppm. The addition of adsorbents had no obvious trend on the uranium leachability. The addition of BFS did not improve the uranium leachability. The addition of flyash at low cement loadings may increase the uranium leachability. There is a trend of decreasing uranium leachability with increasing cement loading.

The uranium concentration in the MTCLP of the untreated waste was 948 ppm. The cement-based stabilization treatment reduced the leachability of uranium down to below 0.13 ppm when only 60 and 80 percent cement was used (formulation numbers 19 and 23). Therefore, the treatment can reduce the concentration of leachable uranium removed from the waste.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.2, all uranium values were below 0.2 ppm. This trend is graphically demonstrated in Figure 4-41.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed and low temperature rise (less than or equal to 3°C). The rate of set, as measured with the pocket penetrometer after the 24-hour cure time, was slower than most of the other waste pits in Operable Unit 1. The formulations that achieved a UCS of greater than 500 psi were considered processable.



BAR GRAPH
URANIUM VS. MTCLP pH
PIT 4, STAGES I & II

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FIGURE 4-41

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, lowered the UCS, and had minimal effect on leachability. The effects of sodium silicate additions were ambiguous. Since the addition of these three reagents had minimal positive effects, it is recommended that the three additives not be used with Waste Pit 4 material at the 6 percent loadings for the adsorbents or at any loading for the sodium silicate.

Recommended Formulations For Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-108 and 4-109. Analysis of the results indicates that solidification of the Pit 4 waste can readily achieve the desired UCS. High loadings of cement are necessary to control the uranium leachability. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 3.0 tsf within a 24-hour cure time.

The UCS values, uranium leachability, and BFs were the deciding criteria for determining the formulations for the Remedy Selection (Advanced Phase) studies. The formulations had to exceed the 500 psi UCS criteria, minimize the uranium concentrations in the MTCLPs, and minimize the BFs. Choosing from the formulations presented in Tables 4-108 and 4-109, formulation numbers 17 (cement, flyash, and clinoptilolite) and a modification of number 23 (cement and clinoptilolite) were selected. These formulations had the lowest uranium concentrations in the MTCLPs.

Remedy Selection Tests

The formulations for the cement stabilizations of Waste Pit 4 are presented in Tables 4-110 and 4-111. All UCSs were considered high with the highest given by the Zone 3, Formulation 2 sample (>3157 psi), while the lowest was found in the Zone 2, Formulation 2 sample. The average UCS was 2005 psi, well above the stated goal of >500 psi. Bulking factors were considered higher than the other pits, with the highest shown by the Zone 1, Formulation 1 sample and the lowest from the Zone 2 and 3, Formulation 2 sample. Average bulking factor was 136 percent. Permeabilities were very low, with the highest result coming from Zone 1, Formulation 2 (1.0×10^{-7} cm/s) and the lowest from Zone 3, Formulation 2 (2.3×10^{-9} cm/s).

Table 4-110

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 4
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	51	31	0	4	34-59
2	100	80	0	0	6	33-61

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

Table 4-111

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY
PIT 4
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
1	1	1862	173	136	1.5×10^{-8}
1	1	1981	170		
2	1	1289	132		2.3×10^{-8}
2	1	1626	130		
3	1	1470	129		5.6×10^{-9}
3	1	2171	126		
1	2	2608	168		1.0×10^{-7}
1	2	1812	169		
2	2	1957	120		2.8×10^{-9}
2	2	>3131	118		
2	2	1026	119		4.2×10^{-9}
2	2	832	118		
3	2	>3157	118		2.3×10^{-9}
3	2	>3149	118		

Dilution adjusted TCLP results for Waste Pit 4 TCLP radionuclides for the two formulations are shown in Table 4-112. Results for metals are shown in Table 4-113. Both formulations pass the TC regulatory criteria. The leachability of Formulations 1 and 2 were nearly identical. The leachability of radionuclides for Formula 2 on the average was better than for Formula 1.

Waste Pit 4 Cement Solidification - Radon Emissions

All radon results for Figures 4-42 and 4-43 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in these figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. Figure 4-42 shows that Formulation 2 appeared to be slightly more effective in reducing the rate at which radon diffuses from the treatability samples into water. The emanation in air (Figure 4-43) also showed Formulation 2 to have a lower radon emission rate than Formulation 2. The emanation rate for untreated waste was approximately double that of the treated waste.

The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 16.8 pCi/g.

TABLE 4-112

WASTE PIT 4 SOLIDIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	3.630	0.910	0.320
Plutonium-238	ND	0.220	0.310
Plutonium-239/240	ND	ND	0.150
Radium-226	48.960	34.050	ND
Radium-228	76.900	37.480	ND
Strontium-90	19.680	2.200	ND
Technetium-99	95.910	23.350	21.370
Thorium-228	ND	5.210	6.020
Thorium-230	ND	1.690	2.380
Thorium-232	ND	ND	ND
Uranium-234	8518.000	3.430	12.070
Uranium-235/236	1891.500	ND	1.390
Uranium-238	67550.000	6.620	79.360
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	ND	ND	ND

* See Table 4-93

\+ See Table 4-93

TABLE 4-113

WASTE PIT 4 SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.400	ND	ND	
Arsenic	ND	ND	ND	5.000
Barium	3.744	3.092	6.165	100.000
Beryllium	0.047	ND	ND	
Boron	0.401	0.586	0.241	
Cadmium	0.046	ND	ND	1.000
Chromium	1.276	0.047	0.027	5.000
Cobalt	0.193	ND	ND	
Copper	0.439	0.033	0.025	
Cyanide	ND	ND	ND	
Lead	0.007	ND	ND	5.000
Manganese	28.344	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	0.111	ND	ND	
Nickel	0.365	ND	ND	
Selenium	ND	ND	ND	1.000
Silicon	11.457	11.885	3.075	
Silver	0.706	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.508	ND	ND	
Zinc	0.484	ND	0.074	

* See Table 4-93

\+ See Table 4-93

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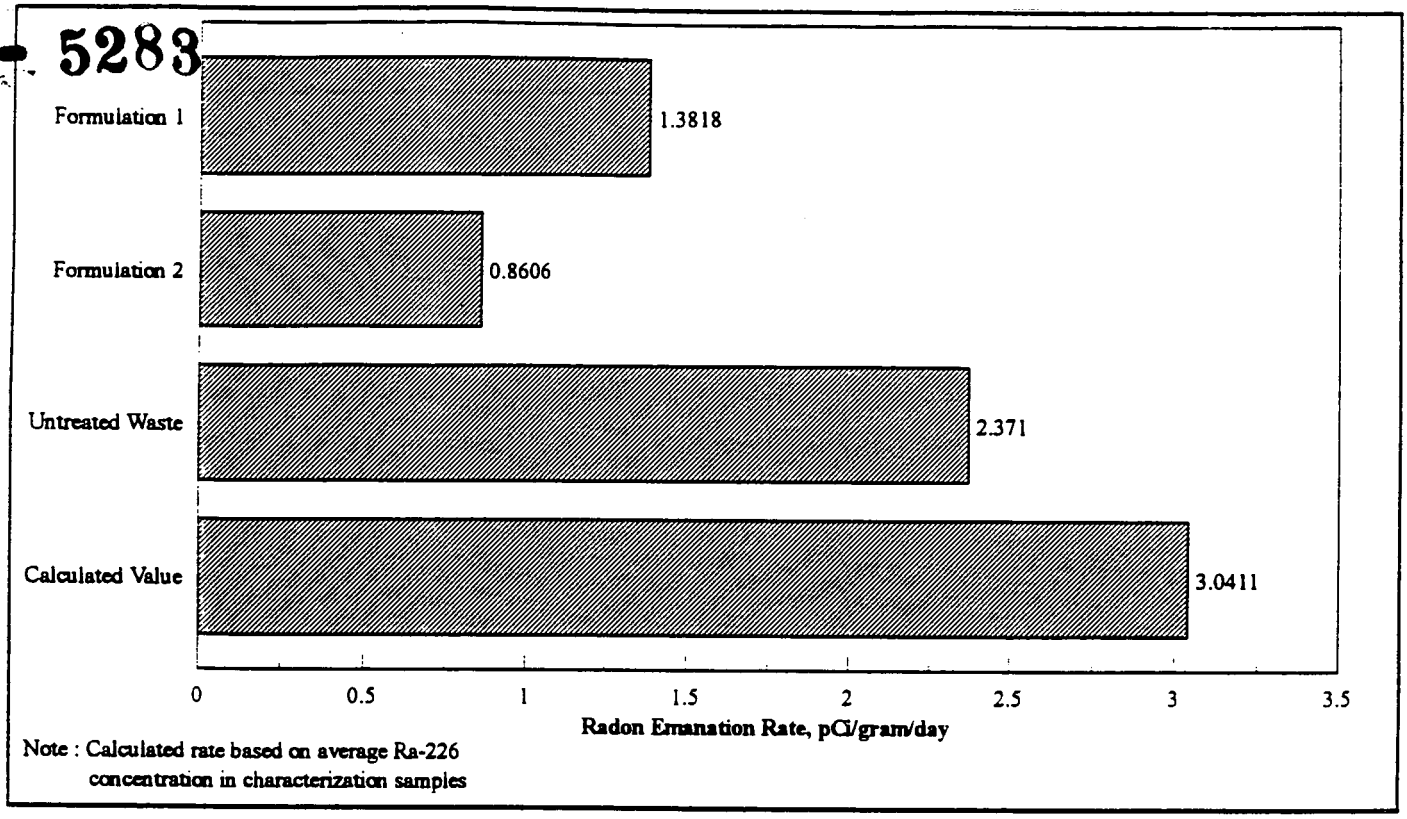

FIGURE 4-42 - PIT 4 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

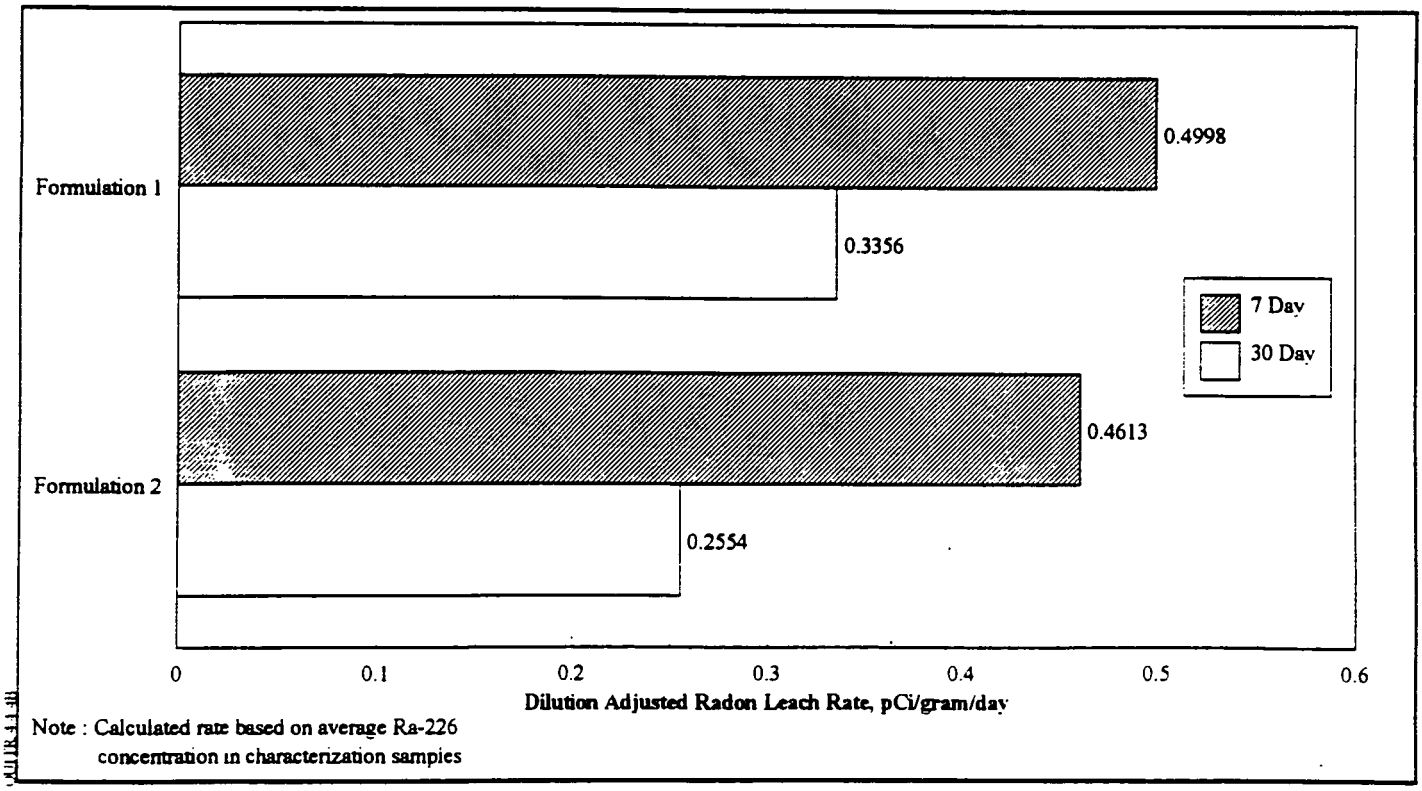

FIGURE 4-43 - PIT 4 STABILIZATION - COMPA
OF DILUTION ADJUSTED RADON LEACH RA

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WASTE PIT 5

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are presented in Tables 4-114 and 4-115. The formulation numbers in the tables are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and Appendix A of this appendix, are also listed for reference.

Unconfined Compressive Strength(UCS)

The UCS values ranged from approximately 65 psi to greater than 650 psi and the values are graphically presented in Figure 4-44. The formulation numbers in the figure correspond to Table 4-114. A horizontal line is added to Figure 4-44 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbents, attapulgite and clinoptilolite, and formulations with activated BFS addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 10 (43 percent cement), 8 (43 percent cement), and 14 (51 percent cement), respectively.

General observations and trends noted for UCS follow:

- Analysis of statistical trends shows that with adsorbents added to waste, the UCS generally increases with cement loading and that at least 43 to 45 percent cement was necessary to meet the UCS requirement.

- The untreated Waste Pit 5 material had a high moisture content (84 percent). The percent water in the cured treated samples were higher than most of the other Operable Unit 1 treated material. The Waste Pit 5 moisture content of the treated material normally ranged from upper 30 to 40 percent, with a few above 50 percent. At a percent moisture in the cured material above approximately 42 percent, the UCS decreased rapidly. Most of these latter samples used formulations with less than 43 percent cement in them.

- Addition of adsorbents increased the UCS for a given cement loading. The increase in UCS was likely the result of attapulgite and clinoptilolite adsorbing excess water from the

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 5 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	0	0	0	0	3	1	66	27
2	100	26	26	0	6	6	3	0	1	1	267	36
3	100	27	20	7	6	6	0	0	1	1	329	34
4	100	31	51	0	6	6	10	0	1	1	455	60
5	100	33	54	7	6	6	13	0	1	1	393	73
6	100	43	43[c]	4	6	6	0	0	2	1	412	59
7	100	43	43[c]	0	6	6	0	0	2	1	422	55
8	100	43	43	0	0	0	0	0	4	1	541	42
9	100	43	43	4	12	0	4	0	3	1	591	61
10	100	43	43	4	6	6	5	0	1	1	603	56
11	100	43	43	4	6	6	6	0	4	1	650	58
12	100	43	43	0	6	6	4	0	4	1	650	54
13	100	43	43	4	0	12	0	0	3	1	650	54
14	100	51	15	0	0	0	0	25	-	2	650	40
15	100	51	31	0	0	4	0	0	-	2	374	44
16	100	51	31	0	6	6	10	0	1	1	650	56
17	100	54	33	7	6	6	15	0	1	1	531	70
18	100	60	0	0	0	0	0	0	5	1	408	27
19	100	64	64	0	6	6	12	0	1	1	650	81
20	100	64	64	0	0	0	0	0	3	1	650	65
21	100	65	31	0	0	4	0	0	-	2	522	47
22	100	68	68	7	6	6	12	0	1	1	650	100
23	100	80	0	0	0	0	0	0	5	1	650	32

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study [illegible]

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FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 5 - REMEDY SCREENING (PRELIMINARY PHASE) CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	18.6	61.6	ND	11.24
2	LLD	28.7	ND	11.14
3	LLD	30	ND	10.75
4	LLD	35.3	ND	10.2
5	LLD	29.4	ND	9.99
6	18.4	33.9	ND	11.68
7	19.3	27.7	ND	11.85
8	28.1	0.4	ND	11.42
9	25.9	45.6	ND	11.2
10	33.7	33.2	ND	11.74
11	LLD	30	ND	9.27
12	35.5	47.2	ND	9.87
13	LLD	40.8	ND	11.1
14	LLD	LLD	ND	11.72
15	25.5	28.1	0.17	12.34
16	LLD	30.4	ND	12.29
17	LLD	22.3	ND	12.21
18	40.9	53	ND	12.34
19	LLD	18.4	ND	11.96
20	18.7	37.9	ND	11.93
21	19.4	20.4	ND	12.43
22	LLD	16	ND	11.97
23	47.8	58.6	ND	12.39

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level

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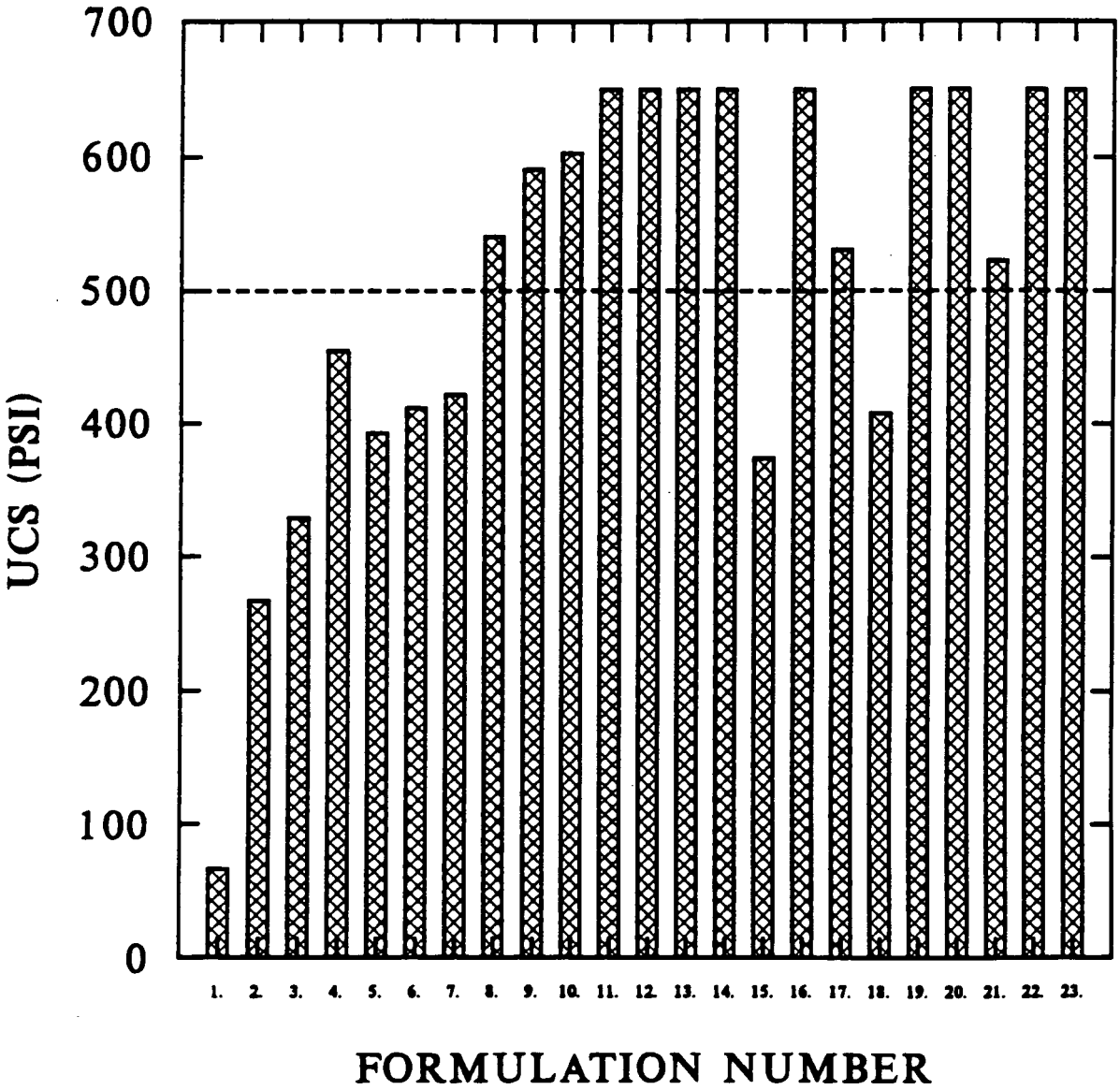

BAR GRAPH
UCS VS. FORMULATION NUMBER
PIT 5, STAGES I & II

Figure 4-44

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waste. At the lower free water concentration in the wet reagent/waste paste, the water to cement ratio would be closer to the optimum ratio. The effect of adsorbent addition was greatest with the lower cement loadings.

- Addition of BFS increased the UCS.
- Portland Type 1 and 2 cements had similar results.
- Formulations using commercial flyash had higher UCS values than those with site flyash.
- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash were investigated. Sixty percent cement loading without addition of other reagents successfully solidified the waste. The cement only formulations did not control the release of the gross alpha and beta components in the MTCLP of the treated material.

Bulking Factor(BF)

The BFs for Waste Pit 5 samples are listed in Table 4-114 and graphically presented (bar graph) in Figure 4-45. The data are ordered by formulation number. The BFs range from approximately 25 to 100 percent for the formulations investigated.

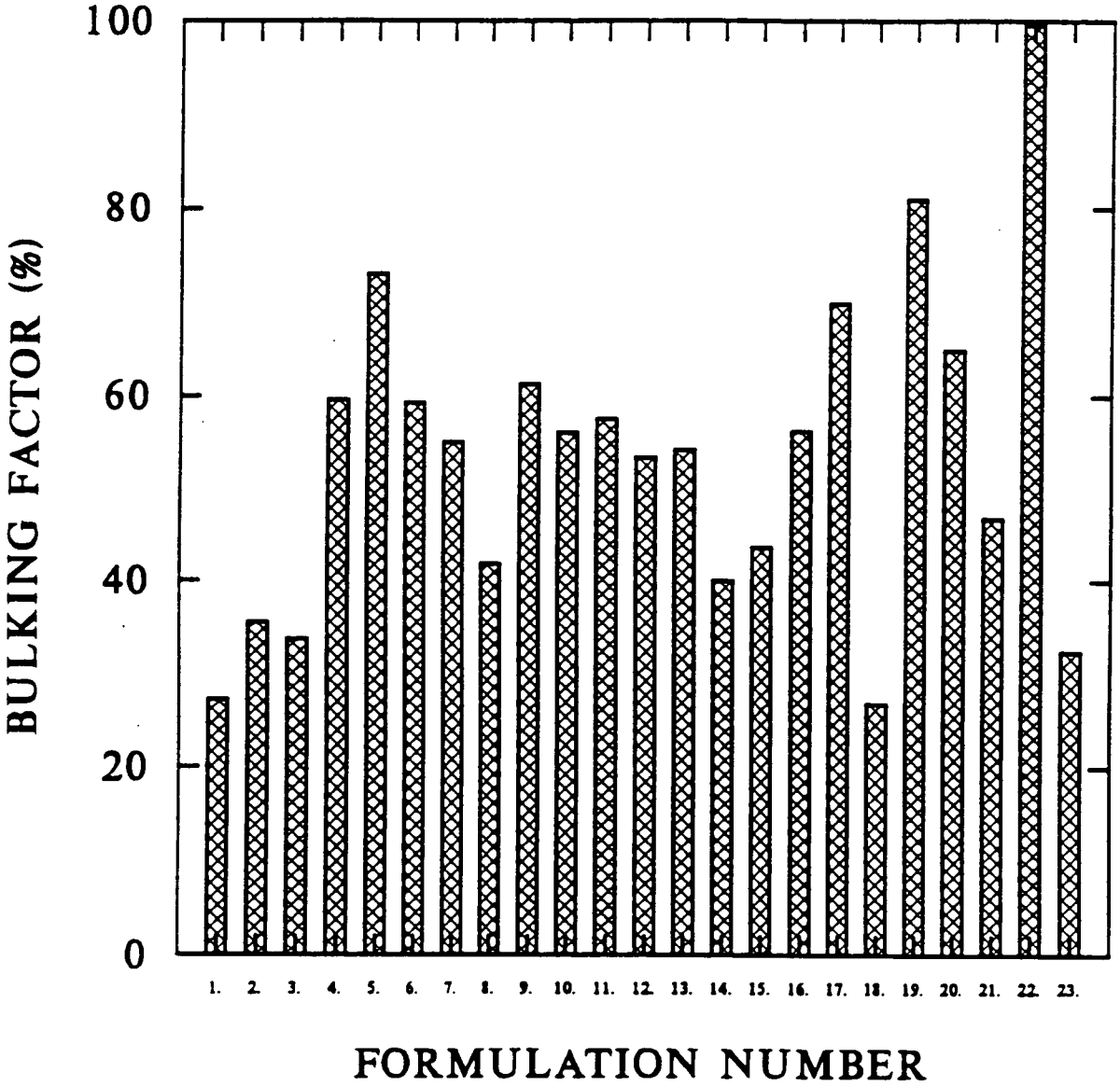
The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Pit 5 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the Remedy Selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-115 for those values. The gross alpha



BAR GRAPH

B.F. VS. FORMULATION NUMBER

PIT 5. STAGES I & II

Figure 4-45

and beta values ranged from lower limits of detection to approximately 50 and 60 dpm/4 cc, respectively. The uranium concentration was below detection limit except for one sample at 0.17 ppm uranium. As previously stated, the addition of 60 and 80 percent cement without other additives did not significantly reduce the gross alpha and beta values in the MTCLP. Addition of adsorbents at 6 percent each of attapulgite and clinoptilolite reduced the gross alpha and beta values in the extract. Analysis of the data shows that high flyash loading lowers the gross alpha and beta values.

The one BFS formulation investigated, formulation number 14, had a lower limit of detection for leachable gross alpha, beta, and uranium. This was the only formulation that had no positive hits for all three analytes.

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). Generally, at cement loadings below 43 percent, the samples set slower. The formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, increased the UCS, and decreased the leachability of gross alpha and beta in the MTCLP. The effects of sodium silicate additions were ambiguous.

Recommended Formulations for Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-114 and 4-115. Analysis of the results indicates that solidification of the Pit 5 waste can readily be

achieved. Only one formulation lowered the gross alpha, beta and uranium levels to nondetectable levels. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within a 24-hour cure time.

The UCS values, gross alpha and beta leachability, and BFs were the deciding criteria for selecting the formulations for the Remedy Selection (Advanced Phase) studies. The formulations had to exceed the 500 psi UCS criteria, have gross alpha and beta levels in the MTCLP at nondetectable levels, and minimize the BFs. Formulation numbers 14 (cement, flyash, and BFS) and augmented formulation number 14 (cement, flyash, and additional BFS) were chosen from the formulations presented in Tables 4-114 and 4-115.

Remedy Selection Tests

Formulations for the Remedy Selection tests can be found in Tables 4-116 and 4-117. No zone samples were tested. Only a composite was tested with duplicate Formulations 1 and 2. UCSs were much higher than the stated goal of 500 psi. The largest UCS value was 2257 psi for the Formulation 2 samples, with a low of 1294 psi for one of the Formulation 1 samples. Bulking factors were considered good, with the highest result found in the Formulation 2 sample (49 percent) and the lowest results in two Formulation 1 samples (37 psi). The average bulking factor was 41 psi. Permeabilities were also low, with the highest value in the two Formulation 1 samples (7.2×10^{-8} cm/s), and the low in the Formulation 2 sample (3.2×10^{-8} cm/s).

Dilution adjusted TCLP results for Waste Pit 5 TCLP radionuclides for the two formulations are shown in Table 4-118. Results for metals are shown in Table 4-119. Both formulations pass the TC regulatory criteria. The leachability of the two formulations was almost identical.

However, a comparison of the dilutions adjusted results for Formulas 1 and 2 shows that for most of the radionuclides Formula 2 performed better than Formula 1. Th-232, Th-total, U-235/236, U-238, and U-total for Formula 1 had dilution adjusted concentrations reported, while formula 2 had NDs. Formula 2 also had lower concentrations for Np-237, Pu-238, Ra-226, Ra-228, Sr-90, Th-228, Th-

Table 116 Table 117

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 5
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	51	15	25	0	0
2	100	51	30	25	0	0-4

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY
PIT 5
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
Composite	1	1535	37	41	7.2×10^{-8}
		1870	37		
Composite	1	1991	38		7.2×10^{-8}
		1294	37		
Composite	2	2257	49		3.2×10^{-8}
		2067	48		

TABLE 4-118

WASTE PIT 5 SOLIDIFICATION TCLP RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	103.000	ND
Neptunium-237	NA	0.535	0.420
Plutonium-238	NA	0.573	0.420
Plutonium-239/240	NA	0.172	0.252
Radium-226	NA	352.000	273.000
Radium-228	NA	68.000	38.900
Ruthenium-106	NA	ND	ND
Stontium-90	NA	79.000	65.300
Technetium-99	NA	199.000	206.000
Thorium-228	NA	5.120	3.300
Thorium-230	NA	204.000	0.483
Thorium-232	NA	2.580	ND
Uranium-234	NA	9.900	0.441
Uranium-235/236	NA	0.401	ND
Uranium-238	NA	3.930	ND
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	NA	0.023	ND
Uranium (Total)	NA	0.012	ND

* See Table 4-93

\+ See Table 4-93

TABLE 4-119

WASTE PIT 5 SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.082	ND	ND	
Arsenic	0.027	ND	ND	5.000
Barium	3.904	14.745	8.736	100.000
Beryllium	0.006	ND	ND	
Cadmium	0.003	ND	ND	1.000
Chromium	0.014	ND	ND	5.000
Cobalt	0.032	ND	ND	
Copper	1.916	ND	ND	
Cyanide	ND	ND	ND	
Lead	0.035	ND	ND	5.000
Manganese	2.307	ND	ND	
Mercury	0.002	ND	ND	0.200
Molybdenum	0.190	0.810	1.117	
Nickel	0.296	ND	ND	
Selenium	ND	ND	ND	1.000
Silver	0.099	ND	ND	5.000
Thallium	0.223	0.015	0.015	
Vanadium	0.815	ND	ND	
Zinc	0.326	0.094	0.160	

* See Table 4-93

\+ See Table 4-93

230 and U-234. Formula 1 had lower concentrations for Pu-239/240 and Tc-99, although the difference (199 versus 206) is not significant.

Waste Pit 5 Cement Stabilization - Radon Emissions

All radon results for Figures 4-46 and 4-47 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the waste pit. The radon emanation rate from the raw waste may be lower than the rates from the treated waste because the Pit 5 waste was extremely wet and soupy. Radon will not diffuse through water as readily as it will through a porous or semiporous substrate.

The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 83.8 pCi/g.

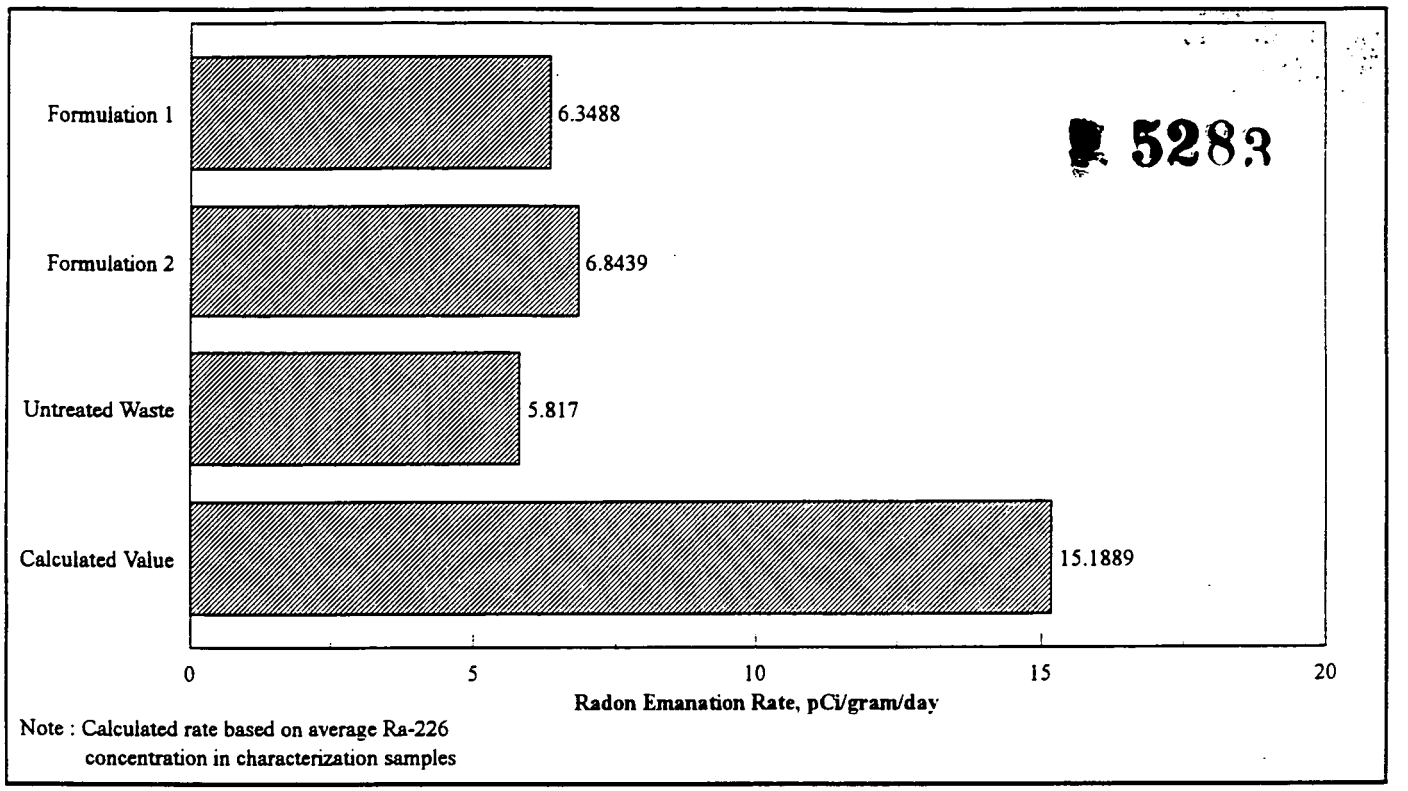


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FIGURE 4-46 -PIT 5 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

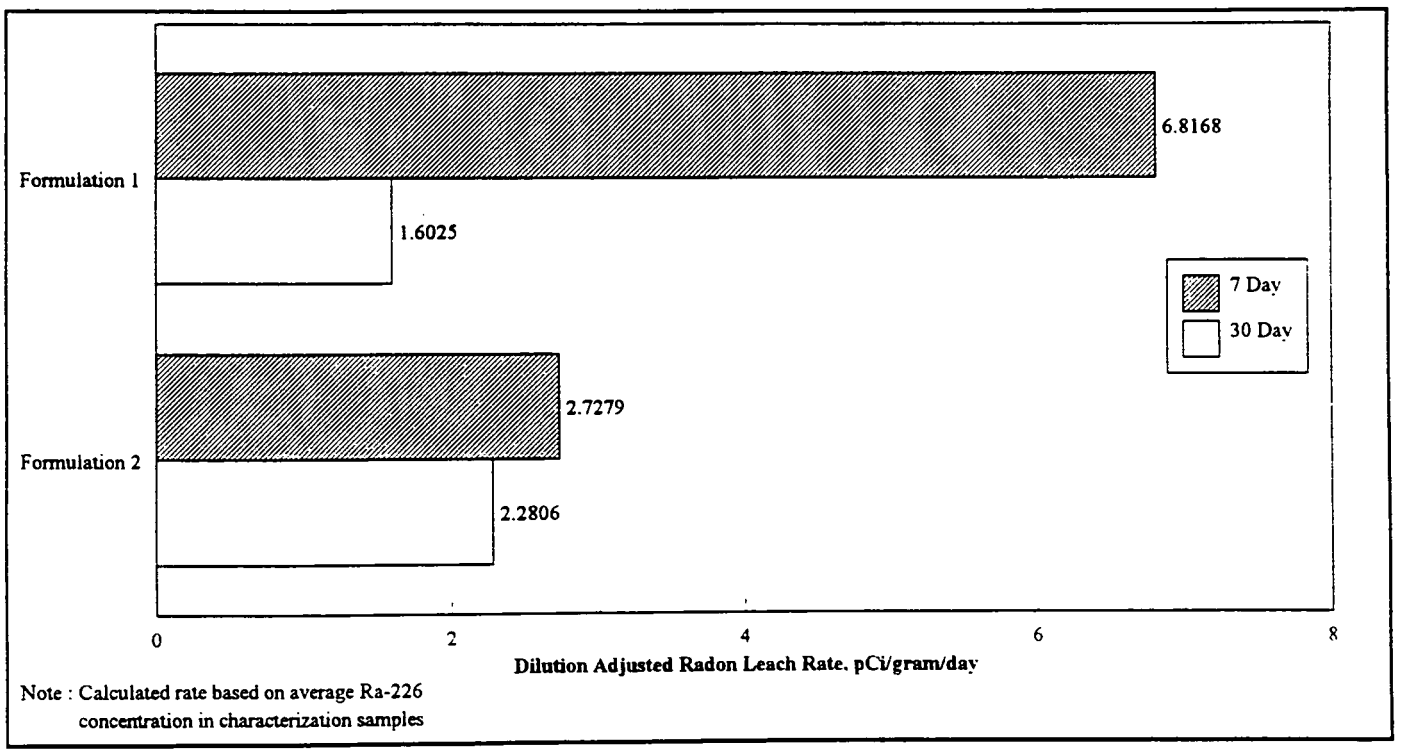

FIGURE 4-47 -PIT 5 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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WASTE PIT 6

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are presented in Tables 4-120 and 4-121. The formulation numbers in the tables are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and in Appendix A of this report, are also listed for reference.

Unconfined Compressive Strength(UCS)

The UCS values ranged from approximately 240 psi to greater than 700 psi and the values are graphically presented in Figure 4-48. The formulation numbers in the figure correspond to Table 4-120. A horizontal line is added to Figure 4-48 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into two sets: formulations with and without the addition of adsorbents, and attapulgite and clinoptilolite. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 4 (31 percent cement), and 13 (43 percent cement), respectively.

General observations and trends noted for UCS follow:

- Analyses of these figures show that almost all formulations achieved a UCS value greater than 500 psi. Only at the lowest cement loadings did the UCS not exceed 500 psi.
- The untreated Waste Pit 6 material had a high moisture content (63 percent). The percent water in the cured treated samples ranged from approximately 25 to 38 percent. Addition of adsorbents increased the UCS for a given cement loading. The increase in UCS was likely the result of attapulgite and clinoptilolite adsorbing excess water from the waste. At the lower free water concentration in the wet reagent/waste paste, the water to cement ratio would be closer to the optimum ratio. The effect of adsorbent addition was greatest with the lower cement loadings.
- Portland Type 1 and 2 cements had similar results.
- Commercial and site flyash had similar results.

Table 4-120

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

PIT 6 - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Forumlation Number	Waste	Type II Portland Cement	Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	26	26	0	0	0	0	3	1	240	24
2	100	26	26	0	6	6	0	1	1	467	31
3	100	27	20	7	6	6	3	1	1	397	36
4	100	31	51	0	6	6	8	1	1	700	58
5	100	33	54	7	6	6	12	1	1	700	74
6	100	43	43	4	12	0	17	3	1	473	76
7	100	43	43[c]	0	6	6	3	2	1	607	59
8	100	43	43	4	6	6	3	1	1	700	58
9	100	43	43[c]	4	6	6	3	2	1	700	63
10	100	43	43	4	0	12	3	3	1	700	62
11	100	43	43	4	6	6	4	4	1	700	61
12	100	43	43	0	6	6	2	4	1	700	49
13	100	43	43	0	0	0	0	4	1	700	42
14	100	51	31	0	6	6	9	1	1	700	53
15	100	54	33	7	6	6	15	1	1	700	70
16	100	60	0	0	0	0	0	5	1	700	23
17	100	64	64	0	6	6	19	1	1	700	94
18	100	64	64	0	0	0	6	3	1	700	80
19	100	68	68	7	6	6	25	1	1	385	116
20	100	80	0	0	0	0	0	5	1	700	30

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

Table 4-121

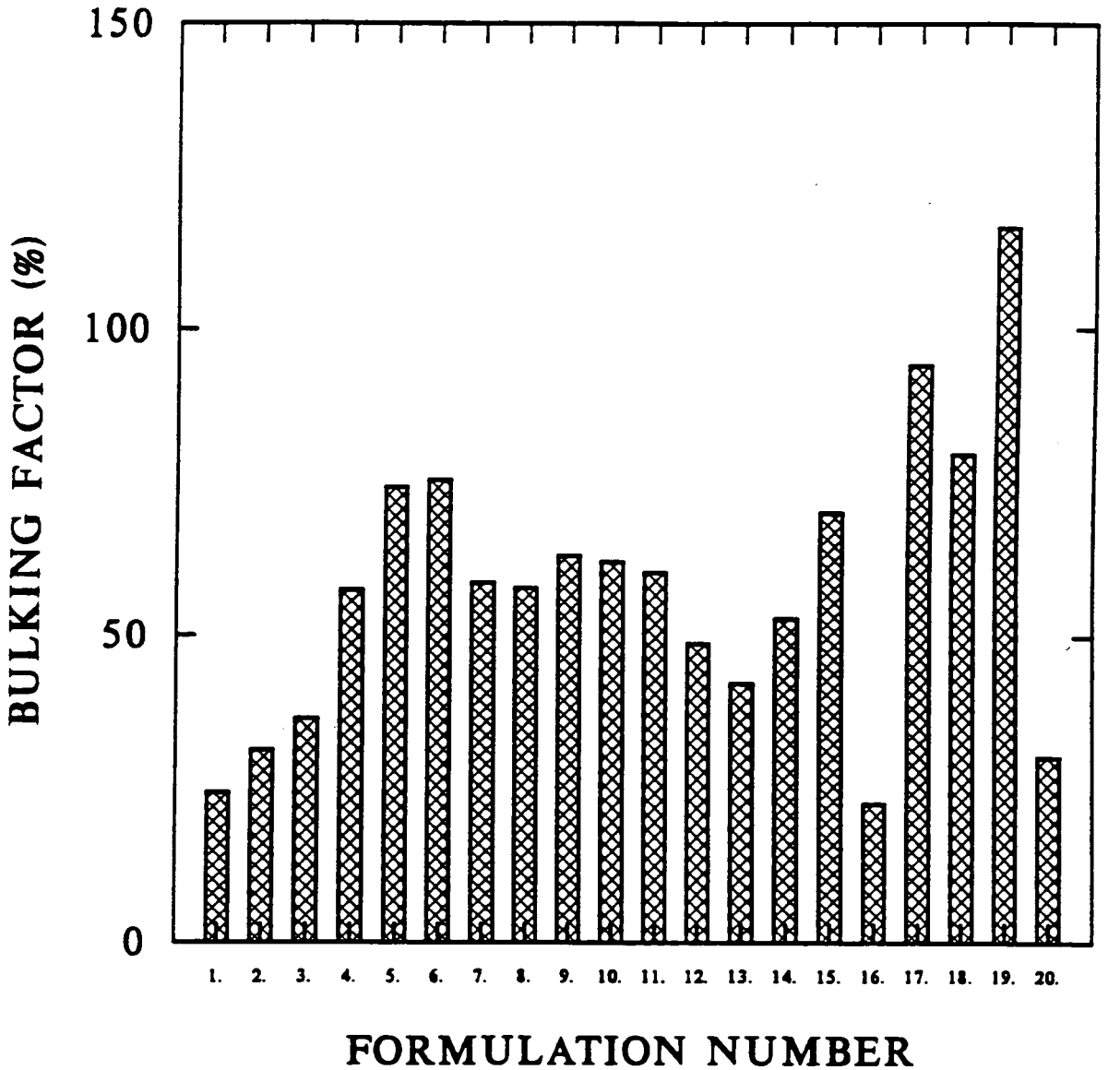
FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

PIT 6 - REMEDY SCREENING (PRELIMINARY PHASE)
CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH MTCLP Extraction Fluid (std. units)
1	LLD	LLD	ND	11.16
2	LLD	LLD	ND	10.46
3	LLD	LLD	ND	9.71
4	LLD	LLD	ND	10.94
5	LLD	LLD	0.1679	9.63
6	LLD	LLD	ND	11.54
7	LLD	LLD	ND	11.79
8	LLD	LLD	ND	11.5
9	LLD	LLD	ND	11.75
10	LLD	LLD	ND	10.5
11	LLD	LLD	ND	11.21
12	32.6	LLD	17.7111	6.25
13	LLD	LLD	ND	11.48
14	LLD	LLD	ND	12.12
15	LLD	LLD	ND	11.77
16	LLD	LLD	ND	12.57
17	LLD	LLD	ND	11.92
18	LLD	LLD	ND	12.2
19	7.8	LLD	ND	11.23
20	LLD	LLD	ND	12.74

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level

Figure 4-48



BAR GRAPH
B.F. VS. FORMULATION NUMBER
PIT 6, STAGES I & II

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- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash were investigated. Sixty percent cement loading without addition of other reagents successfully stabilized the waste.

Bulking Factor(BF)

The BFs for Waste Pit 6 samples are listed in Table 4-120 and graphically presented (bar graph) in Figure 4-48. The data are ordered by formulation number. The BFs range from approximately 25 to 120 percent for the formulations investigated. The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Pit 6 waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the remedy selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-121 for these values. The gross alpha and beta numbers are all below the limit of detection except for one sample using formulation number 12. The uranium concentration was below detection limit, except for two samples. The uranium concentrations were 0.17 and 17.7 ppm for formulation numbers 5 and 12.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.5, all uranium values were below detection limit.

This trend is graphically demonstrated in Figure 4-49. The uranium concentration in the MTCLP of the untreated waste was 263 ppm. Therefore, the treatment significantly reduced the leachability of uranium.

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As previously noted, the site and commercial flyash also had similar effect on the UCS results. Thus, site flyash could be considered for stabilizing the waste in Pit 6 instead of using commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). The shear strength of the wet reagent/waste paste was slightly higher for this pit material than for the other OU1 waste materials. The formulations that achieved a UCS of greater than 500 psi were considered processable.

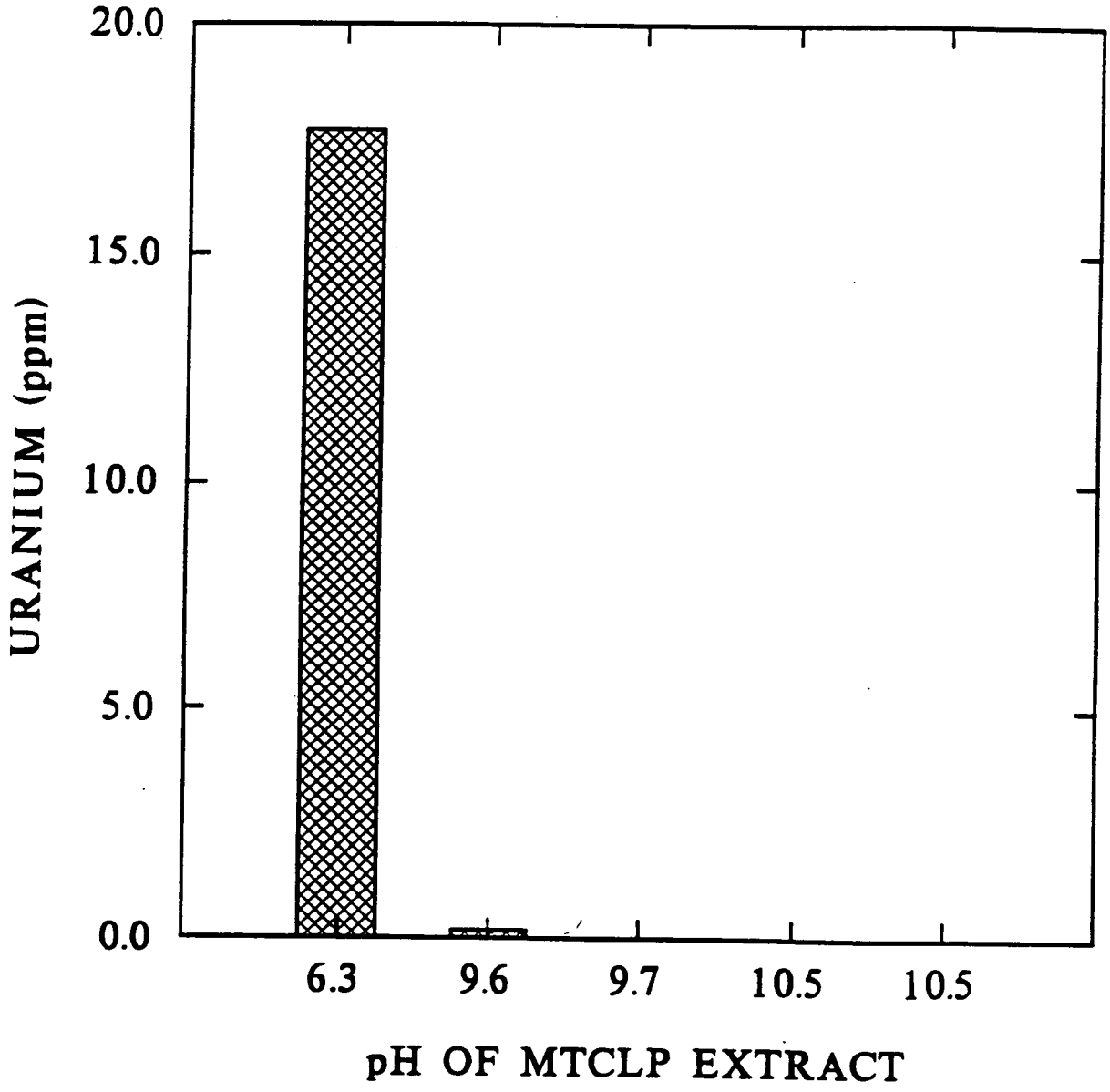
Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, increased the UCS, and had minimal effect on leachability. The effects of sodium silicate additions were ambiguous.

Recommended Formulations for Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-120 and 4-121. Analysis of the results indicates that stabilization of the Pit 6 waste can readily achieve the desired UCS and leachability values. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within the 24-hour cure time.

Figure 4-49



BAR GRAPH

URANIUM VS. MTCLP pH

PIT 6, STAGES I & II

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The UCS values, uranium leachability, and BFs were the deciding criteria for determining the formulations for the Remedy Selection (Advanced Phase) studies. The formulations had to exceed the 500 psi UCS criteria, have uranium concentrations and gross alpha and beta in the MTCLP at non-detectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without adsorbents additions which met the above requirements were selected. Formulation number 13 (cement, flyash) was chosen from the formulations presented in Tables 4-120 and 4-121. A cement/flyash/BFS formulation not previously tested with Pit 6 material was also selected. This formulation had proven to be successful in other Operable Unit 1 pit material.

Remedy Selection Tests

Formulations for the Waste Pit 6 solidification can be found in Table 4-122. UCS results, bulking factors, and permeabilities are given in 4-123. No zone samples were tested for Pit 6. Duplicate composite samples were tested with Formulation 2 and a single sample by Formulation 1. UCSs for the samples were considered acceptable, with the highest given by a sample tested with Formulation 1 (>3142 psi). Lower results were given by the two Formulation 2 samples, with the lowest having a UCS of 697 psi. The average UCS was 1662 psi. Bulking factors were low, with all samples having a bulking factor of approximately 40 percent. Permeabilities were also low, with the highest result given by the Formulation 1 sample (6.5×10^{-9} cm/s) and the lowest by one of the Formulation 2 samples (1.1×10^{-9} cm/s).

Dilution adjusted TCLP results for Waste Pit 6 TCLP radionuclides for the two formulations are shown in Table 4-124. Metals results are shown in Table 4-125. Both formulations pass the TC regulatory criteria. The leachability of the two formulations was almost identical.

A comparison of the dilutions adjusted results shows that Formula 1 seems to give the better overall results. Formula 1 had NDs for Pu-239/240 and Tc-99 while Formula 2 had dilution adjusted concentrations reported. Formula 2 had a relatively high Tc-99 dilution adjusted concentration of 65 pCi/L. Formula 1 also had lower values for Th-228, Th-230, U-238, and U-Total. Formula 2 had better results than Formula 1 with Pu-238, Sr-90, and U-234 (NDs for Formula 2). Formula 2 also had slightly lower dilution adjusted concentration of Np-237.

Table 4-122

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
PIT 6
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	53	15	25	0	4
2	100	43	43	0	0	2

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

Table 4-123

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY
PIT 6
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
Composite	1	>3139	41	41	6.5×10^{-9}
		>3142	41		
Composite	2	697	41		1.1×10^{-9}
		936	41		
Composite	2	1032	40		4.1×10^{-9}
		1028	39		

TABLE 4-124

WASTE PIT 6 SOLIDIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization + (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	ND	ND
Neptunium-237	NA	0.670	0.649
Plutonium-238	NA	0.197	ND
Plutonium-239/240	NA	ND	0.254
Radium-226	NA	ND	ND
Radium-228	NA	ND	ND
Stontium-90	NA	11.879	ND
Technetium-99	NA	ND	65.330
Thorium-228	NA	2.049	2.538
Thorium-230	NA	1.497	2.726
Thorium-232	NA	ND	ND
Uranium-234	NA	1.281	ND
Uranium-235/236	NA	ND	ND
Uranium-238	NA	3.211	7.652
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	NA	ND	ND
Uranium (Total)	NA	0.010	0.023

* See Table 4-93

\+ See Table 4-93

TABLE 4-125

WASTE PIT 6 SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION*

	Raw Waste Characterization+ (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	ND	ND	ND	
Arsenic	0.550	ND	ND	5.000
Barium	1.731	1.324	1.058	100.000
Beryllium	0.009	ND	ND	
Cadmium		ND	ND	1.000
Chromium	ND	ND	0.028	5.000
Cobalt	ND	ND	ND	
Copper	ND	0.024	0.036	
Cyanide	ND	ND	ND	
Lead	0.596	ND	ND	5.000
Manganese	1.255	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	ND	ND	0.098	
Nickel	0.095	ND	ND	
Selenium	ND	ND	ND	1.000
Silver	0.047	ND	ND	5.000
Thallium	0.660	ND	ND	
Vanadium	ND	ND	ND	
Zinc	1.551	ND	ND	

* See Table 4-93

\+ See Table 4-93

Waste Pit 6 Cement Solidification - Radon Emissions

All radon results shown in Figures 4-50 and 4-51 were multiplied by the reagent dilution factor so that all results are expressed relative to the amount of pit waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. Figures 4-50 and Figure 4-51 both show very low or undetectable radon emission rates. This result was not unexpected because the calculated emission rate was so low. The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 3.9 pCi/g. An emanation rate from the untreated waste was not reported because the test was inadvertently overlooked and was not performed.

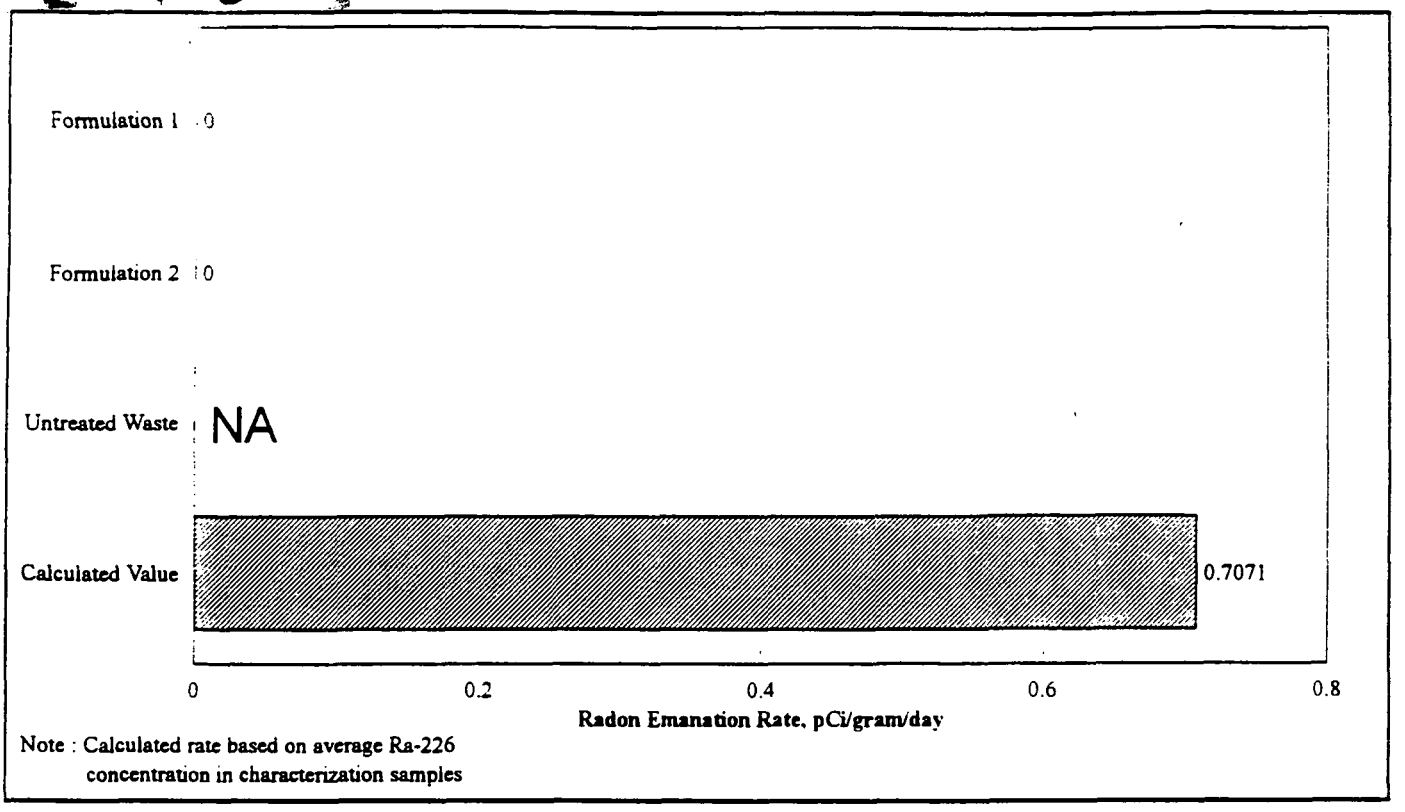

FIGURE 4-50 -PIT 6 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

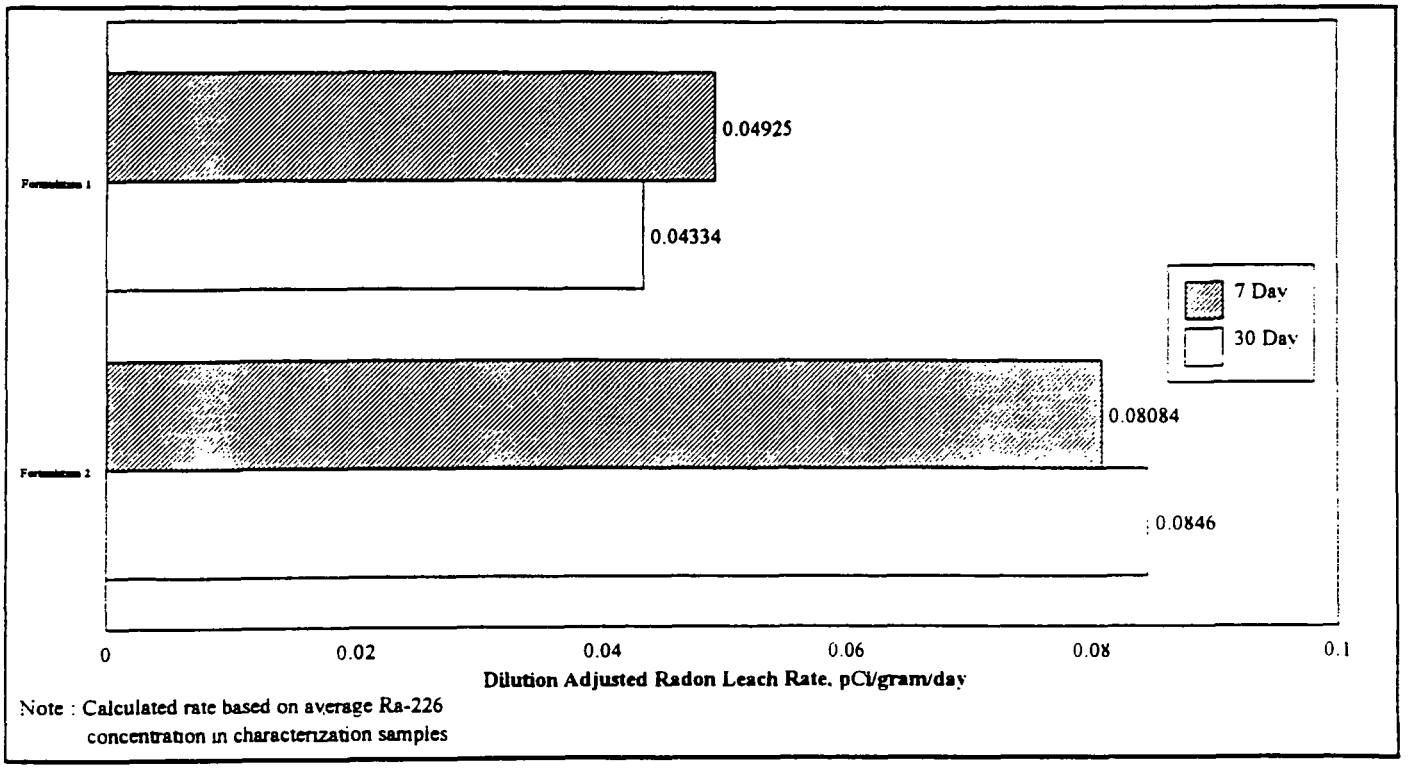

FIGURE 4-51 -PIT 6 STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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BURN PIT

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are presented in Tables 4-126 and 4-127. The formulation numbers in the tables are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and Appendix A, are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 55 psi to greater than 700 psi and the values are graphically presented in Figure 4-52. The formulation numbers in the figure correspond to Table 4-126. A horizontal line is added to Figure 4-52 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. None of the original 20 formulations from Stage 1 met the UCS criteria. This includes the 80 percent cement loading formulation and the 68/68 percent cement/flyash loading formulation. In Stage II, multiple formulations with BFS, calcium hydroxide, or ferrous chloride supplementation were tested. In addition, since 6 to 12 percent adsorbent loading appears to lower the UCS, a test with reduced levels of clinoptilolite was performed.

General observations and trends noted for UCS follow:

- Analyses of statistical trends in the data show that with adsorbents added to the waste, the UCS generally increases with cement loading and that 80 to 90 percent cement loading was necessary to meet the UCS criteria. When both attapulgite and clinoptilolite are at six (6) percent loading, none of the formulation met the UCS criteria. The highest cement and flyash loadings investigated with the adsorbents added was 68 percent cement and flyash.
- Addition of adsorbents lowered the UCS for a given cement loading.
- Addition of BFS increased the UCS. All BFS formulations had UCS values greater than 500 psi.
- The UCS value was higher with Type 1 portland cement than with Type 2 portland cement.

TABLE 4-126

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

BURN PIT - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Calcium Hydroxide	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	20	27	7	6	6	53	0	0	1	1	110	126
2	100	26	26	0	6	6	50	0	0	1	1	56	118
3	100	26	26	0	0	0	33	0	0	3	1	268	79
4	100	31	51	0	6	6	61	0	0	1	1	255	161
5	100	33	54	7	6	6	83	0	0	1	1	55	208
6	100	43	43	4	6	6	72	0	0	4	1	165	186
7	100	43	43[c]	0	6	6	57	0	0	2	1	187	161
8	100	43	43	4	0	12	67	0	0	3	1	207	173
9	100	43	43	4	12	0	79	0	0	3	1	209	189
10	100	43	43	4	6	0	59	0	0	1	1	241	165
11	100	43	43[c]	4	6	6	60	0	0	2	1	274	172
12	100	43	43	0	6	6	67	0	0	4	1	277	165
13	100	43	43	0	0	0	53	0	0	4	1	337	139
14	100	51	15	0	0	0	55	31	0	_	2	700	132
15	100	51	31	0	6	6	60	0	0	1	1	329	155
16	100	51	31	0	0	0	53	15	0	_	2	700	139
17	100	54	33	7	6	6	67	0	0	1	1	289	181
18	100	54	33	0	0	4	54	0	0	_	2	700	129
19	100	60	0	0	0	0	38	0	0	5	1	393	86
20	100	64	50	0	0	0	79	50	0	_	2	700	222

TABLE 4-126

(Continued)

BURN PIT - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Type F Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Calcium Hydroxide	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
21	100	64	64	0	6	6	80	0	0	1	1	374	222
22	100	64	64	0	0	0	65	0	0	3	1	441	183
23	100	68	68	7	6	6	93	0	0	1	1	315	253
24	100	72	44	0	0	0	70	21	0	_	2	700	192
25	100	73	21	0	0	0	70	44	0	_	2	700	181
26	100	75	50	0	0	6	66	0	0	_	2	700	182
27	100	80	0	0	0	0	43	0	0	5	1	313	107
28	100	80	0	0	0	0	55	0	1	_	2	700	118
29	100	80	80	0	0	0	79	0	0	_	2	700	217
30	100	100	0	0	0	0	52	0	0	_	2	700	127
31	100	100	0	0	0	0	49	0	0	_	2	700	120
32	100	100	100	0	0	0	90	0	0	_	2	700	266
33	100	120	0	0	0	0	60	0	1	_	2	700	152
34	100	150	0	0	0	0	68	0	0	_	2	700	176
35	100	150	0	0	0	0	66	0	0	_	2	700	174

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

TABLE 4-127

FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

BURN PIT - REMEDY SCREENING (PRELIMINARY PHASE)
CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	46.7	21.1	5.9965	7
2	LLD	LLD	1.049	8.5
3	41	LLD	4.6705	7.09
4	LLD	LLD	3.9751	7.5
5	28	11.5	3.8658	7.5
6	LLD	LLD	0.1015	8.5
7	LLD	LLD	0.5132	10.01
8	25	LLD	3.9338	7.19
9	34.9	LLD	4.1633	6.91
10	48	13.3	5.005	7
11	LLD	LLD	1.5787	7.41
12	LLD	10.2	2.4832	7.5
13	LLD	LLD	1.1178	8.5
14	LLD	LLD	ND	11.4
15	LLD	LLD	0.1803	10.5
16	LLD	LLD	ND	10.21
17	LLD	LLD	ND	10
18	LLD	LLD	ND	10.21
19	35.1	10.8	0.2291	10.5
20	LLD	LLD	ND	9.96
21	LLD	LLD	0.1704	10.26
22	LLD	LLD	2.4937	8.23
23	LLD	0.6	ND	9.58
24	LLD	LLD	ND	11.25
25	LLD	LLD	ND	11.12
26	LLD	LLD	ND	11.49
27	23.2	11.8	ND	10.5
28	LLD	LLD	ND	11.95
29	LLD	LLD	ND	10.1

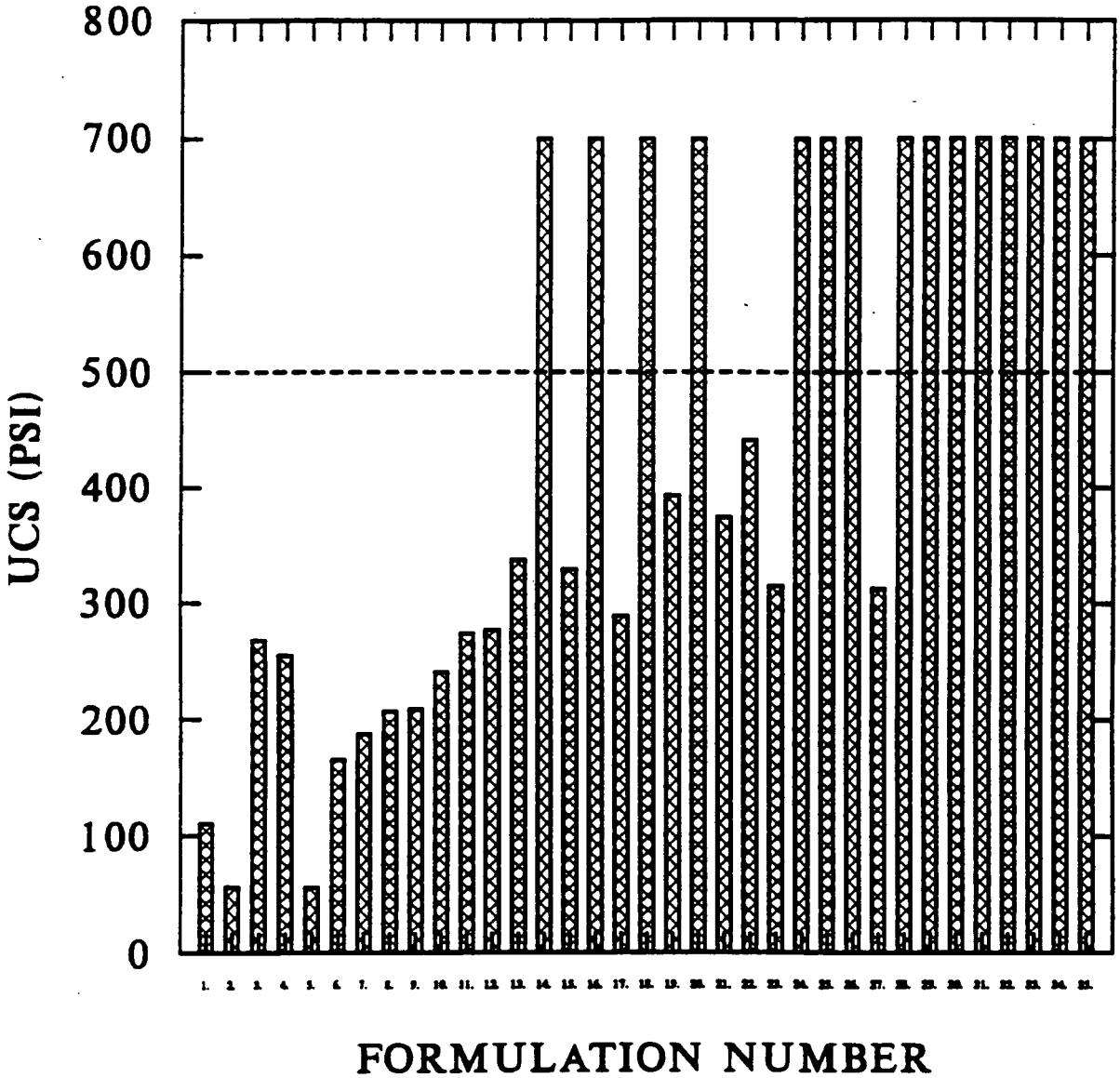
TABLE 4-127

(Continued)

BURN PIT - REMEDY SCREENING (PRELIMINARY PHASE)
CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
30	LLD	LLD	ND	12
31	LLD	LLD	ND	11.88
32	LLD	LLD	ND	11.08
33	LLD	LLD	ND	12.02
34	LLD	LLD	0.05	11.91
35	LLD	LLD	ND	11.98

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown
ND - Not detected
LLD - Under the lower limit detection level



BAR GRAPH
UCS VS. FORMULATION NUMBER
BURN PIT, STAGES I & II

Figure 4-52

- Commercial and site flyash had similar results.
- In this study, 60, 80, 100, and 150 percent cement loadings without addition of adsorbents, BFS, or flyash were investigated. One hundred percent cement loading without addition of other reagents successfully stabilized the waste.
- Addition of 1 percent calcium hydroxide to 80 percent cement improved the UCS of the treated sample.

Bulking Factor (BF)

The BFs for the Burn Pit samples are listed in Table 4-126 and graphically presented (bar graph) in Figure 4-53. The data are ordered by formulation number. The BFs range from approximately 80 to 265 percent for the formulations investigated.

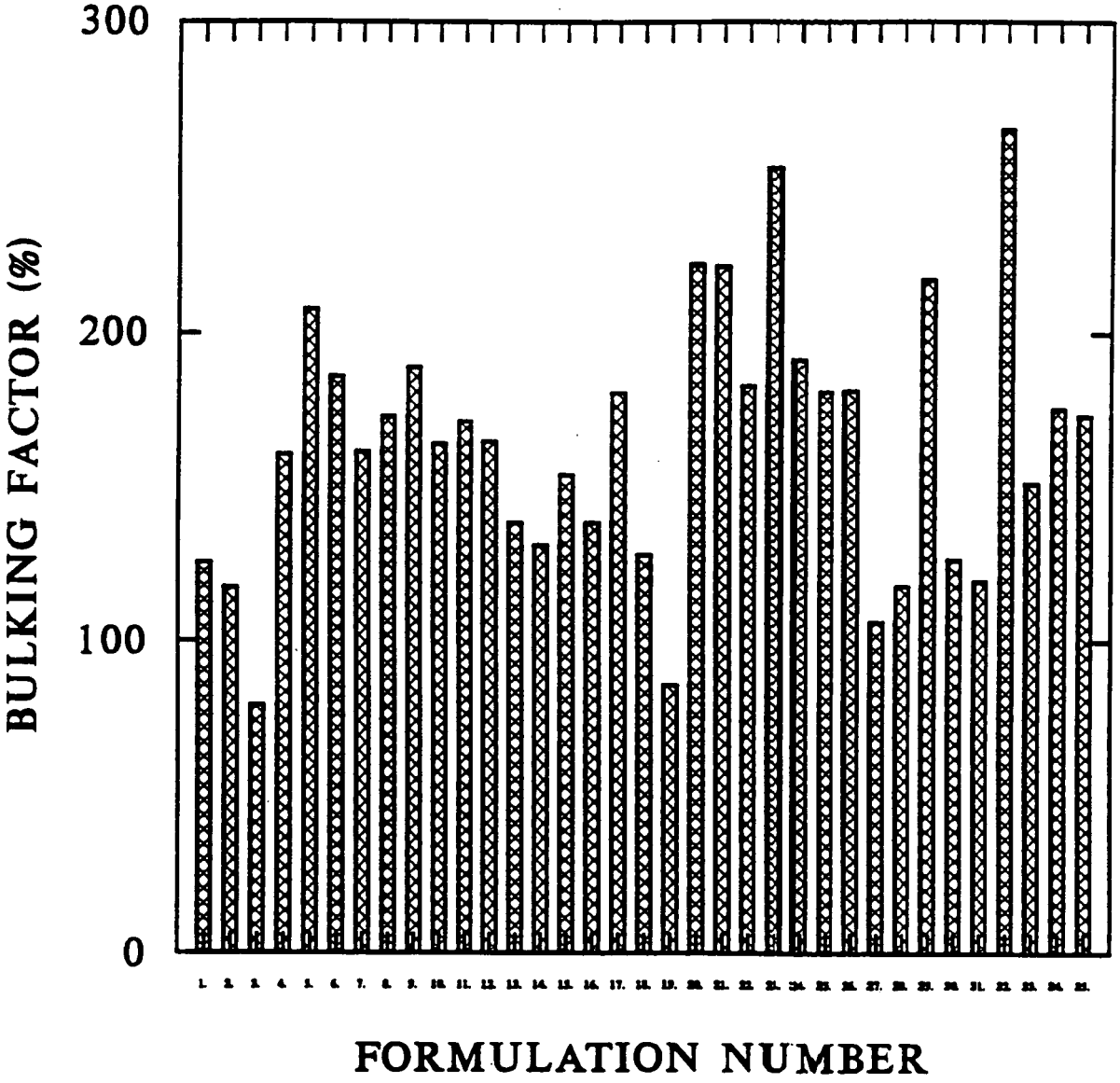
The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than did the addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase the cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Burn Pit waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the Remedy Selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Tables 4-127 for these values. The gross alpha and beta values ranged from lower limits of detection to approximately 47 and 21 dpm/4 cc. The uranium concentrations varied between below the detection limit to 6 ppm.



BAR GRAPH

B.F. VS. FORMULATION NUMBER

BURN PIT, STAGES I & II

0524

Figure 4-53

Analysis of data contour plots (see Appendix A) shows that cement loadings greater than approximately 50 percent and flyash greater than zero percent loadings lower the gross alpha and beta and uranium values to their minimum values.

The addition of BFS to the formulation lowered the radionuclide leachability. Also, the addition of clinoptilolite at 4 percent loading reduced the radionuclide leachability.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.5, all uranium values were below detection limit.

The uranium concentration in the MTCLP of the untreated waste was 19 ppm. Therefore, the treatment significantly reduced the leachability of uranium.

Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As previously noted, the site and commercial flyash also had similar effect on the UCS results. Thus, site flyash could be considered for stabilizing the waste in Burn Pit instead of using commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). The formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, lowered the UCS, and had minimal effects on leachability. The effects of sodium silicate additions were ambiguous.

Recommended Formulations for Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-126 and 4-127. Analyses of the results indicates that stabilization of the Burn Pit waste could be achieved. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within a 24-hour cure time.

The UCS values, uranium, gross alpha and beta leachability, and BFs were the deciding criteria for determining the formulations for the Remedy Selection (advanced phase) studies. The formulations had to exceed the 500 psi UCS criteria, have uranium, gross alpha and beta concentrations in the MTCLP at nondetectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without adsorbent additions which met the above requirements were selected. Choosing from the formulations presented in Tables 4-126 and 4-127, formulation numbers 14 (cement, flyash, and BFS) and 18 (cement, flyash, and clinoptilolite) were selected.

Remedy Selection Tests

Formulations for the Burn Pit stabilization samples can be found in Table 4-128. Bulking factors, UCS results, and permeabilities are given in Table 4-129. The UCSs for the Burn Pit were lower than for most of the other pits. The highest value was exhibited by the sample of Zone 1, Formulation 1, which was 1828 psi. The lowest was given by the Zone 2, Formulation 2 sample, which was 522 psi, very near the lower limit of approximately 500 psi. The average UCS was 1080 psi. Bulking factors were considered high, with the highest given by the Zone 1, Formulation 1 sample (148 percent), and the lowest given by the Zone 3, Formulation 2 sample (123 percent). Average bulking factor was 132 percent. All permeabilities were at least 3.0×10^{-7} cm/s.

Results for the Burn Pit TCLP radionuclides for the two formulations are shown in Table 4-130. Both formulations pass the TC regulatory criteria. The leachability of the two formulations was almost identical. There was not much difference in the leachability of Formulations 1 and 2 for metals shown in Table 4-131.

TABLE 4-128

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
BURN PIT
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Normalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	51	15	31	0	44-69
2	100	54	33	0	4-6	42-63

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

TABLE 4-129

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY
BURN PIT
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
1	1	1828	148	132	5.3×10^{-9}
2	1	770	126		5.0×10^{-7}
3	1	1656	135		8.1×10^{-9}
1	2	530	138		1.2×10^{-8}
2	2	522	124		3.0×10^{-7}
3	2	1171	123		7.3×10^{-8}

TABLE 4-130
BURN PIT SOLIDIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Neptunium-237	ND	0.904	0.507
Plutonium-238	ND	0.293	0.333
Plutonium-239/240	ND	0.426	0.320
Radium-226	23.600	46.079	44.050
Radium-228	4.500	17.051	16.450
Stontium-90	ND	ND	ND
Technetium-99	25.000	79.800	ND
Thorium-228	2.010	1.498	2.190
Thorium-230	2.160	1.117	0.614
Thorium-232	ND	ND	ND
Uranium-234	10200.000	1.104	2.610
Uranium-235/236	643.000	ND	ND
Uranium-238	11000.000	1.020	2.140
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	ND	0.001	ND
Uranium (Total)	23.920	0.003	0.008

* See Table 4-93

\+ See Table 4-93

TABLE 4-131

BURN PIT SOLIDIFICATION TCLP METALS DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.095	ND	ND	
Arsenic	0.078	ND	ND	5.000
Barium	1.395	3.130	3.660	100.000
Beryllium	0.005	ND	ND	
Cadmium	0.017	ND	ND	1.000
Chromium	0.176	0.069	0.054	5.000
Cobalt	0.050	ND	ND	
Copper	0.053	0.059	0.054	
Cyanide	ND	ND	ND	
Lead	0.065	0.013	0.031	5.000
Manganese	3.820	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	0.025	0.067	ND	
Nickel	0.081	ND	ND	
Selenium	0.190	0.005	ND	1.000
Silicon	4.760	5.300	4.370	
Silver	0.121	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.070	ND	ND	
Zinc	0.513	0.081	0.198	

* See Table 4-93
\+ See Table 4-93

Burn Pit Cement Solidification - Radon Emissions

All radon results shown in Figures 4-54 and 4-55 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the waste pit. The figures show radon emission rates from the treated waste in the same range as the untreated waste in air, and significantly lower than the calculated rate. For radon emanation rates for the levels reported, the differences detected by the instrument for the emanation in air cannot be considered significant because changing background levels could account for the difference.

The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average concentration of Ra-226 in the characterization samples was 8.9 pCi/g.

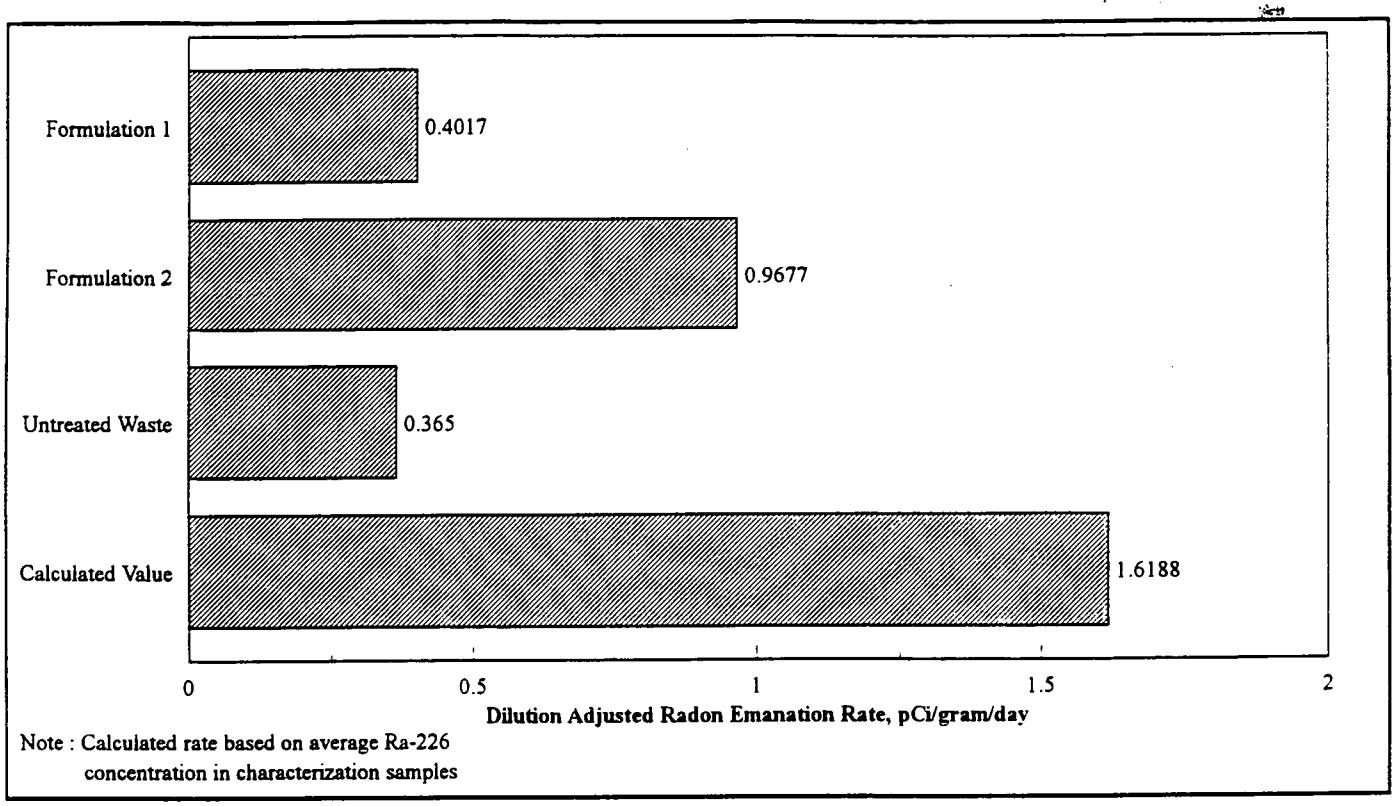


FIGURE 4-54 BURN PIT STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

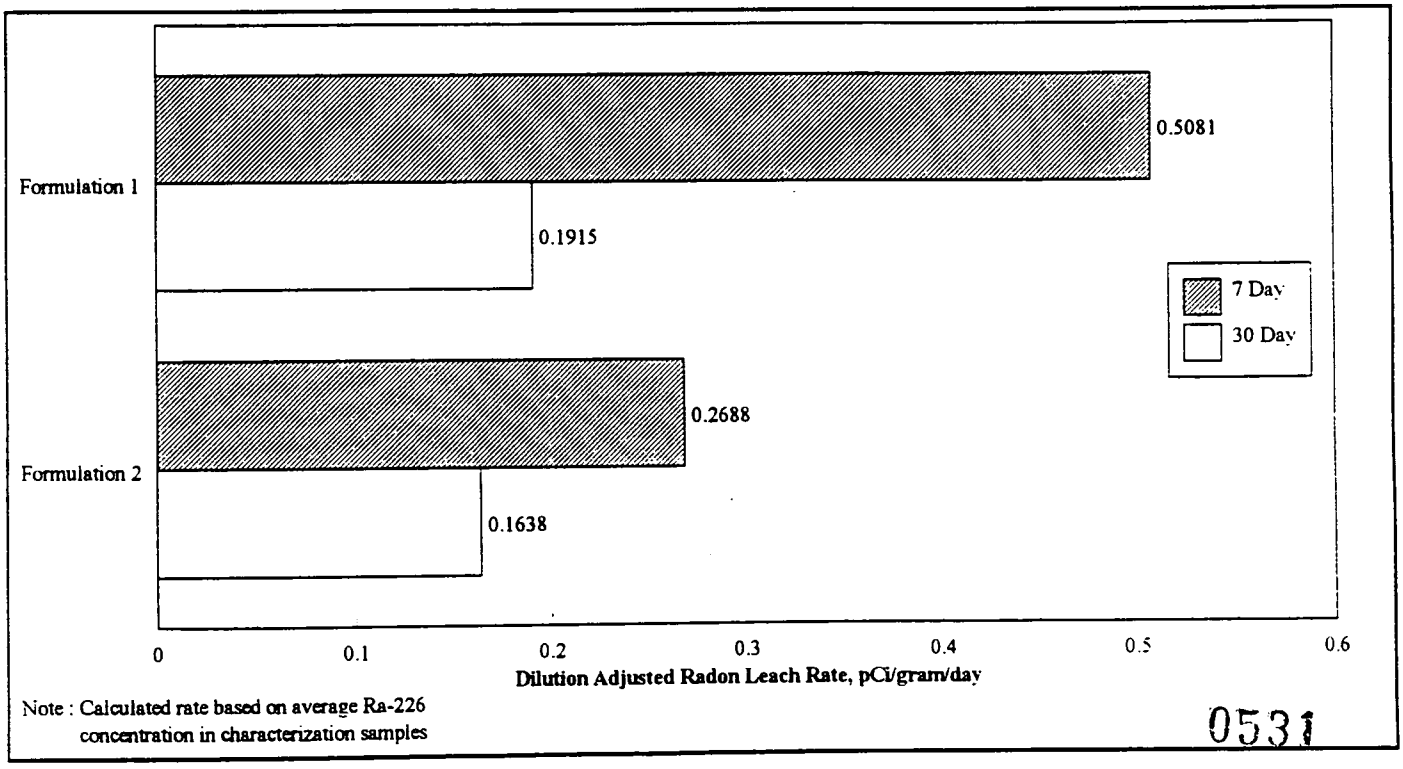


FIGURE 4-55 BURN PIT STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

CLEARWELL

Remedy Screening Tests

The formulations investigated, UCSs, BFs, and MTCLP radiological results from the preliminary phase are presented in Tables 4-132 and 4-133. The formulation numbers in the tables are in order of increasing cement loading, flyash loading, and UCS values. The group and stage values, as defined in the Operable Unit 1 Treatability Work Plan (DOE 1991) and Appendix A, are also listed for reference.

Unconfined Compressive Strength (UCS)

The UCS values ranged from approximately 40 psi to greater than 700 psi; the values are graphically presented in Figure 4-56. The formulation numbers in the figure correspond to Table 4-132. A horizontal line is added to Figure 4-56 at 500 psi to assist in visualizing the number of formulations that had UCS values greater than 500 psi. The UCS discussion can be grouped into three sets: formulations with and without the addition of adsorbents, attapulgite and clinoptilolite alone, and formulations with activated BFS in addition to the cement/flyash reagents. The formulation numbers (and cement loadings) for the lowest level of reagent addition in each group to meet the UCS requirements are 8 (31 percent cement), 6 (26 percent cement), and 1 (15 percent cement), respectively.

General observations and trends noted for UCS follow:

- Analysis of statistical trends in the data show that with adsorbents, cement, and flyash added to the waste, the UCS generally increases with cement loading and that at least 70 percent cement is necessary to meet the UCS requirement. It is important to note that these samples have adsorbents in them which lower the UCS, especially at the lower cement loading. When the adsorbents are not added to the sample (see formulation numbers 5 versus 6), the UCS is significantly higher.
- Addition of adsorbents lowered the UCS for a given cement loading.
- Addition of BFS increased the UCS.
- Portland Type 1 and 2 cements had similar results.

FORMULATIONS[a] WITH UCS AND BULKING FACTOR RESULTS

CLEARWELL - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
1	100	15	0	0	0	0	11	15	_	2	700	45
2	100	15	15	0	0	0	11	0	_	2	268	44
3	100	26	0	0	0	0	11	26	_	2	41	58
4	100	26	0	0	0	0	9	0	_	2	623	35
5	100	26	26	0	6	6	40	0	1	1	338	113
6	100	26	26	0	0	0	24	0	3	1	511	79
7	100	27	20	7	6	6	40	0	1	1	227	123
8	100	31	51	0	6	6	49	0	1	1	554	151
9	100	33	54	7	6	6	50	0	1	1	549	170
10	100	43	43	4	6	6	0	0	4	1	342	114
11	100	43	43	4	6	6	50	0	1	1	426	156
12	100	43	43	4	0	12	53	0	3	1	491	167
13	100	43	43[c]	0	6	6	47	0	2	1	515	160
14	100	43	43	4	12	0	58	0	3	1	534	177
15	100	43	43	0	6	6	50	0	4	1	601	158
16	100	43	43	0	0	0	31	0	4	1	700	116
17	100	43	43[c]	4	6	6	48	0	2	1	700	166
18	100	51	31	0	6	6	47	0	1	1	700	146
19	100	54	33	7	6	6	45	0	1	1	499	160

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(Continued)

CLEARWELL - REMEDY SCREENING (PRELIMINARY PHASE) - CEMENT STABILIZATION

Formulation Number	Waste	Type II Portland Cement	Flyash	Sodium Silicate	Attapulgite	Clinoptilolite	Water	Blast Furnace Slag	Group[b]	Stage[b]	UCS (psi)	Bulking Factor
20	100	60	0	0	0	0	23	0	5	1	700	77
21	100	64	64	0	6	6	61	0	1	1	665	207
22	100	64	64	0	0	0	48	0	3	1	700	180
23	100	68	68	7	6	6	67	0	1	1	627	230
24	100	80	0	0	0	0	31	0	5	1	700	100

[a]Reagent loadings in grams per 100 grams of wet weight of waste
[b]As listed in the Operable Unit 1 Treatability Study Work Plan
[c]Site flyash used

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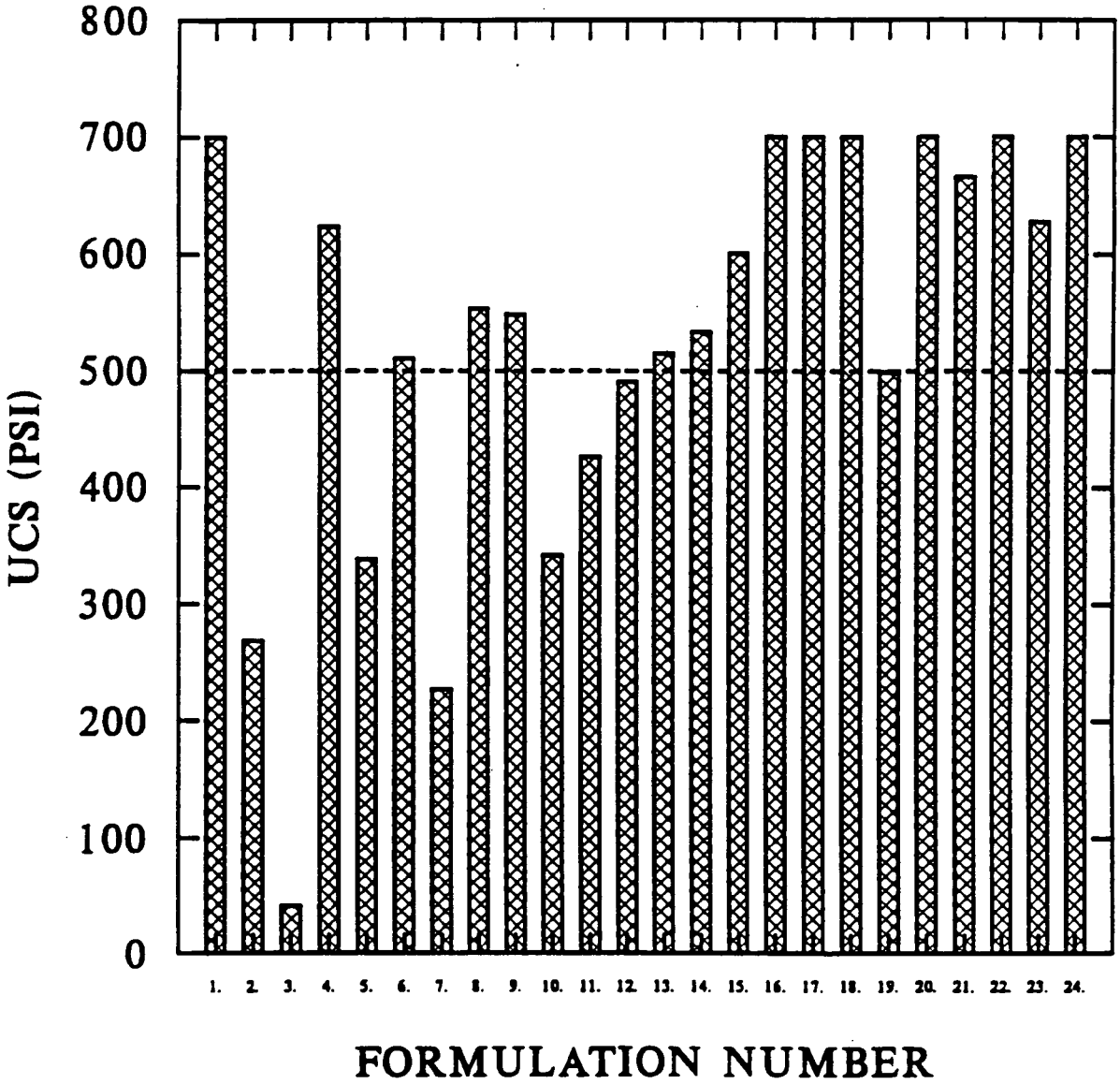
FORMULATIONS[a] WITH ANALYTICAL RESULTS[b]

CLEARWELL - REMEDY SCREENING (PRELIMINARY PHASE) CEMENT STABILIZATION

Formulation Number	Gross Alpha (dpm/4cc)	Gross Beta (dpm/4cc)	Uranium by IC (ppm)	pH of MTCLP Extraction Fluid (std. units)
1	LLD	LLD	2.46	7.42
2	22.7	18.4	4.72	7.34
3	LLD	9.8	5.46	7.47
4	LLD	16.8	ND	9
5	LLD	11.2	3.0543	7.67
6	LLD	18.1	ND	10.62
7	LLD	LLD	2.8642	7.83
8	LLD	LLD	1.0186	8.24
9	LLD	LLD	2.5685	7.76
10	LLD	LLD	2.5986	7.7
11	LLD	LLD	2.6424	7.63
12	LLD	LLD	3.0242	7.65
13	LLD	LLD	ND	10.22
14	LLD	11.2	0.7884	8.64
15	LLD	LLD	2.039	7.87
16	17.5	LLD	2.271	8
17	LLD	LLD	ND	8.88
18	LLD	10.6	ND	11.18
19	LLD	LLD	0.9521	9.05
20	LLD	LLD	ND	12.07
21	LLD	LLD	ND	11.17
22	LLD	LLD	ND	10.7
23	LLD	LLD	0.3223	9.22
24	LLD	LLD	ND	12.05

[a]Reagent loading per 100 grams of wet weight of waste
[b]Only metals that have results above detection limits are shown.
ND - Not detected
LLD - Under the lower limit detection level



BAR GRAPH
UCS VS. FORMULATION NUMBER
CLEARWELL, STAGES I & II

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Figure 4-56

- Samples with site flyash had larger UCS values than samples with commercial flyash.
- In this study, 60 and 80 percent cement loadings without addition of adsorbents, BFS, or flyash were investigated. Sixty percent cement loadings without addition of other reagents successfully stabilized the waste.

Bulking Factor (BF)

The BFs for Clearwell samples are listed in Table 4-132 and graphically presented (bar graph) in Figure 4-57. The data are ordered by formulation number. The BFs range from approximately 35 to 230 percent for the formulations investigated.

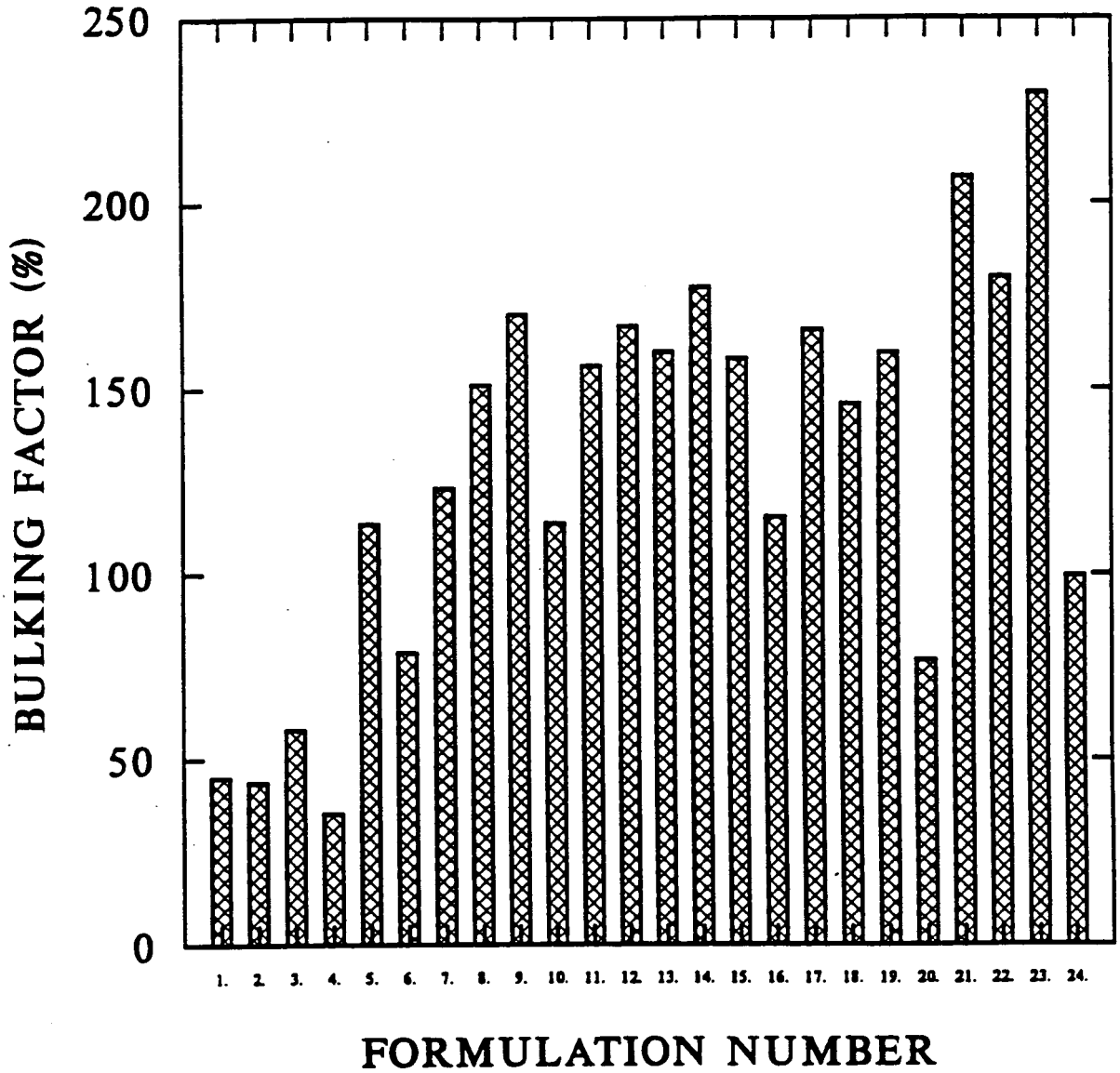
The BF was increased by addition of all solid reagents and water. The lowest BFs were measured with the lowest loading of reagents. Typically, flyash, attapulgite, and clinoptilolite additions had a larger effect on the BF than addition of cement or BFS. Therefore, to minimize the BF, it is preferable to increase cement loading instead of flyash.

MTCLP - RCRA Metals

All of the metal concentrations in the MTCLP for both the untreated and treated Clearwell waste were below one-half the TC regulatory criteria for these samples. The RCRA metal concentrations in the MTCLP were, therefore, not a selection criteria for determining the formulations to test in the remedy selection (advanced) phase.

MTCLP - Radionuclides

Indicators of radionuclides leachability for the MTCLP leach test include gross alpha, gross beta, and uranium concentrations in the MTCLP leachates. See Table 4-133 for these values. The gross alpha and beta values range between lower limits of detection to 23 and 18.5 dpm/4 cc, respectively. Most of the values are lower limits of detection. The uranium concentration varies between below the detection limit and approximately 3 ppm.



BAR GRAPH
B.F. VS. FORMULATION NUMBER
CLEARWELL. STAGES I & II

Figure 4-57

Analysis of the data plots (see Appendix A) shows that cement loadings greater than approximately 50 percent are required to lower the gross beta and uranium values to their minimum values when adsorbents are added to the stabilization formulation.

The water solubility of uranium compounds is normally lower at higher pHs. This trend was observed for the MTCLP samples. At pH values above 10.5, all uranium values were below the detection limit. This trend is graphically demonstrated in Figure 4-58. The pH of the MTCLP extract is unusually low for the cement loadings that were used in these experiments. It is presumed that this is due to an unidentified material in the waste which slowly neutralizes part of the alkalinity of the added portland cement.

The uranium concentration in the MTCLP of the untreated waste was 4.9 ppm. Therefore, the treatment reduced the leachability of uranium.

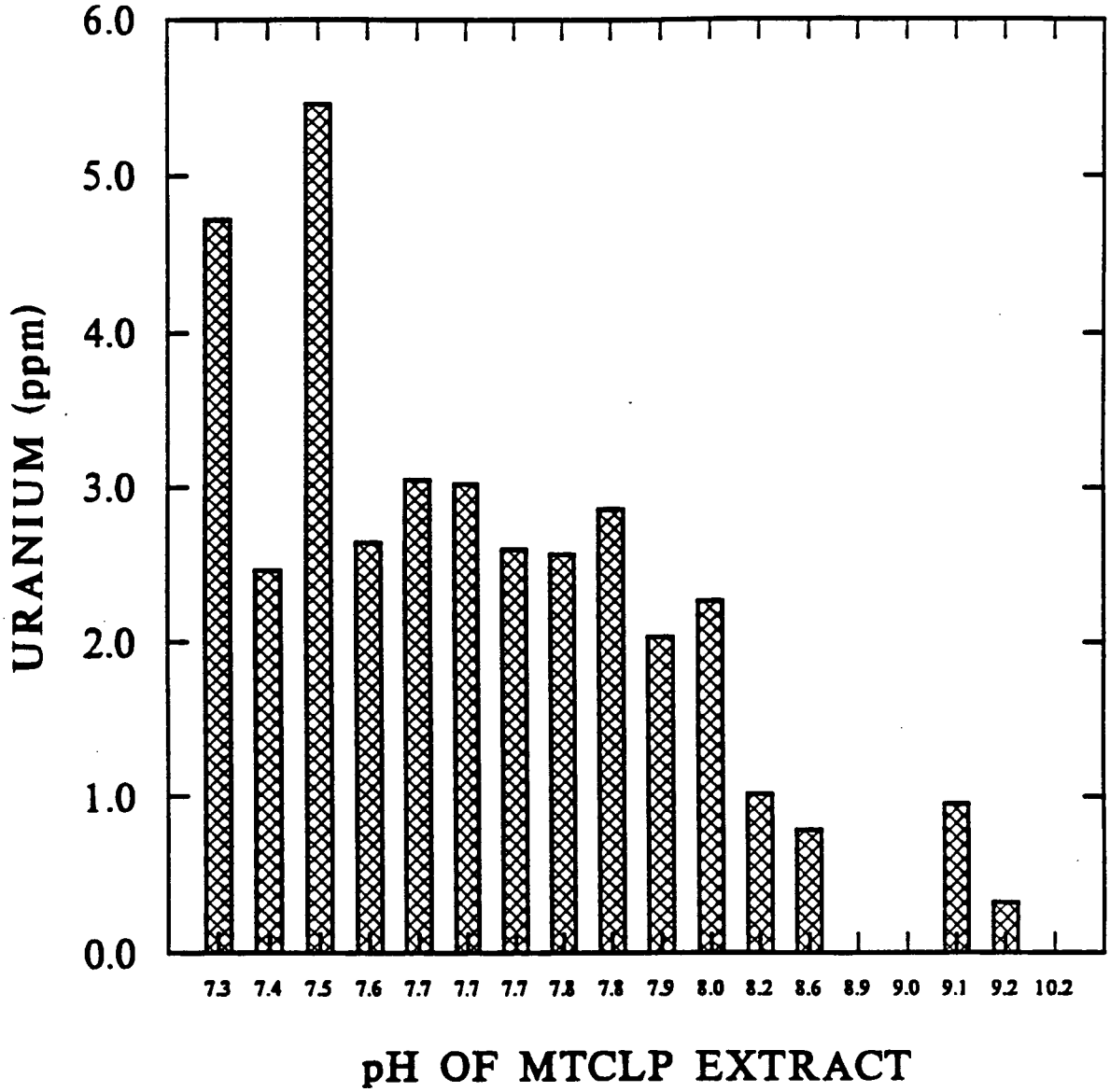
Commercial Type F flyash and site flyash were equally effective at controlling the leachability of the treated waste. As noted above, the site and commercial flyash also had similar effect on the UCS results. Thus, site flyash could be considered for stabilizing the waste in the Clearwell instead of buying commercial flyash.

Processability

The processability of the treated waste was determined by measuring the shear strength, PR, and temperature rise when the reagents were added to the waste. The wet paste had low shear strength when mixed, had acceptable structural integrity (greater than 3.0 tsf PR at a 24-hour cure time), and low temperature rise (less than or equal to 3°C). Formulations that achieved a UCS of greater than 500 psi were considered processable.

Effect of Attapulgite, Clinoptilolite, and Sodium Silicate

The addition of attapulgite and clinoptilolite increased the BF, lowered the UCS, and had minimal effect on leachability. The addition of sodium silicate increased the UCS.



BAR GRAPH
URANIUM VS. MTCLP pH
CLEARWELL, STAGES I & II

Figure 4-58

Recommended Formulations for Remedy Selection (Advanced Phase)

The performance of the Remedy Screening (preliminary phase) samples are summarized in Tables 4-132 and 4-133. Analysis of the results indicates that stabilization of the Clearwell waste can achieve the desired UCS and leachability values. All formulations passed the TC regulatory requirements. The wet reagent/waste paste was readily mixable and set to greater than 4.5 tsf within a 24-hour cure time.

The UCS values, uranium and gross beta leachability, and BFs were the deciding criteria for determining the formulations for the Remedy Selection (Advanced Phase) studies. The formulations had to exceed the 500 psi UCS criteria, have uranium concentrations in the MTCLP at nondetectable levels, and minimized BFs. In order to minimize the BF, the lowest cement, flyash, and BFS loadings without adsorbent additions which met the above requirements were selected. Choosing from the formulations presented in Tables 4-132 and 4-133, Formulations 1 (cement and BFS) and 4 (cement only) were selected.

Remedy Selection Tests

No zone samples were tested for the Clearwell. Formulations for the Clearwell stabilizations can be found in Tables 4-134 and 4-135. The UCS values were the lowest of the eight waste streams investigated, the lowest UCS value being below the stated goal of 500 psi. This came from a composite sample stabilized using Formulation 2 (451 psi). The sample with the highest was stabilized using Formulation 1 (1250 psi). The average UCS was 696 psi. Bulking factors were generally very near one another, with a high of 49 percent and a low of 44 percent. The average was 47 percent. Permeabilities were considered adequate, with the lowest given by the sample stabilized with Formulation 1 (8.9×10^{-8} cm/s) and the highest given by the Formulation 2 sample (1.6×10^{-7} cm/s).

Dilution adjusted TCLP results for Clearwell TCLP radionuclides for the two formulations are shown in Table 4-136. Metals results are shown in Table 4-137. Both formulations pass the TC regulatory criteria.

Table 4-134

CEMENT STABILIZATION
ADVANCED PHASE FORMULATIONS
CLEARWELL
FOR FERNALD OPERABLE UNIT 1

Formulation	Normalized Waste	Normalized Cement	Normalized Flyash	Noramalized Blast Furnace Slag	Normalized Clinoptilolite	Normalized Water (Range)
1	100	15	0	15	0	20
2	100	26	0	0	0	20-22

NOTE: All quantities are normalized to express quantities of reagents in grams used per 100 grams of waste. Waste was not dried before mixing.

Table 4-135

CEMENT STABILIZATION
ADVANCED PHASE
RESULTS OF UCS, BULKING FACTOR, AVERAGE BULKING FACTOR, AND PERMEABILITY
CLEARWELL
FOR FERNALD OPERABLE UNIT 1

Zone	Formulation	UCS (psi)	Bulking Factor (Percent Volume Increase)	Average Bulking Factor (Percent Volume Increase)	Permeability (cm/s)
Composite	1	824	48	47	8.9×10^{-8}
		1250	48		
Composite	2	593	44		1.6×10^{-7}
		525	45		
Composite	2	451	49		1.5×10^{-7}
		536	48		

TABLE 4-136

CLEARWELL SOLIDIFICATION TCLP
RADIONUCLIDES DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (pCi/l)	Formula 1 (pCi/l)	Formula 2 (pCi/l)
Cesium-137	NA	ND	ND
Neptunium-237	NA	0.120	0.592
Plutonium-238	NA	ND	0.548
Plutonium-239/240	NA	ND	ND
Radium-226	NA	21.600	19.011
Radium-228	NA	18.300	19.802
Stontium-90	NA	12.300	15.281
Technetium-99	NA	114.300	333.740
Thorium-228	NA	2.025	2.923
Thorium-230	NA	0.615	2.760
Thorium-232	NA	ND	0.414
Uranium-234	NA	0.225	0.370
Uranium-235/236	NA	ND	0.148
Uranium-238	NA	0.345	0.703
	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)
Thorium (Total)	NA	ND	0.004
Uranium (Total)	NA	0.002	0.001

* See Table 4-93

\+ See Table 4-93

TABLE 4-137

CLEARWELL SOLIDIFICATION TCLP
METALS DILUTION ADJUSTED CONCENTRATION

	Raw Waste Characterization (mg/l)	Formula 1 (mg/l)	Formula 2 (mg/l)	TC REG LIMITS (mg/l)
Antimony	0.101	ND	ND	
Arsenic	ND	ND	ND	5.000
Barium	2.001	2.640	4.360	100.000
Beryllium	ND	ND	ND	
Cadmium	0.010	ND	ND	1.000
Chromium	0.010	ND	0.020	5.000
Cobalt	0.100	ND	ND	
Copper	0.822	0.687	0.570	
Cyanide	ND	ND	ND	
Lead	0.123	ND	0.010	5.000
Manganese	66.990 0	ND	ND	
Mercury	ND	ND	ND	0.200
Molybdenum	0.037	0.273	0.160	
Nickel	0.886	0.081	0.110	
Selenium	ND	0.005	ND	1.000
Silver	0.049	ND	ND	5.000
Thallium	ND	ND	ND	
Vanadium	0.040	0.024	ND	
Zinc	0.609	0.039	0.070	

* See Table 4-93

\+ See Table 4-93

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A comparison of the dilution adjusted results shows that Formulation 1 seems to give the better overall results. The dilution adjusted concentrations for every radionuclide were lower for Formulation 1, with the exception of Ra-226, which was slightly lower for Formulation 2.

Clearwell Cement Stabilization - Radon Emissions

All radon results in Figures 4-59 and 4-60 were multiplied by the reagent dilution factor so that all results were expressed relative to the amount of pit waste in the stabilized sample. The results in the figures were based on the average result of measurements made on a cylindrical test specimen from each zone of the pit. Figures 4-59 and 4-60 show that both formulations had roughly the same effectiveness in reducing the rate at which radon was emitted. The relatively low emanation rates from the untreated waste were probably due to the wet, clay-like nature of the waste tested. Such material would be expected to have extremely low porosity, reducing the ability of radon to diffuse through it.

The calculated radon emission rate given for comparison in both figures was based on the average Ra-226 concentration found in characterization samples. Each pCi of Ra-226 generates Rn-222 at a rate of 0.1813 pCi per day. The average Ra-226 concentration in the characterization samples was 55 pCi/g.

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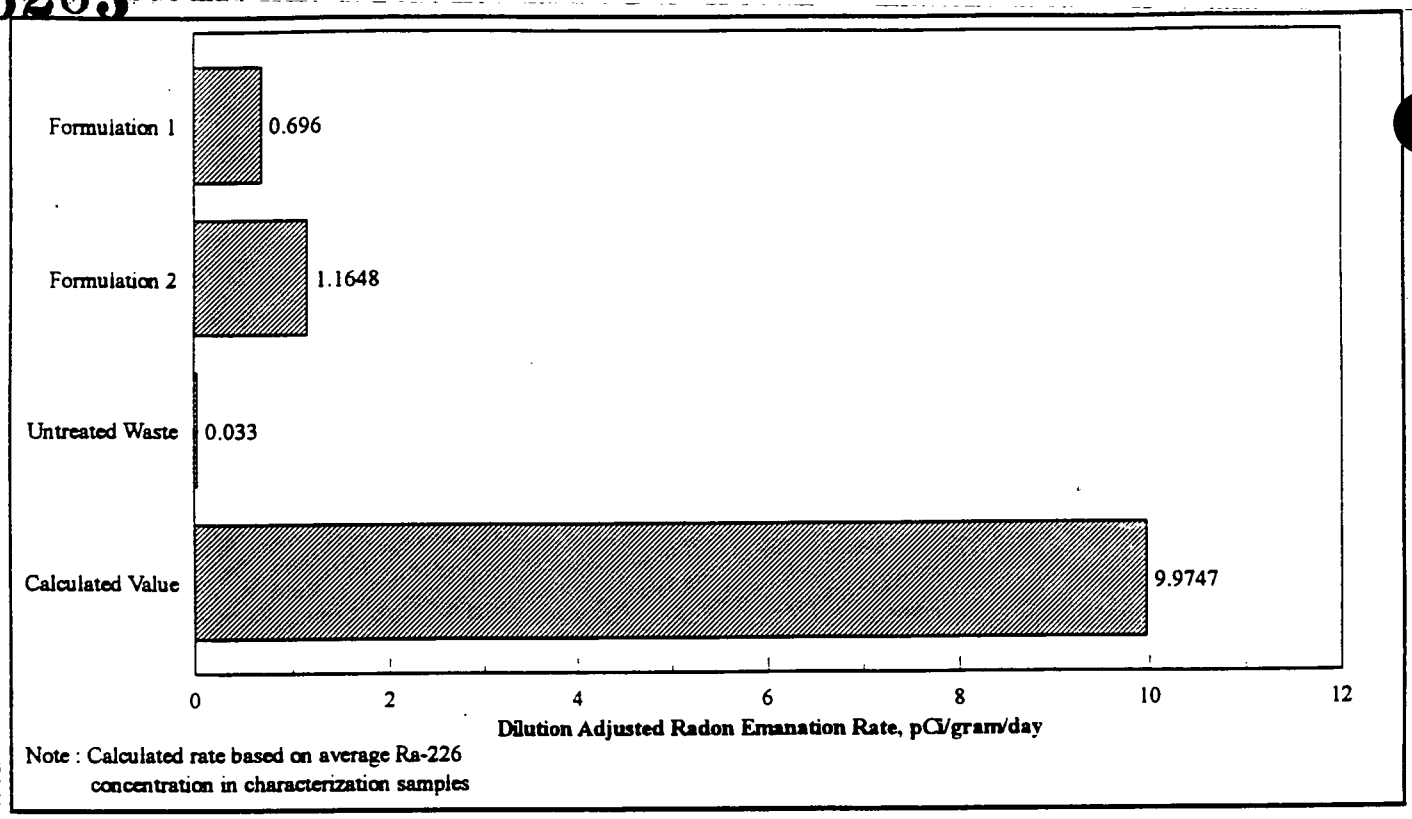

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Figure 4-59 -CLEARWELL STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON EMANATION RATES

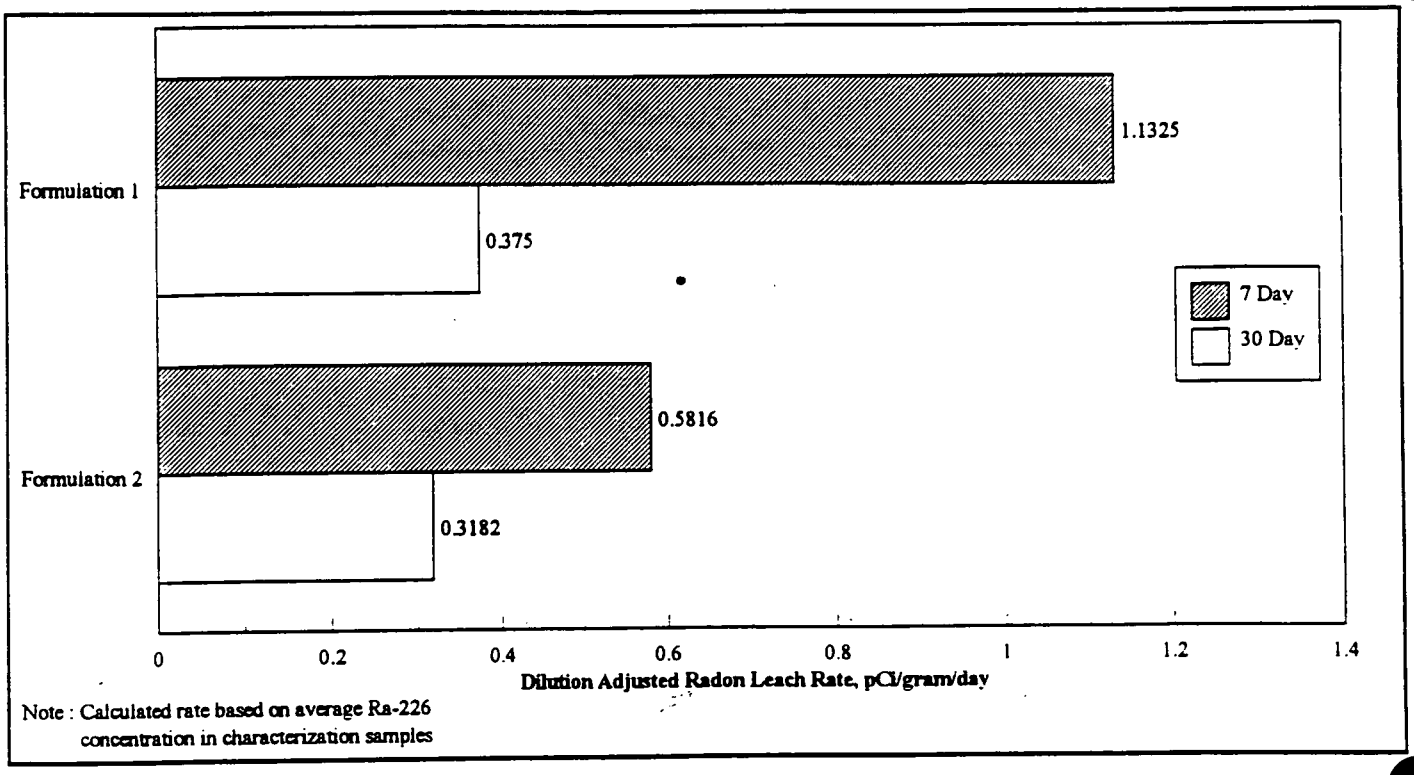

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Figure 4-60 -CLEARWELL STABILIZATION - COMPARISON OF DILUTION ADJUSTED RADON LEACH RATES

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Durability Testing of Cement Stabilized Samples

Wet/Dry and Freeze/Thaw testing was performed by the University of Cincinnati on two formulations for each waste pit with the exception of Waste Pit 4. The test procedures for both the wet/dry and freeze/thaw tests require the test specimens to be subjected to 12 cycles of alternating environmental conditions. Each two day testing cycle consisted of two 24 hours periods of different temperature and humidity conditions. After each cycle, the weight loss from each specimen was determined by the weight of the residue remaining in the beaker that had contained the specimen during that testing cycle. The weight loss of each test specimen is adjusted later to reflect the weight loss in the control specimens. The ASTM procedures for both durability tests specify that when the specimen weight loss exceeds 30 percent, the test is to be terminated.

The physical description of the test specimens is provided in Appendix M. It should be noted that sufficient pit waste material was not available to cast all specimens to the desired 44mm.x 74mm. size. The sample numbering designation used internally was the last four digits of IT's extended specimen number, e.g., IT specimen #1141401 became UC specimen #1401. Typically, the last two digit for the ten specimens provided for each sample were numbered from 01 to 10, e.g., #1401 thru # 1410.

A listing of the final corrected weight loss data for the wet/dry and freeze/thaw tests for all the mix designs is provided in Table 4-138. This information is also presented graphically in Figures 4-61 to 4-64. The data for the weight loss for each cycle of both the wet/dry and freeze/thaw durability testing is provided in Appendix M. The summary of the relative weight loss (average of three specimens), along with the visual observations, for each cycle of each set of three specimens is also provided there. Figures 4-65 and 4-66 graphically present the twelve cycles of the freeze/thaw weight loss data for the two mix designs for Pit #1. This response is typical of most of the specimens tested.

Both ASTM D4842 and D4843 specify that the tests for a mix design is to be terminated if the cumulative mass loss of any of the three specimens exceeds 30% (failure). However, no criteria currently exists to certify that the stabilized waste sample has passed these durability tests. The literature does propose that weight loss in excess of 15% is unacceptable (U.S. Environmental

Table 4-138 Summary of CRUDD Results

Pit	Mix	Total Weight Loss, in %		Final Visual Observations	
		Wet/Dry	Freeze/Thaw	Wet/Dry	Freeze/Thaw
1	1-BFS	0.02%	0.00%	Pinhole cracking and crazing	Pinhole cracking and slight cracking
	1-FA	-0.06%	0.04%	Pinhole cracking and slight crazing	Pinhole cracking and slight crazing
2	2-BFS	0.04%	0.07%	Surface cracking and 20 air voids	Slight cracking and 30 air voids
	2-FA	0.07%	0.22%	Pinhole cracking, slight crazing and slight cracking	Pinhole cracks, crazing and about 30 air voids
3	3-BFS	0.09%	24.24%	Crazing, pinhole cracking, and slight cracking	1407: hunks fell off , other ready to do same
	3-FA	-0.13%	0.24%	Crazing, pinhole cracking, and slight cracking	Pinhole cracking and slight crazing
5	5-BFS	1.05%	0.22%	Pinhole cracking and slight crazing	Pinhole cracking, 1" crack near end on one and slight crazing
	5-FA	0.38%	15.73%	Pinhole cracking, crazing on ends and about 15 air voids	Pinhole cracking and slight crazing, except 2009 split in half
6	6-BFS	0.04%	30.27%	Pinhole cracking and crazing	Specimens practically disintigrated
	6-FA	-0.08%	0.27%	Pinhole cracking, crazing and surface cracking	Pinhole cracking, few air voids and surface flaking
Clearwell	CW-1	-0.44%	4.50%	3-3/8" cracks, pinhole cracks and few air voids	Pinhole cracking, 3-1/4" cracks, slight cracking and obvious surface flaking
	CW-BFS	0.01%	-0.08%	Pinhole cracks, few air voids and 3-1/4" cracks	Pinhole cracking, 2-1/4" cracks, slight cracking and surface flaking
Burn Pit	BP-BFS	0.01%	-0.01%	Pinhole cracking and surface cracking	Pinhole cracking and cracking
	BP-FA	0.01%	-0.04%	Pinhole cracking, few air voids and slight crazing	Pinhole cracking, 1/4" crack, few air voids and slight crazing
3 (dup.)	3-BFS	-0.04%	0.04%	Crazing and pinhole cracking	Few air voids and slight cracking
6 (dup.)	6-BFS	0.07%	1.39%	Crazing and pinhole cracking	Pinhole cracking and cracking

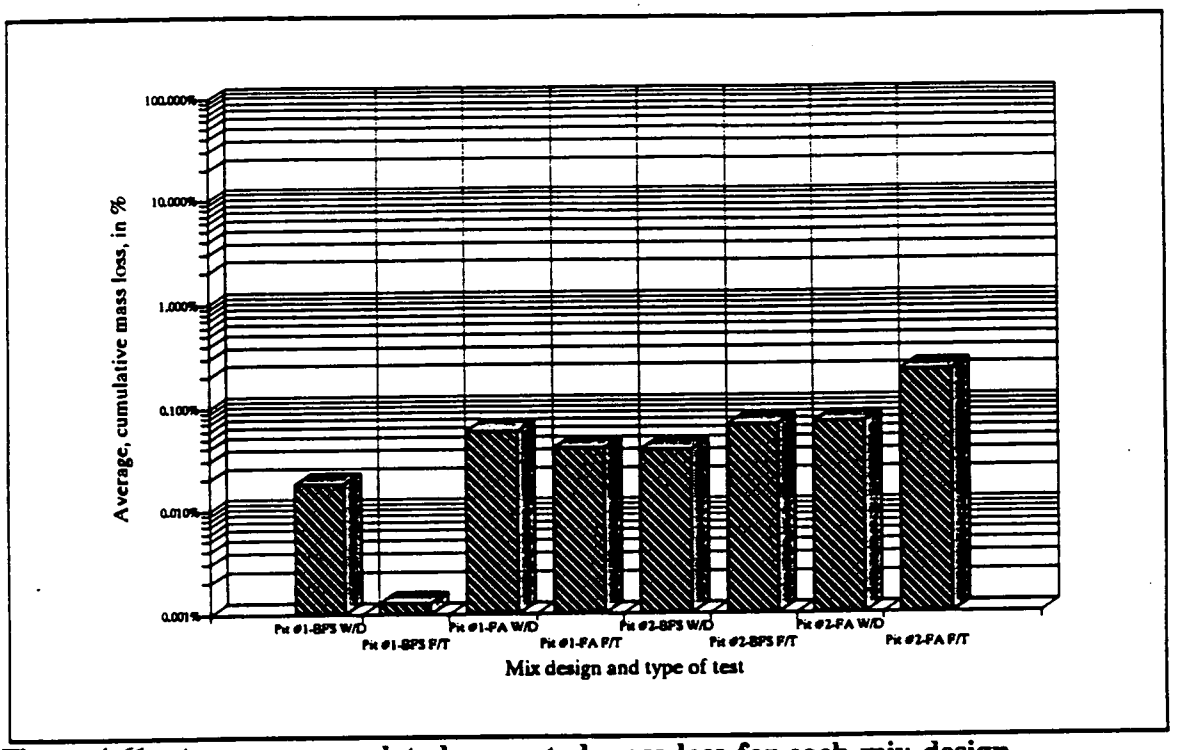

Figure 4-61 Average, cumulated corrected mass loss for each mix design.

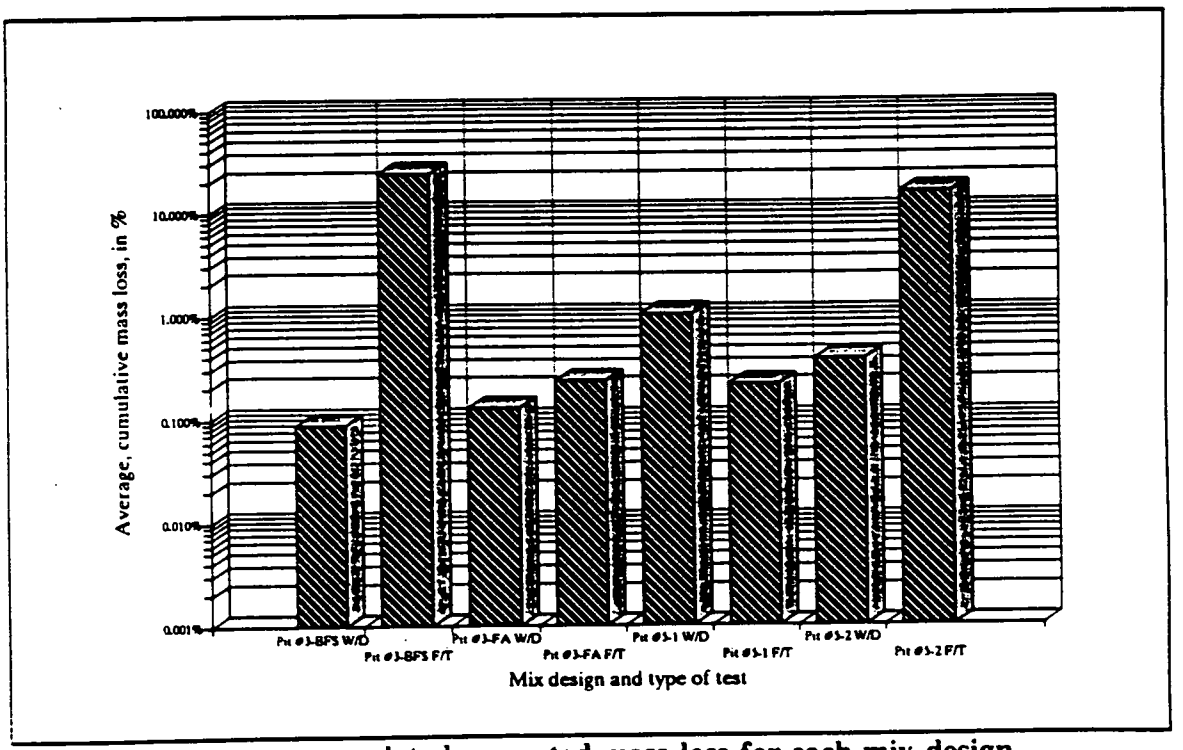

Figure 4-62 Average, cumulated corrected mass loss for each mix design.

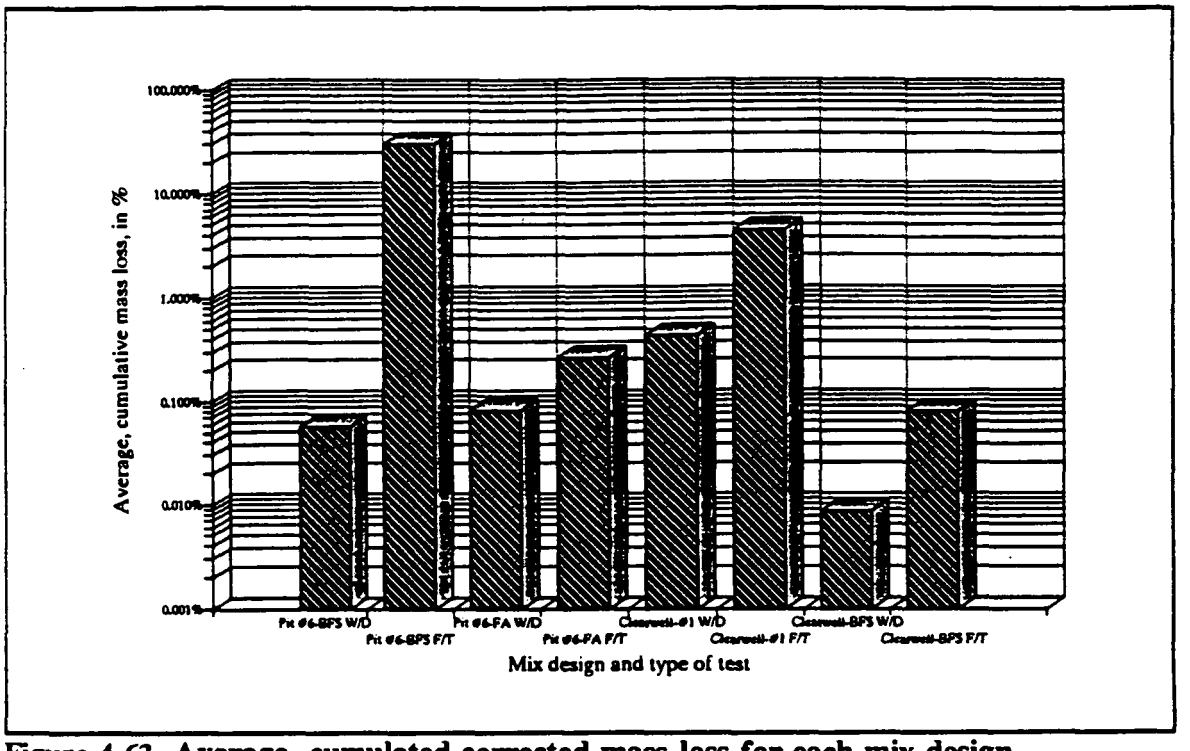

Figure 4-63 Average, cumulated corrected mass loss for each mix design.

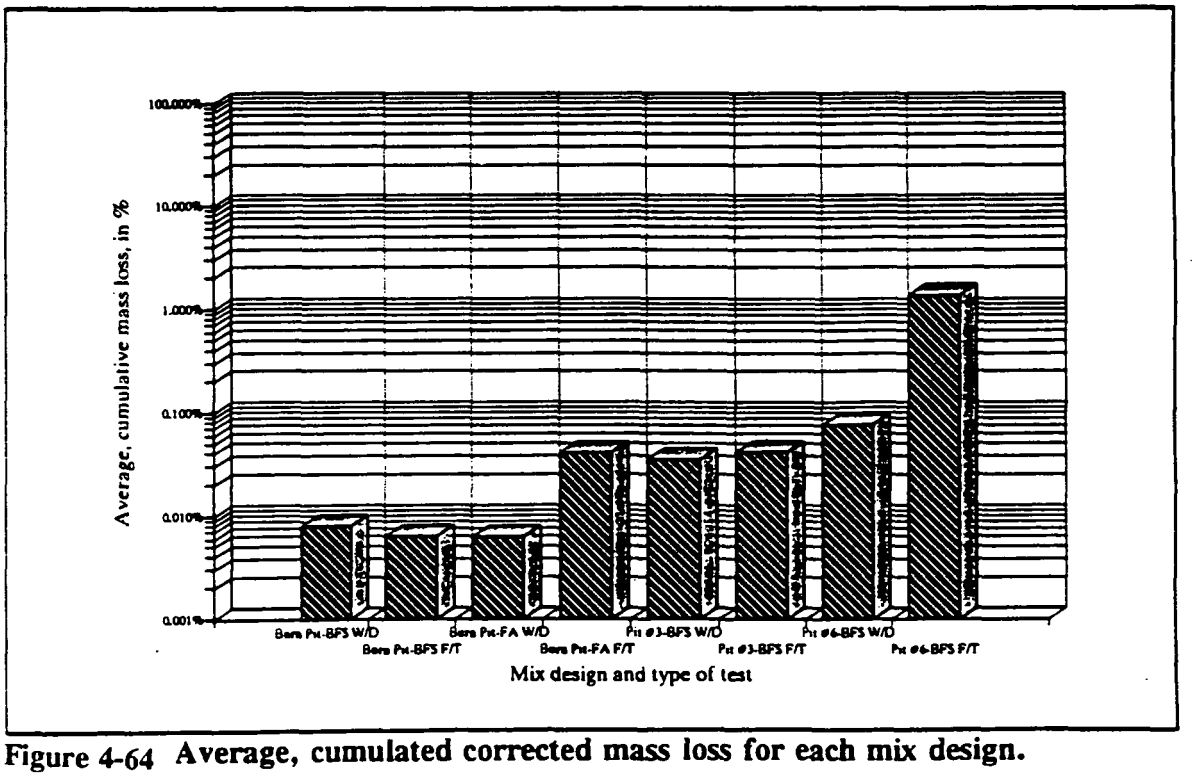

Figure 4-64 Average, cumulated corrected mass loss for each mix design.

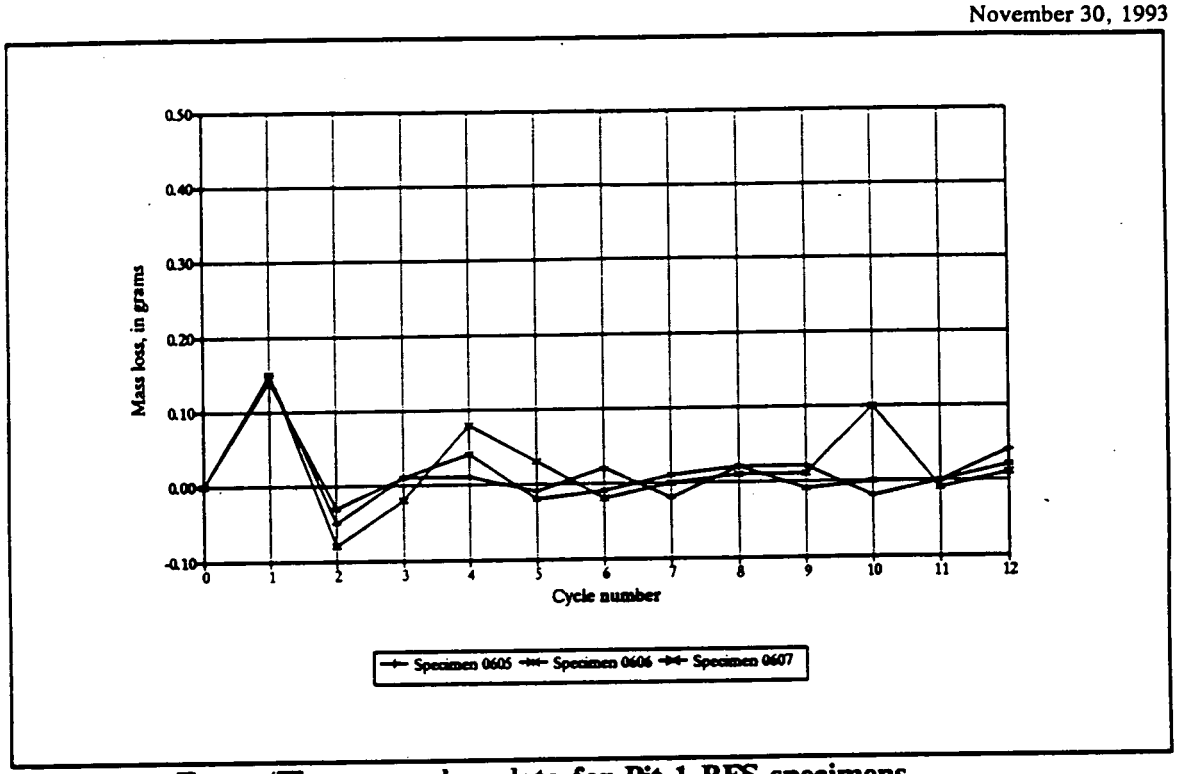

Figure 4-65 Freeze/Thaw mass loss data for Pit 1-BFS specimens.

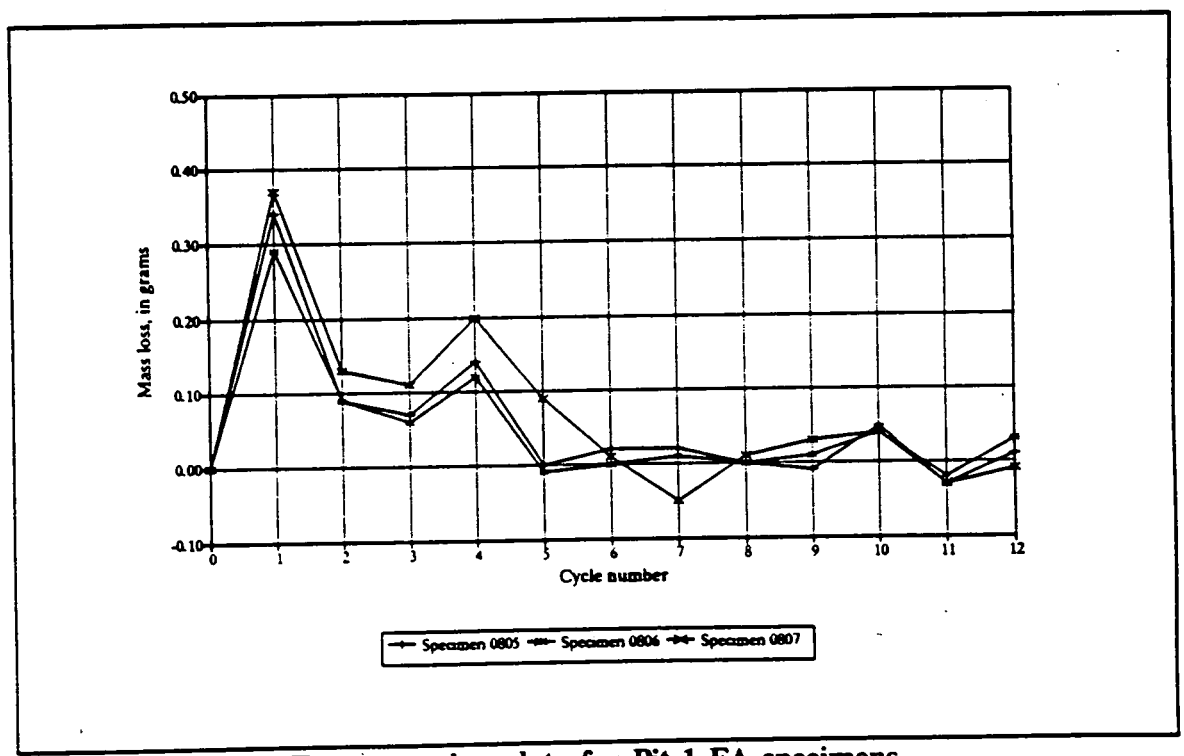

Figure 4-66 Freeze/Thaw mass loss data for Pit 1-FA specimens.

Protection Agency [EPA] 1989). It should be emphasized that significant cracking can be present in a specimen that has exhibited only nominal weight loss during the durability testing. When evaluating each specimen, considerable value should be given to the visual information recorded for each specimen.

Additionally, non-destructive acoustic procedure and unconfined compression tests were performed on the test specimens as a part of a research effort to develop improved evaluation techniques for identifying deterioration during durability testing. These results are to be integrated with and reported under contract #2-15526-003, Long Term Durability.

None of the mix designs failed the wet/dry tests. However, the mix design containing blast furnace slag for Pit 6, 6-BFS, failed the ASTM freeze/thaw durability test as even the average of the weight loss for the three specimens slightly exceeded 30 percent. While the average of the weight loss for the Pit 3 mix design containing blast furnace slag, 3-BFS, did not exceed 30 percent for the freeze/thaw test, a single specimen lost over 44 percent weight. Thus mix design 3-BFS also failed the freeze/thaw tests. Note that while the duplicate samples provided for the blast furnace slag mix designs for Waste Pits 3 and 6 did not exhibit the same large weight loss, the visual observation of cracks at the surface of these specimens due to freeze/thaw testing also showed significant degradation.

The large average weight loss during the freeze/thaw testing for the mix design for Pit 5 that does not contain blast furnace slag, 5-FA, resulted from a unique occurrence. While being transferred from a beaker, specimen number 2009 unexpectedly cracked completely through the cross-section with no other signs of significant deterioration. The smaller portion of the specimen was recorded as the amount of weight lost for that cycle. Visual examination of the crack plane gave no indication as to the cause of the separation. An explanation for this behavior is that the crack plane could be a cold joint that occurred during the casting of the specimen. The other two specimens from the same mix had minimal deterioration throughout the testing cycles, therefore, it is suggested that the large average weight loss value for this mix design is not representative of its durability.

In summary, the freeze/thaw tests typically, but not always, had a more detrimental effect than the wet/dry tests on the proposed mix designs. For nominally the same weight loss, different specimens can exhibit significantly varied degrees of cracking. Generally for a given pit waste, the mix formulation without blast furnace slag performed significantly better than those mix designs containing blast furnace slag, especially for the freeze/thaw tests.

Comparison to Test Objectives

Analysis of the results from Remedy Screening Stage 1, indicated that solidification of the waste in Waste Pits 4, 5, 6, and Clearwell readily achieved the desired UCS. Pits 1, 2, and 3 required higher loadings of reagents to solidify the waste because less then 50 percent of the formulations achieved 500 pounds per square inch (psi) UCS. The remaining pits, Pit 2 and Burn Pit, required re-formulations in Stage 2 because less then 20 percent of the initial 20 formulations in Stage 1 achieved the desired 500 psi UCS. Uranium was more leachable in Pits 4 and 5 then all other pits. The MTCLP leachate for all formulations of all the pit materials passed the TC regulatory requirements.

In Stage 2, the results indicated that solidification of the waste in all pits can readily achieve the desired 500 psi UCS. All pits except Pit 6 had blast furnace slag in the Stage 2 formulations. In all cases, the blast furnace slag improved UCS. The most promising formulations derived from the Remedy Screening (Stage 2) testing program were used in the Remedy Selection phase of the program. These formulations had a UCS greater than 500 psi, met the TC regulatory limits, had relatively low uranium, had gross alpha and beta values in the MTCLP extraction fluid, and had a relatively low bulking factor.

The overall objectives of the treatability study were met. All cement stabilized waste forms in the Advanced Phase passed the TCLP and attained an UCS of greater than 500 psi. Sufficient information on permeability and durability was generated to assess cement stabilization as a treatment technology.

4.1.2.3 THERMAL TREATMENT

Thermal treatment studies underway include physical characterization of each waste pit material and baseline crucible studies. The physical characterization is the first step in the thermal processing treatability study.

Results of various tests will be provided as they become available. Although numerical results have not yet been produced, many differences in the raw, the dried, and the heat treated wastes and soil became apparent as the testing proceeded. These are summarized in Table 4-139. Moisture content in Table 4-139 is defined as the wt. of water/wt. of dry solids x 100 percent.

Portions of the dried and the heat treated samples were set aside for further analysis. These analyses include TCLP. TCLP analysis will be performed on the raw, the dried, and the heat treated samples.

Physical characterization testing includes visual classification, natural moisture content, grain size distribution, Atterberg limits, hydrometer analysis, specific gravity, shrinkage factors, soil moisture-density relationships, unconfined compressive strength, direct shear, and possibly other tests. The purpose of physical characterization is to classify the pit wastes as to their expected engineering behavior under different moisture and stress environments as well as disposal environments. Engineering properties have been found to correlate well with the index and classification properties of a given soil deposit.

Waste pit materials were visually classified using the classifications in Table 4-140. This table was developed by a University of Cincinnati geotechnical engineering professor as an outgrowth of ASTM D2488-90. The table does not cover all possible outcomes but is meant to serve as a simple means to visually classify most soils in the laboratory or in the field.

Results of the 55 visual classification tests performed are summarized as in Table 4-139.

TABLE 4-139

Summary of Waste Characteristics

	Pit 3	Pit 5	Pit 6	Soil
Sampling notes	clumps of grassy material, several small sticks, and many rocks in waste	weak ammonia odor, few pieces of grassy material in waste	few pieces of grassy material in waste	rocks observed in raw sample
Wet frisk* (counts per minute)	1200	1200	11,500	<20 above background
Wet appearance	very viscous, dark brown	medium thickness, light brown, many air bubbles	thin & grainy, drab olive green	dark brown with malt colored powder interspersed
Average moisture content	110%	352%	169%	24%
Dry frisk* (counts per minute)	2000	4000	20,000	<20 above background
Dry appearance	light to medium brown	light pinkish brown with darker colored ring around edge, sticky	light avocado with darker ring around edge	light brown
Appearance after being heated to 400°C	medium brown, same consistency as dried waste	light orangish brown, same consistency as dried waste	light pea greenish brown, same consistency as dried waste	light to medium brown with orangish tint, same consistency as the dried soil
Appearance after being heated to 800°C	light grey, easy to crush, softly clumped together, craters on surface	medium to dark brown with white flecks, same consistency as dried waste	bright yellow, same consistency as dried waste	orangish brown, same consistency as the dried soil
Appearance after being heated to 1000°C	medium grey mottled with orange, layered, craters on surface hard, adhered to crucible	very dark brown with few white flecks, clumped but easy to break and crush	brown with slight reddish tint, shrunken from sides of crucible and very hard	orange, agglomerated but easy to break and crush

* Note that the samples were frisked while in the evaporating dishes (wet and dry).

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TABLE 4-140
Visual Classification Tests On
Soil Fraction Less Than 1/8 Inch Size

General Characteristics When Wet	Breaking or Dry Strength	Shine	Plasticity (Thread)	Shaking Reaction (Dilatancy)	Odor	Color (Wet)	USCS Symbol
practically non-plastic, non-cohesive	none to slight, gritty	none to very dull	very weak, easily crumbled	moderate to quick	none	gray, yellow, tan to reddish, blue	ML
moderately plastic and cohesive	significant to high, may be gritty	medium to dull	medium to tough, adheres to hand	none	earthy	dark brown, reddish, dark gray, tan	CL
slightly plastic and cohesive	slight, gritty	none to very dull	soft, weak; adheres somewhat to hand	none to very slow	decayed organic matter	black, dark gray, dark brown	OL
slightly plastic and cohesive	slight to medium, powdered soil feels like talc	none to dull	very soft, weak to medium	slow to quick	none	blue, pink, green, white, yellow, orange	MH
very plastic and cohesive	high to very high, cannot be powdered by finger pressure	very glossy	very tough, very sticky to the hand	none	strong earthy	dark brown, red, blue, yellow	CH

Table 4-140 (Continued)

Visual Classification Tests On Soil Fraction Less Than 1/8 Inch Size

General Characteristics When Wet	Breaking or Dry Strength	Shine	Plasticity (Thread)	Shaking Reaction (Dilatancy)	Odor	Color (Wet)	USCS Symbol
moderately to very plastic and cohesive	moderate to high, may be fibrous	medium to very glossy	weak to medium, often soft and fibrous	none	decayed organic matter	black, dark brown, dark gray	OH
fibrous and highly organic, very plastic	low to medium, fibrous when powdered	none to dull	very soft, fibrous, slimy	none	decayed organic matter	black, dark brown, dark gray	Pt

Waste Pit 1

Waste Pit 1 is a homogeneous non-plastic silt (Unified Soil Classification System (USCS) Symbol NP). The majority of the eight samples (samples 1A through 7A) from Pit 1 have 70 to 91% fines, 9 to 27% sand, and a trace of gravel (up to 3%). Sample 8A is a sandy silt containing 58% fines, 38% sand, and 4% gravel. All the samples are gray black in color. The samples consistently display quick shaking (dilatancy) reactions, slight cohesion, and low dry strength. An odor of petroleum is present in most samples. In their received and settled state in the sample cans the samples are firm and display a dull shine; the moisture contents range from 20 to 39%. A few vegetative fibers are present in the samples.

Waste Pit 2

Waste Pit 2 contains low plasticity clays, high plasticity silts, and silty sand (USCS Classifications CL, MH and SM). Four samples were taken from this pit. Sample 9A is a silty sand with 44% fines, 55% sands and 1% gravel. Samples 10A and 12A are sandy lean clays (CL) with 66 to 74% fines, 22 to 26% sand, and 4 to 8% gravel. Sample 11A is a high plasticity silt with 67% fines, 28% sand and 5% gravel. The samples range from light to medium brown in color. Samples 9A and 11A show slow to medium dilatancy, moderate cohesion, and moderate to high dry strength. Samples 10A and 12A show slow to no dilatancy reactions, high cohesion, and high dry strength. Shine varies from dull to medium. Some fibrous matter is present in the samples. The samples are soft with moisture contents ranging from 35 to 70%; an exception is Sample 12A which had no free water in the can, the moisture content being 16.7%.

Waste Pit 3

Waste Pit 3 varies between low plasticity clay, low plasticity silt, and high plasticity silt (USCS Classifications CL, ML and MH). Samples 13A, 14A, 16A and 17A are sandy silts (MH) with 63 to 84% fines, 15 to 34% sand, and up to 4% gravel. Samples 15A and 18A appear to be low plasticity silts (ML) with approximately 57 to 68% fines, 26 to 41% sand and 3 to 7% gravel. Sample 19A appears to be a sandy lean clay (CL) with 74% fines, 20% sand, and 6% gravel. The samples are mottled light brown to gray black in color; samples 13A, 16A and 17A are predominantly reddish-brown, samples 14A, 15A and 19A are predominantly medium brown and sample 18A is medium gray. The gray-black material has the characteristics of silt. The samples display moderate to no dilatancy and variable dry strengths. Samples 14A and 17A have moderate to low dry strength, 15A and 16A have moderate to high dry strengths, and samples 13A, 18A and 19A have high dry strengths. All the samples show

moderate to high cohesion. As received the samples are wet and soft having moisture contents ranging from 36 to 153%. Samples 15A, 18A and 19A had no free water on them and define the lower bound ranging from 36 to 42%. Some fibrous organic matter is present. Samples 16A and 17A contain considerable organic matter resembling peat (Pt).

Waste Pit 4

Waste Pit 4 varies from low plasticity clay to nonplastic silt (USCS Classifications CL and NP). Samples 21A, 24A and 25A are sandy lean clays (CL) with 62 to 64% fines, 25 to 35% sand, and from 1 to 13% gravel. Samples 22A, 23A and 26A are nonplastic (NP) silts with 81 to 89% fines, 12 to 18% sand, and a trace of gravel. The samples are gray black in color with sample 23A being mottled with light brown. Samples 21A and 25A are moderately cohesive, have slow dilatancy reactions and have moderate to high dry strength. Samples 22A and 26A have slight cohesion, quick dilatancy reactions, and have low to moderate dry strengths. Sample 23A has slight cohesion, a moderate to quick dilatancy reaction, and moderate dry strength. As received the samples are firm and range in moisture content from 10 to 29%. Samples 24A and 21A had no standing water in the can and defined the lower bound of the water content range. A few roots are present in the samples and an odor of petroleum is noticeable in samples 23A and 26A.

Waste Pit 5

Waste Pit 5 is predominantly high plasticity silt with some nonplastic silts (USCS Classifications MH and NP). Samples 30A through 39A, 57A and 58A are silts (MH) with approximately 85 to 100% fines and 0 to 15% sand. Samples 40A and 41A are nonplastic silts (NP) with 94% fines and 6% sand. The samples ranged in color from brownish-gray to salmon with the majority being mottled with light brown, white and gray. The natural moisture contents range from 109 to 620% making cohesion and dilatancy difficult to assess. Samples 31A, 35A and 41A show signs of being cohesive and appear to have slow to no dilatancy reactions. Sample 30A appears to have moderate cohesion and a moderate dilatancy reaction. Samples 33A and 36A seem to have a moderate dilatancy reaction while samples 32A, 34A, 57A and 58A have slow to no reaction. Samples 30A, 39A, 40A, 41A, and 57A have low dry strength; samples 35A and 36A have moderate dry strength; samples 31A through 34A, 37A and 58A have high

dry strength. As received the samples are wet and soft. An odor of ammonia is present in all the samples. Small soft white nodules of unknown material are also present throughout all the samples.

Waste Pit 6

Waste Pit 6 varies between low plasticity to non-plastic silt, high plasticity silt and silty sand (USCS Classifications ML, NP, MH and SM). Samples 43A and 45A are nonplastic silts (NP) with 72 to 96% fines and 4 to 28% sand. Samples 45C is a nonplastic silty sand (SM) with 49% fines and 51% sand. Sample 46A is a low plasticity silt (ML) with 86% fines and 14% sand. Sample 47A is a high plasticity silt with 90% fines and 10% sand. No gravel was found in any of the samples. The samples range in color from pea green to gray black. Samples 43A, 45A and 45C have slight to moderate cohesion, quick dilatancy reactions, and low to moderate dry strength. Samples 46A and 47A have moderate cohesion, slow to moderate dilatancy, and moderate to high dry strength. As received the samples are wet and soft with moisture contents ranging from 27 to 425%. A trace of fine fibrous organic matter is present in these samples.

Burn Pit

The Burn Pit varies from a low plasticity silt to a low plasticity clay (USCS Classifications ML and CL). Sample 27A is a low plasticity clay (CL) with 71% fines, 26% sand and 3% gravel. Samples 28A and 29A are low plasticity silts (ML) with 53 to 59% fines, 37 to 38% sand and 4 to 8% gravel. The samples range in color from light to dark brown in sample 27A and gray black with light brown for samples 28A and 29A. Sample 27A is cohesive, has a slow dilatancy reaction, and high dry strength. Samples 28A and 29A have slight cohesion, moderate to quick dilatancy reactions, and high dry strength. As received the samples are moist with moisture contents ranging from 25 to 30%. A trace a fibrous organic matter is present.

Clearwell

The Clearwell consists of low plasticity clay, high plasticity silt and silty sands (USCS Classifications CL, MH, and SM). Samples 49A and 53A are sandy lean clays (CL) with approximately 61 to 66% fines, 31 to 39% sand, and up to 3% gravel. Samples 50A, 54A, 55A and 56A are high plasticity sandy silts (MH) with 53 to 77% fines, 22 to 36% sand and 1 to 11% gravel. Sample 54A is a silt with sand (MH)

having 77% fines, 22% sand and 1% gravel. Samples 51A and 52A are silty sands with 45 to 49% fines, 47 to 52% sand, and 0 to 9% gravel. The color of the samples ranges from medium to dark brownish-gray to light brown. All the samples are cohesive, have dilatancy reactions ranging from none to slow, and possess moderate to high dry strengths. As received the samples are wet and range in moisture content from approximately 35 to 74%. Some fibrous organic matter is present. Sample 49A contains a considerable percentage of organic matter similar to fine wood mulch (Pt).

A summary of the laboratory data generated to date appears in Table 4-141. It should be noted the visual classification summaries may need to be modified as further Atterberg limit determinations are made. Many of the samples are borderline in the USCS classification system, meaning they either have liquid limits near 50 percent which divides low from high plasticity, or their liquid limit plasticity index combination plots near the A-line which separates silts from clays on the plasticity chart.

Thermal Treatment Results

Very little data is currently available. Based on the work completed to date the pit wastes appear to be predominantly fine-grained (silts and clays) in nature. Only four of the 55 samples classify as sands. The gravel content found in the one-gallon cans is practically negligible. Pits 3, 5 and 6 have relatively high water contents (107 to 620 percent). Most of the samples have been found to air-dry quickly. Extreme shrinkage has been observed with a number of samples, particularly those from Waste Pits 5 and 6. The pit wastes are amenable to standard ASTM soil classification testing.

4.1.2.4 Particle Agglomeration

Technical investigations into drying (thermal treatment) indicate the technology is a feasible alternative for treatment of the pit wastes. However, the end product of this type of treatment can be a fine dusty material. The main purpose of this technology is to reduce dusting problems during handling for load-out, on-site storage, transportation, and off-site storage. Particle agglomeration is one method of eliminating dusting. The two types of particle agglomeration tested includes pelletizing and polymer encapsulation.

TABLE 4-141

Geotechnical Laboratory Material Property Testing Results

Sample Number	Pit	Moisture Content %	% Gravel	% Sand	% Fines	% < 2μ	G_s	Liquid Limit %	Plastic Limit %	PI %	pH of Solids In H_2O	Liquidity Index	Activity Index	USCS Symbol
1A	1	20.3	0.0	14.2	85.8			--	--	--		--		NP
2A	1	24.7	0.0	13.2	86.8			--	--	--		--		NP
3A	1	39.1	2.9	26.8	70.3			--	--	--		--		NP
4A	1	18.0	0.0	9.0	91.0			--	--	--		--		NP
5A	1	20.7	0.4	10.8	88.8	0.0	3.02	--	--	--	7.27	--	--	NP
6A	1	21.1	0.0	9.0	91.0			--	--	--		--		NP
7A	1	20.7	1.1	9.8	89.1			--	--	--		--		NP
8A	1	22.7	3.9	37.6	58.5			--	--	--		--		NP
9A	2	35.4	1.0	55.1	43.9			33.1	23.2	9.9		1.23		SM
10A	2	38.3	7.6	26.1	66.3	22.2	2.72	42.3	23.1	19.2	7.67	0.79	0.86	CL
11A	2	70.5	5.5	27.8	66.7	11.7	2.67	66.8	42.2	24.6	7.53	1.15	2.10	MH
12A	2	16.7	4.2	22.3	73.5			44.1	16.2	27.9		0.01		CL
13A	3	145.4	3.2	33.7	63.1			89.7	55.8	33.9		2.64		MH
14A	3	152.7	3.5	23.8	72.7			81.8	58.9	22.9		4.10		MH
15A	3	42.2	6.5	25.8	67.7	3.1	2.69	46.9	31.7	15.1	7.74	0.70	4.87	ML
16A	3	96.8	3.3	27.0	69.7	15.7	2.72	77.8	44.3	33.5	7.76	1.57	2.13	MH
17A	3	142.0	1.0	15.3	83.7			69.9	53.9	16.0		5.51		MH
18A	3	41.9	2.5	40.9	56.6			37.9	30.5	7.4		1.54		ML
19A	3	36.1	6.0	19.9	74.1			44.1	25.2	18.9		0.58		CL

Table 4-141 (Continued)

Geotechnical Laboratory Material Property Testing Results

Sample Number	Pit	Moisture Content %	% Gravel	% Sand	% Fines	% < 2μ	G_s	Liquid Limit %	Plastic Limit %	PI %	pH of Solids In H_2O	Liquidity Index	Activity Index	USCS Symbol
21A	4	18.0	6.4	29.5	64.1	6.6	3.25	28.4	18.5	9.9	7.79	-0.05	1.50	CL
22A	4	23.3	0.0	12.0	88.8			--	--	--		--		NP
23A	4	22.2	0.8	15.2	84.0	8.4	3.02	--	--	--	7.73	--	--	NP
24A	4	10.1	13.4	24.7	61.9			33.9	16.7	17.2		-0.38		CL
25A	4	25.4	1.2	34.7	64.1			34.1	21.8	12.3		0.29		CL
26A	4	29.3	1.2	18.0	80.8			--	--	--		--		NP
30A	5	173.0	0.0	5.0	95.0			70.7	57.7	13.0		8.87		MH
31A	5	497.5	0.0	5.2	94.8			94.2	50.6	43.6		10.25		MH
32A	5	483.0	0.0	3.4	96.6			102.2	80.5	21.7		18.55		MH
33A	5	507.3	0.0	1.3	98.7			108.4	71.8	36.6		11.90		MH
34A	5	451.7	0.0	1.9	98.1			102.2	64.6	37.6		10.30		MH
35A	5	161.1	0.0	11.9	88.1	14.5	2.70	90.9	60.2	30.7	8.53	3.29	2.12	MH
36A	5	342.4	0.0	8.1	91.9			103.8	75.6	28.2		9.46		MH
37A	5	620.0	0.0	0.2	99.8			93.0	58.0	35.0		16.06		MH
38A	5	495.7	0.0	2.7	97.3		2.74	112.3	68.1	44.2	8.72	9.67	--	MH
39A	5	448.5	0.0	5.9	94.1			112.0	69.6	42.4		8.94		MH
40A	5	114.5	0.0	5.5	94.5			--	--	--		--		NP
41A	5	109.3	0.0	6.0	94.0	8.9	2.71	--	--	--	8.34	--	--	NP
57A	5	242.3	0.0	14.6	85.4			87.7	60.9	26.8		6.77		MH
58A	5	295.7	0.0	10.4	89.6	10.2	2.70	77.1	52.7	24.4	8.22	9.96	2.37	MH

Table 4-141 (Continued)

Geotechnical Laboratory Material Property Testing Results (Continued)

Sample Number	Pit	Moisture Content %	% Gravel	% Sand	% Fines	% < 2μ	G_s	Liquid Limit %	Plastic Limit %	PI %	pH of Solids In H_2O	Liquidity Index	Activity Index	USCS Symbol
43A	6	425.1	0.0	3.7	96.3			--	--	--		--		NP
45A	6	26.8	0.0	27.6	72.4	9.6	3.21	--	--	--	9.19	--	--	NP
45C	6	117.6	0.0	51.3	48.7			--	--	--		--		SM
46A	6	107.4	0.0	13.8	86.2	27.9	2.98	47.0	28.4	18.6	9.43	4.25	0.67	ML
47A	6	111.4	0.0	9.8	90.2	35.2	2.85	64.9	33.1	31.8	9.40	2.46	1.45	MH
49A	CW	53.4	3.3	31.1	65.6			43.9	25.6	18.3		1.52		CL
50A	CW	65.1	10.9	36.4	52.7			50.6	32.5	18.1		1.80		MH
51A	CW	61.9	0.0	51.5	48.5			45.0	28.0	17.0		1.99		SM
52A	CW	40.2	8.5	47.0	44.5			39.3	24.9	14.4		1.06		SM
53A	CW	35.4	0.0	39.4	60.6	22.3	2.69	35.1	18.0	17.1	8.35	1.02	0.77	CL
54A	CW	73.9	0.5	22.5	77.0			54.7	39.2	15.5		2.24		MH
55A	CW	71.7	1.8	23.7	74.5	23.8	2.78	52.4	38.0	14.4	8.24	2.34	0.61	MH
56A	CW	68.5	3.3	31.3	65.4			53.3	40.2	13.1		2.16		MH
27A	BP	25.5	2.6	26.2	71.2			41.3	24.7	16.6		0.05		CL
28A	BP	25.6	4.4	37.0	58.6			35.1	31.0	4.1		-1.32		ML
29A	BP	30.0	8.5	38.2	53.3	15.0	2.50	37.8	26.7	11.1	7.74	0.30	0.74	ML

Preliminary tests were performed using surrogate soils prepared by the University of Cincinnati. The soils were made to resemble the particle size distribution of the wastes in Pits 5 and 6.

Pelletizing

Agglomeration technology is a process of size enlargement or upgrading of otherwise finer particles. The forms of product, depending on the reason for agglomeration, can be spheres, pellets, irregular extrusions, or merely loosely bound aggregates or clusters.

Tests were performed at a vendor test facility using a disc pelletizer. Initial tests used water as the binder to create pellets from the surrogate waste. These tests were not successful in creating durable pellets. The pellets disentigrated upon discharge from the pelletizer. A water-based polymer was then tried as a binder to create pellets in three different size ranges. This polymer was diluted 50 percent with water to improve spraying properties. The smallest pellets created resembled coffee grounds. The next larger size resembled aquarium gravel. And the largest size were pellets about 2.0 to 2.5 cm. in diameter. All three pellet forms virtually eliminated dusting. The smaller pellets or granules appeared to yield the best packing ratio. The composition of the waste material, with the exception of large, physically unsuitable material, appeared to have effect on the agglomeration.

Polymer Encapsulation

Brookhaven National Laboratory (BNL) has done some extensive work using polyethylene in a single screw extruder to encapsulate nitrate salt waste. Due to the limited waste stream that was studied and the limitations of a single-screw extruder, the decision was made to investigate other types of processing equipment using a surrogate waste mixed with polyethylene.

Visits to three manufactures were scheduled to investigate equipment for polyethylene encapsulation and agglomeration. The purposes of these visits was to observe the use of the equipment with a surrogate waste matching the particle size characteristics of OU1 pit waste. The surrogate waste had a moisture content of 6-8%. The three manufacturers visited were Draiswerke Inc. in Allendale, New Jersey, on August 19, 1993, Teledyne Readco in York, Pennsylvania on September 8-9, 1993 and Farrel Corporation in Ansonia, Connecticut on November 8, 1993.

UC and FERMCO representatives went to Draiswerke, Inc. and observed the use of their GELIMAT® Model G 40S compounding unit. This model was reported to create the least amount of dust of all of the GELIMAT® models. It is not designed for use with hazardous materials, but can be used with them if modifications are made (such as the addition of a HEPA filtered exhaust system). The GELIMAT® unit used was a one-liter laboratory size unit.

The test runs were made using 250-300 ml batches of surrogate waste and polyethylene (PE) beads from Chevron Chemical (PE 1409). A total of thirty-five batches were run with waste loadings ranging from 50% to 92% by weight. The product exited the machine in a pile that was usually pressed into a pancake-like shape and placed in a container of water to cool. A typical batch took about 20 seconds to process. Eleven of the thirty-five batches were not pressed but were left loose so the size of the agglomerates formed could be seen.

Three of the batches had water added to them (6.5% by weight) to observe the effect of moisture on the process. The added water created a significant amount of steam and the pancake formed was generally smoother (less porous) than others in which water had not been added. The Draiswerke representative noted that the material inside the unit was fluxing at approximately 300 °F, well above the boiling point of water. Most of the water will be evaporated inside the compounding chamber and vented from the machine before the material fluxes and will not affect the final product significantly. The final three batches were run without any polyethylene. The highest waste loading achieved was 92%. At this waste loading, most of the surrogate waste was bound in the PE and there were no signs of respirable fines on the surface of the final product. Several times during the course of the test runs, the GELIMAT® was purged and a relatively small amount of surrogate that had not been bound to PE was expelled. This is viewed as a minor issue that can be resolved since the surrogate was not released with the PE/waste matrix as respirable fines, but remained inside the unit. Surrogate waste (89%) and water (11%) were also run in the unit to see what kind of binding could be achieved. Although this resulted in a product not bound by PE, it did result in much larger waste particles and virtually eliminated any respirable fines.

On September 8 and 9, UC and FERMCO personnel visited Teledyne-Readco and performed lab trials using the 2-inch continuous processor with a heating cooling jacket. Again, a surrogate waste was used and two different polymers were tested for their ability to encapsulate this surrogate. The surrogate used for these trials was spiked with 1% table salt (NaCl) so the leaching potential can be evaluated on the final products. The two polymers tested were polyethylene, PE 1409, and a polyethylene terephtalate (PET). Also tested during the visit was a disk pelletizer to look at agglomerating the waste using a polymer-based binder.

A total of twenty-five waste loading/polymer combination runs were made using the continuous processor over the two day period. The surrogate waste and polymers were fed through volumetric feeders into the solids inlet port of the processor. The polymer feed rate was kept constant while the surrogate waste feed rate was varied in order to provide samples of various waste loading. The speed of the machine was varied form 100 rpm to 300 rpm. The jacket temperature was varied from 105°C to 250°C.

The product exited the processor in a viscous state, similar to thick cake batter. It was collected and compressed into cylinders while still warm and moldable. At higher processing temperatures the product tended to have a smoother surface finish. Using the PE 1409, the highest waste loading rate achieved was 88%. Using the PET polymer, a jacket temperature of 260°C was required and the highest waste loading rate was 80%. As with the batch mixer, most of the surrogate waste was bound in the polymer and there were no signs of respirable fines on the surface of the final product. One observation made concerning the final products was that the PET product was much more brittle and glossier than the PE product. Although no attempts were made to vary the moisture content of the surrogate, the continuous processor was able to vent the moisture that was present in the surrogate, estimated at about 6%. The material was being processed at a rate of about 45 kg/hr (100 lb/hr).

A disk pelletizer was also tested with the surrogate waste at Teledyne-Readco. Using both water and an acrylic binder, the waste was agglomerated into spheres of varying size; the longer the surrogate

was kept in the pelletizer, the larger the agglomerates. Using the acrylic binder and oven drying, the waste was formed into very hard agglomerates with no signs of waste on the surface.

A Banbury® batch mixer model BR1600 was tested at Farrel Corporation to observe how well it encapsulated the surrogate waste (spiked with NaCl) in polymer. The polymers tested with the BR1600 were polyethylene, PE 1409, and ethyl vinyl acetate (EVA). Initial trials to determine the optimal batch size were performed. From these, it was decided that 4.9 lbs was the optimal size. After this determination was made, a total of twelve batches were run using the BR1600.

The product exited the machine as a very thick substance and was collected on a pan. It was then placed, piecewise as it came out, in a cylindrical mold and compacted. Due to the low temperature of the exiting product the final, molded product was stratified between the piecewise additions of product. After all of the encapsulated material exited the machine, a portion of the dry surrogate itself would exit. The stratified product and this expulsion of dry surrogate indicate the BR1600 was not operated at a temperature high enough to successfully encapsulate our waste and form a fairly uniform product. A Farrel representative indicated a continuous process would be better for encapsulating the surrogate waste. Using the PE polymer, the highest waste loading achieved was 80%. Using the EVA, 90% waste loading rate was achieved. These numbers, however, are over-estimates of the true loading rate since not all of the surrogate was encapsulated in the polymer, but was expelled dry. The samples made at Teledyne-Readco and Farrel will be subject to a leach test to obtain a general idea of their leach potentials.

Comparison to Test Objectives

The purpose of these studies is to determine whether drying the waste to a certain temperature for a specified period of time will produce a waste product which may be bulk handled and shipped and meet WAC at selected disposal sites. These WAC may include TCLP, moisture content and free liquid content. Should further treatment be required to mitigate a dusting or handling problem which cannot be mitigated with engineering controls, agglomeration of the dried waste particles may be required. Agglomeration appears capable of creating a waste form which is essentially dust free and is durable. Further testing may be performed to define agglomeration process parameters and the

agglomerated waste form requirements for transportation. These tests would determine the appropriate moisture level, waste loading, and polymer type to meet the requirements.

4.2 QUALITY ASSURANCE/QUALITY CONTROL

The treatability study results presented in this report cover a several year period. QA/QC procedures and requirements changed over the time period these studies were performed. The work performed by IT Corporation was governed by the RI/FS QAPP. The later Duratek studies were governed by by an NQA-1 program already in practice. Later treatability studies were performed according to the Draft and Final Sitewide CERCLA Quality Assurance Project Plan (SCQ).

4.2.1 Remedy Screening/Remedy Selection Studies -- Vitrification and Cement Stabilization

The FEMP RI/FS QAPP, Revision 3, is the governing document for the remedial investigation at the FEMP. The QAPP includes the DQOs, the performance requirements to meet these objectives, and the methods for verifying that the objectives have been met. To meet the analytical DQOs of the QAPP, strict documentation procedures are used in conjunction with blanks, duplicate samples, and spiked samples to determine the data precision, accuracy, and completeness.

Daily laboratory activities were recorded in laboratory notebooks specifically assigned to this project. Logbooks used to record equipment maintenance, daily checks, and standards preparation, were assigned to specific functions or equipment. These notebooks and logbooks are returned to the quality assurance officer (QAO) after completion of the project or when the book is filled. Data recording and verification procedures are described in the Treatability Study Work Plan for Operable Unit 1, Section 7.0, Data Management.

Analyte specific QA/QC requirements for analytical work are specified in the FEMP RI/FS QAPP, Sections 4.0 and 9.0. Three types of routine quality control samples were analyzed; blanks, analytical duplicates (or spike duplicates), and spike samples. The purpose and results of these quality control samples are explained in this section.

Other quality control samples that are not included in the RI/FS QAPP are experimental duplicate and triplicate samples. Experimental duplicate samples are used to determine if a particular process produces consistent results. Experimental triplicate samples were used to determine the quality of glass produced by vitrification.

The FEMP RI/FS QAPP also specifies that data be greater than or equal to 90 percent complete. Percent completeness is a measure of how many good data points were collected from the total number of data points requested.

Five separate tasks are discussed: 5-day static leach of cement stabilized samples, TCLP of cement stabilized samples, TCLP of vitrified samples, leachability (PCT test) of vitrified samples, and triplicate analysis of PCT leachates. Each task is further divided into analytical categories. Each of the QC samples for these tasks and analytical categories are discussed separately. Data for percent completeness combines all analytical categories within a task.

Three analytical procedures are not discussed in this section; unconfined UCS, emanation, and durability (freeze/thaw and wet/dry) tests.

Three categories of analyses were requested for the 5-day static leach samples and vitrification TCLP and PCT extracts; radionuclides, metals, and general chemistry.

Six categories of analyses were requested for the cement stabilized TCLP extracts; TCL volatiles, TCL semivolatiles, TCL pesticides/polychlorinated biphenyls (PCBs), metals, radionuclides, and general chemistry.

In addition to total uranium and thorium, isotopic uranium and thorium data were reported. Isotopic uranium and thorium were not requested, and data are not used in this report, except for calculating uranium and thorium spike recoveries. Thorium-232 and uranium (U)-238 were used to spike radiological samples.

Analyses of cyanide, reactivity, and alkalinity were cancelled. The data for these analyses are not discussed in this section.

Analysis results for analytes other than those listed on the Request for Analysis are not discussed.

Section 3.0 lists the specific analytes for each analysis category. This table was taken from the Treatability Study Work Plan for Operable Unit 1, Table 3-4. Because cement is highly alkaline, the alkalinity analysis of cement stabilized 5-day static leach samples and TCLP extracts was deleted. Due to the small sample volume available for analysis, the reactivity analysis was also deleted for all samples.

Not all of the QC sample data were available for review. When QC sample data are unavailable, it is mentioned in the discussion of that QC sample.

Analysis results were to be validated prior to writing this report. However, some of the general chemistry results were not validated. For this section, the unvalidated data are treated the same as validated data, except when calculating percent completeness. Percent completeness calculations use validated data only.

The volume of data precludes listing all QC sample analytical results. Only those results that exceed tolerances specified in the RI/FS QAPP will be listed.

Blank Samples

Blank samples are analyzed to determine if detectable quantities of an analyte are being introduced into samples from either the reagents used or laboratory apparatus. Blank contamination does not automatically invalidate sample results, and must be judged on a case-by-case basis. No data were rejected due to blank contamination.

There are three general types of blank samples; extraction, sample preparation, and method. Sample preparation blanks are usually very clean, and positive results for any analyte are normally near the detection limit.

Extraction and method blanks are handled considerably more than preparation blanks and come into contact with more laboratory apparatus. It is not unusual to find low levels of contaminants in these types of blanks.

Analysis of TCLP leachates includes a reagent blank that is subjected to the same extraction and measurement process as samples. This blank is intended to show the presence of contamination present in reagents or test apparatus, and will be referred to as an extraction blank.

Prior to analysis, samples are extracted (organics), digested (metals), or otherwise prepared. A sample preparation blank, consisting of laboratory deionized water, is prepared in the same manner as the samples and is also used to show the presence of contaminates in reagents or apparatus.

Method blanks are generated by the treatability laboratory from laboratory deionized water, and submitted for analysis as a regular analytical sample. Method blanks provide information about sample shipping container cleanliness, treatability and analytical laboratory water purity, and sample preparation and measurement contamination.

During data validation, blank sample results are checked for contamination. Sample results associated with contaminated blanks are qualified according to the level of blank contamination and level of analyte in the sample. Gross blank contamination (greater than 100 times the detection limit) indicates a serious problem, and may invalidate sample results. Sample results greater than ten times blank contamination levels are not qualified. Sample results less than the blank contamination are qualified as nondetected. Sample results greater than the contamination, but less than ten times the contamination level, are qualified as estimated.

Large (greater than the negative detection limit) negative blank results normally indicate an instrument calibration problem. This problem is usually caused by using a contaminated calibration blank, or contamination in the measurement system during calibration. This causes the zero concentration point of the calibration curve to be artificially high. When an uncontaminated blank is analyzed, the instrument "sees" less than was in the calibration blank, giving a negative result. Analysis results near the detection limit are affected more (results are low) than results at medium concentrations, and results at high concentrations may not be much at all.

Calibration check blanks are analyzed periodically. If they also indicate large negative results, it is a sure indication that there is a calibration problem.

Blank sample results for each analytical category are discussed in the following sections. Tables 4-142 through 4-145 list blank results with detectable quantities of analyte. The data are grouped by task and further divided by analytical category. Only analytes with detectable quantities are listed; analytes that were not detected are not listed.

Blank data for pH measurements serve no purpose and are not included.

The following section presents a discussion of blank sample results by tasks.

Cement Stabilization 5-Day Static Leach

A total of 47 cement stabilization 5-day static leach samples were submitted for analysis of radiological, metals, and general chemistry parameters. These samples were submitted in five batches. Each batch contained a method blank. Analytes detected in both method and sample preparation blanks are presented in Table 4-146.

None of the reported radiological results contained data for laboratory sample preparation blanks. All of the metals analyses contained data for one preparation blank per sample group. Preparation blank data for general chemistry parameters are incomplete.

Most preparation blank contamination was slightly above the detection limit. Only one blank contained contamination in excess of two times the detection limit, and that contaminant, calcium, is commonly found in laboratory deionized water. None of the preparation blank contaminants were present in a quantities large enough to be of concern.

All of the contaminants found in method blanks are common laboratory contaminants, and are not present in large enough quantities to be of concern.

Two preparation blanks showed significant negative results; one for boron, and the other for aluminum. The continuing calibration blanks (blanks analyzed periodically throughout the analysis) also had large negative results for both analytes. These results would normally indicate a calibration problem with the ICP, but the method blanks associated with both analyses indicate results that are nondetected (less than detection limit, and greater than the negative value of the detection limit) for each analyte. A review of the ICP raw data would be required before a good judgment could be made as to the impact of the negative blanks on analysis data. Worst case is that samples analyzed under the same calibration curve would show slightly low results. Aluminum and boron are usually present in large enough quantities to make the calibration problem insignificant.

Cement Stabilization TCLP

Forty-two samples, in five batches, were submitted for radiological, metals, general chemistry, pesticide/PCBs, semivolatiles, and volatiles analysis.

A total of six extraction blank results were reported from four of the five radiological sample batches. One blank contained 1.16 mg/L of total uranium. This contamination is very close to the uranium detection limit and is insignificant. Other radiological analytes in all blanks were below the detection limits.

Sample preparation and extraction blank data are incomplete for the general chemistry parameters. All analytes are associated with at least one blank sample result. There were no analytes detected in the sample preparation blanks, but the extraction blanks did contain detectable quantities of some analytes.

One extraction blank contained large amounts of chloride (13615.6 micrograms per liter [μg/L]) and sulfate (18688.8 μg/L). Only one sample, 075033-10729614, is associated with this blank. Chloride was measured in the sample at 76.09 milligrams per liter (mg/L) in the sample, and sulfate at 92.46 mg/L. Neither sample result was qualified during data validation. Due to this gross contamination, chloride and sulfate analysis results for sample 075033-10729614 are invalid and should not be used.

There were six other positive results in the extraction blanks. All six results were at a low level and will have a minimal, if any, effect on sample results.

Vitrification TCLP

A total of 45 samples, in four batches, were submitted for radiological, metals, general chemistry, pesticide/PCBs, semivolatiles, and volatiles analysis. Except for radiological results, an extraction blank was reported for each sample batch. An extraction blank was reported in two of the four radiological sample batches.

There were several analytes detected in the extraction blanks. Many were near the detection limit, and will have minimal or no effect on the analysis data.

Sample preparation blanks are also reported for most of the metals, general chemistry, and organic analyses. Sample preparation blanks were not reported for radiological parameters. There were several analytes detected in the preparation blanks. Chloride and sulfate contamination may be significant. Contamination of other analytes is near the detection limit and will have minimal or no effect on the analysis data.

Vitrification PCT

A total of 51 samples, in three batches, were submitted for radiological, metals, and general chemistry analysis. The laboratory divided one batch into two separate batches for radiological analysis, for a total of four radiological batches.

One method blank was analyzed for radiological parameters. No analytes were detected.

One method blank was analyzed for metals. Twelve of 25 analytes were present. Aluminum, potassium, sodium, boron, and silicon were present in large amounts. There was insufficient time to review the sample results to determine the effects of the contamination.

One method blank was analyzed for general chemistry parameters. Phosphorus was detected at the detection limit of 0.02 mg/L. This detection should have no effect on the analytical data.

Three preparation blanks were analyzed for metals. Aluminum, boron, and silicon contamination was present at levels near the detection limit, and will have minimal or no effect on analysis data.

One preparation blank had a negative result (-109.6) for aluminum. No other blanks associated with that measurement indicated a negative result. The sample data are not affected.

Duplicate Samples

In some cases, treatability tests were performed in duplicate or triplicate (vitrification PCT test only). The purpose of these experimental duplicates is to determine the variability in the outcome of the treatment processes. Variability can be caused by several factors, i.e., sample heterogeneity, contamination, and measurement variability. Measurement variability and contamination are also checked with analytical duplicate and blank samples. By comparing analytical duplicate and blank sample results with experimental duplicate results, a general assesment can be made of sample heterogeneity.

There are two different types of duplicate samples; experimental and analytical. Experimental duplicates are two separate samples, prepared by the treatability laboratory from the same raw materials, in exactly the same manner. Experimental duplicates are usually prepared at the same time as the original sample.

Analytical duplicates are prepared by the analytical laboratory. A sample is randomly chosen and split into multiple fractions. One fraction is the "original" sample, another becomes the "duplicate" sample. A statistical calculation is performed to compare the two results.

Organics and general chemistry (except pH) analyses normally use a spike duplicate sample. This sample is prepared as described in the preceding paragraph, except that two duplicate fractions are

spiked with a known quantity of analytes. The analysis results are treated the same way as a regular duplicate sample, except that the amount of spike recovered is compared.

In some cases, blank spike duplicate samples were generated by the analytical laboratory. Blank spike samples contain laboratory deionized water that is spiked similar to a regular spike sample. Blank spike samples are used when there is insufficient sample volume to prepare a separate duplicate sample. Blank spike duplicate samples do not reflect the measurement interferences that may be present in the samples, but do indicate the general precision of the analytical system.

The purpose of analytical duplicate samples is to show measurement precision (repeatability). Experimental duplicates also indicate measurement precision, as well as variabilities in the sample and reagents. Variations in the sample can contribute to a large difference in experimental duplicate results. Comparison of analytical duplicate results to experimental duplicate results may indicate if sample variations or the measurement process are responsible for large duplicate sample variations. Such a comparison is not presented here.

Precision and sample variability are expressed as the relative percent difference (RPD) between the original and duplicate sample results. This variability is calculated according to the following equation:

$$RPD = \frac{C_1 - C_2}{\left(\frac{C_1 + C_2}{2}\right)} * 100$$

where

C_1 = The larger of two measurements

C_2 = The smaller of two measurements

The FEMP RI/FS QAPP, Table 4-1, specifies a 10 percent tolerance for precision of metals and general chemistry parameters. Table 4-2 of the RI/FS QAPP specifies precision tolerances for each

organic parameter. Table 4-3 of the RI/FS QAPP specifies a 20 percent precision tolerance for radionuclides. Precision requirements for other radionuclide parameters are not specified, but are assumed to also be 20 percent. There are no precision requirements for experimental duplicates; any results exceeding 20 percent RPD will be mentioned.

Precision is determined only for those analytes that are greater than the detection limit in both the original and duplicate samples. Precision calculations of analyte concentrations near the detection limit are not statistically valid. Analyte concentration should be greater than five times the detection limit for meaningful comparison.

Tables 4-146 through 4-149 list duplicate sample results that exceed the tolerances specified in the FEMP RI/FS QAPP. The data are grouped by task, and further divided by analytical category.

Cement Stabilization 5-Day Static Leach

Statistical comparison of duplicate results near or less than the detection limits is not valid. Analysis results should be greater than five times the detection limit for meaningful comparison. A comparison was made only when both original and duplicate samples contained measurable amounts of the analyte, even though that amount was less than five times the detection limit.

Cesium (Cs)-137 was the only radiological analyte measured in duplicate. All Cs-137 results were below the detection limit. No statistical comparison can be made.

Seven sets of experimental duplicate samples were submitted for analysis. Except for pH, a spike duplicate sample was used for general chemistry parameters. Five analytical duplicate samples were analyzed for metals and general chemistry parameters.

Generally speaking, the experimental duplicate sample results look favorable. Out of 175 duplicate analysis results, 158 (>90 percent) results met the precision requirement. Eleven of the 17 results outside the precision requirements come from one duplicate sample. Zinc had the worst results, with

five of seven results not meeting the precision requirement. Aluminum is the only other analyte with more than one result (two) not meeting the precision requirement.

Of the 125 analytical duplicate results, 120 (96 percent) met the precision requirement. Lead is the only analyte with more than one result not passing the precision requirement.

These results indicate that the raw pit samples were well homogenized prior to testing, and that analytical precision was very good.

Spike Samples

Spike sample analysis is designed to measure data accuracy, and provide information regarding the effects of sample matrix on sample preparation and analysis. Accuracy is expressed as percent recovery (R) of the spike. Poor spike recovery is usually an indication of measurement interference.

Percent spike recovery is calculated according to the following equation:

$$\%R = \frac{SSR - SR}{SA} * 100$$

where

SSR = Measured concentration of spike sample

SR = Measured concentration of original sample

SA = Concentration of spike added

The FEMP RI/FS QAPP, Revision 3, Table 4-3, lists the accuracy requirements for radiological analysis. Thirty percent accuracy is required for all radiological analytes except Pb-210. Pb-210 is not listed in the table, and the assumed accuracy requirement is thirty percent.

The accuracy requirement for metals and general chemistry data is twenty percent.

Tables 4-150 and 4-151 list those analytes with spike recoveries that do not meet the RI/FS QAPP accuracy requirement. The data are grouped by task and further divided by analytical category.

Cement Stabilization 5-Day Static Leach

Five groups of samples were submitted. One analytical spike sample was analyzed in each analysis category for each group of samples.

All of the Ra-228 spike recoveries were numerically low. This problem appears to be an inherent with the analytical method.

All of the general chemistry spike recoveries were within the 20 percent limit.

In general, spike recoveries were very good, indicating good measurement accuracy.

A blank spike sample was used for the radiological spike in one sample group. A blank spike is composed of laboratory deionized water that is spiked and processed the same way a sample is. Blank spikes do not account for interferences caused by the sample matrix, and data are limited to checking the sample preparation and analysis process. Data from blank spikes should not be used to correct sample analysis results.

PCT Triplicate Analysis

Seven vitrified samples were subjected to triplicate PCT testing to determine the quality of the glass. Each glass sample was ground to meet the PCT particle size requirement. Three separate portions of each sample were removed for PCT testing. Only five metals were measured in the PCT leachate; boron, lithium, sodium, potassium, and silicon. Lithium results are available for only two of the three replicates, and are not addressed.

The percent relative standard deviation (RSD) of the three analytical results was determined using the following equation:

$$\%RSD = \frac{AVERAGE\ SAMPLE\ CONCENTRATION}{MEASUREMENT\ STANDARD\ DEVIATION} * 100$$

A low RSD indicates a good quality glass. The results are presented in Table 4-152.

Results for two samples (075100-10670604 and 000000-10675804) were good. Sample 000000-10675804 is the Catholic University standard glass that was used as a reference. It was expected that good test results would be obtained for this sample.

Data Completeness

Percent data completeness is a measure of how much of the data requested is collected and valid. Percent completeness (percent C) is calculated according to the following equation:

$$\%C = \frac{V}{n} * 100$$

where

V = Number of measurements reported and judged valid

n = Total number of sample measurements

The FEMP RI/FS QAPP, Tables 4-1 through 4-3, specifies that data be ≥90 percent complete.

A summary of data percent completeness is presented in Table 4-153 . All data for samples submitted for analysis are used to calculate percent completeness. Laboratory QC samples and nonrequested analyses are not considered in the percent completeness data. Percent completeness data are calculated for each task and analytical category.

4.2.2 Remedy Design Vitrification Studies

The specific QA/QC requirements for these programs are found in the individual Treatability Study Work Plans for Remedy Design Laboratory Studies by GTS Duratek/CUA and the MAWS Work Plan. These studies were initiated under NQA-1 guidelines which were the existing standard for the site at the initiation of the laboratory project. Procedures and requirements were modified where possible to comply with the Draft SCQ when it was issued. Implementation of the SCQ continued into the MAWS project.

4.2.3 Thermal Processing and Particle Agglomeration

Specific QA/QC requirements are detailed in the Draft Cooperative Remedy Screening Treatability Study Work Plan, June 1993. The requirements of that work plan comply with the provisions of the FEMP Sitewide CERCLA Quality Assurance Project Plan, September 1992.

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Table 4-142

ANALYTES DETECTED IN FIVE-DAY STATIC LEACH BLANKS

Stabilization Five-Day Static Leach Test				
Analysis Category	Type of Blank	Analyte	Contamination Concentration g/l	Detection Limit g/l
Radiological	Preparation - none reported			
	Method (5 reported)	Total Uranium	14.0	Unknown
		Total Uranium	5.78	Unknown
Metals	Preparation (5 reported)	Aluminum	-129.6	30.0
		Boron	-95.8 52.19[a]	50.0
		Calcium	131 53.4	20.0
		Silicon	116.2	100
		Zinc	6.65 9.73	5.0
	Method (5 reported)	Barium	2.4	2.0
		Calcium	53.5 71.6 173 131 78	20.0
		Potassium	208	100
		Magnesium	125	50.0
Metals, continued	Method, continued	Silicon	111	100
		Sodium	241	100
		Zinc	10.2 6.9 7.4 13.2 9.9	5.0
General Chemistry	Preparation (4 reported)	None detected		
	Method (5 reported)	Ammonia	0.15 mg/l	0.1 mg/l
		Chloride	2.2 mg/l	0.5 mg/l
		Nitrate	0.154 mg/l	0.1 mg/l

[a]More than one entry indicates that more than one blank was contaminated.

Table 4-143

ANALYTES DETECTED IN STABILIZATION TCLP BLANKS

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Cement Stabilization TCLP Test				
Analysis Category	Type of Blank	Analyte	Contamination Concentration g/l	Detection Limit g/l
Radiological	Preparation - none reported			
	Extraction (duplicate)	Total Uranium	1.16 (203)	Unknown
Metals		Aluminum	-119.1	30.0
		Calcium	22.6	20.0
		Zinc	7.7	5
	Extraction (8 reported)	Aluminum	306	30.0
			41.8	
			32.5	
			31.2	
			69.4	
		Arsenic	4.4	2.0
		Barium	78.0	2.0
			10.4	
			6.1	
			11.3	
			79.4	
			15.7	
			77.9	
			91.8	
		Boron	72.3	50.0
			65.2	
			68.2	
			68.6	
		Calcium	720	20.0
			1630	
			191	
			109	
			184	
			118	
			287	
			429	
		Magnesium	384	50.0

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Table 4-143

(Continued)

Cement Stabilization TCLP Test				
Analysis Category	Type of Blank	Analyte	Contamination Concentration g/l	Detection Limit g/l
Metals, continued	Preparation, continued	Silicon	635	100
			131	
			273	
			126	
			331	
			218	
		Sodium	814	100
			52300	
			225	
			70800	
			1280	
		Zinc	54.3	5.0
			21.1	
			12.8	
			17.0	
			54.7	
			66.0	
General Chemistry	Preparation (5 reported)	None detected		
	Extraction (5 reported)	Ammonia	0.14 mg/l	0.1 mg/l
			0.22 mg/l	
		Chloride (7 extraction blanks reported)	1.2 mg/l	0.5 mg/l
			0.6 mg/l	
			4.9 mg/l	
			0.54 mg/l	
			0.86 mg/l	
			6.01 mg/l	
			13616 mg/l	
		Sulfate	18689 mg/l	2.0 mg/l

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Table 4-144

ANALYTES DETECTED IN VITRIFICATION TCLP BLANKS

Vitrification TCLP Test				
Analysis Category	Type of Blank	Analyte	Contamination Concentration g/l	Detection Limit g/l
Radiological	Preparation - none reported			
	Extraction (2 reported)	Radium-226	4.44	Unknown
Metals	Preparation (4 reported)	Aluminum	43.8	30.0
		Boron	14.2	50.0
		Calcium	31.6 33.2 22.0	20.0
		Magnesium	52.1 -64.6	50.0
	Extraction (4 reported)	Aluminum	48.9 62.1	30.0
		Barium	34.3 12.1 33.7	2.0
		Boron	52.9 80.2 80.9	50.0
		Calcium	238 164 207 279	20.0
		Magnesium	100 265	50.0
		Potassium	266 286 154 384	100
		Silicon	479 326 352	100
Metals, continued	Extraction, continued	Zinc	34.5 52.5 20.5 29.3	5.0

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Table 4-144

(Continued)

Vitrification TCLP Test

Analysis Category	Type of Blank	Analyte	Contamination Concentration g/l	Detection Limit g/l
General Chemistry	Preparation (2 reported)	Chloride	32.9 mg/l	0.5 mg/l
		Sulfate	22.2 mg/l	0.5 mg/l
	Extraction (3 reported)	Ammonia	0.44 mg/l 0.33 mg/l	0.1 mg/l
		Chloride	27.0 mg/l 53.02 mg/l	0.5 mg/l 0.4 mg/l
		Sulfate	26.36 mg/l	2.0 mg/l

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Table 4-145

ANALYTES DETECTED IN VITRIFICATION PCT BLANKS

Vitrification PCT Test				
Analysis Category	Type of Blank	Analyte	Contamination Concentration µg/l	Detection Limit µg/l
Radiological	Preparation - none reported			
	Method (1 reported)	None detected		
Metals	Preparation (3 reported)	Aluminum	-109.6 35.2	30.0
		Boron	18.1	50.0
		Silicon	129.3	100
	Method (1 reported)	Aluminum	6670	30.0
		Arsenic	4.6	2.0
		Barium	3.3	2.0
		Boron	14100	50.0
		Calcium	53.7	20.0
		Magnesium	172	50.0
		Manganese	57.3	10.0
		Molybdenum	148	20.0
		Potassium	10600	100
		Silicon	49000	100
		Sodium	38300	100
		Zinc	6.1	5.0
General Chemistry	Preparation (3 reported)	None detected		
	Method (1 reported)	Fluoride	0.06 mg/l	0.05 mg/l
		Phosphorous	0.02 mg/l	0.02 mg/l

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Table 4-146

OUT OF TOLERANCE ANALYTICAL DUPLICATE SAMPLES FOR FIVE-DAY STATIC LEACH TEST

Five-Day Static Leach			
Analysis Category	Analyte	Relative Percent Difference	>5 Times The Detection Limit?
Radiological, ±20% (3 Cesium-137 duplicates and 1 blank spike duplicate reported)	Neptunium-237	20.5	Yes
	Radium-228	27.2	Yes
	Strontium-90	124.5	Yes
	Technecium-99	128.8	Yes
Metals, ±10% (5 reported)	Lead	200	No
		11.4	Yes
	Magnesium	15.2	No
	Selenium	10.5	Yes
	Silicon	14.7	Yes
	Thallium	76.1	Yes
General Chemistry, ±10% (5 reported)	Sulfate	17.7	Yes

0590

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Table 4-147

OUT OF TOLERANCE ANALYTICAL DUPLICATE SAMPLES FOR STABILIZATION TCLP TEST

Cement Stabilization TCLP Test			
Analysis Category	Analyte	Relative Percent Difference	Analyte >5 Times the Detection Limit?
Radiological, ±20% (4 cesium-137 duplicates reported)	Cesium-137	0 (analyte not detected)	No
Metals, ±10% (data could not be compared)	NA	NA	NA
General Chemistry, ±10% (5 reported)	Ammonia	15.1 11.0	Yes
	Fluoride	10.3	Yes

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TABLE 4-148

OUT OF TOLERANCE ANALYTICAL DUPLICATE SAMPLES
FOR VITRIFICATION TCLP TEST

Vitrification TCLP Test			
Analysis Category	Analyte	Relative Percent Difference	> 5 Times the Detection Limit?
Radiological, ±20% (4 reported)	Total Uranium	63.3	No
Metals, ±10% (4 reported)	Calcium	13.9	Yes
	Magnesium	22.7	No
	Selenium	10.4 10.4	No
	Thallium	12.3	Yes
General Chemistry, ±10% (2 reported, all blank spike duplicates)	Chloride	13.2	Yes
	Fluoride	73.4	Yes
	Phosphate	10.5	Yes

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TABLE 4-149

OUT OF TOLERANCE ANALYTICAL DUPLICATE SAMPLES
FOR VITRIFICATION PCT TEST

Vitrification PCT Test			
Analysis Category	Analyte	Relative Percent Difference	>5 Times the Detection Limit?
Radiological, ±20% (3 reported)	None out of tolerance		
Metals, ±10% (1 available)	None out of tolerance		
General Chemistry, ±20% (data unavailable)	NA		

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TABLE 4-150

OUT OF TOLERANCE SPIKE SAMPLE RECOVERY FOR FIVE-DAY STATIC LEACH TEST

Five-Day Static Leach			
Analysis Category	Type of Spike	Analyte	Percent Recovery (%)
Radiological, ±30%	Spike	Np-237	52.3
		Ra-228	40.5
			22.7
			47.9
			25.6
		Sr-90	132
			140.8
Metals, ±20%	Spike	Cadmium	77.4
		Mercury	122.7
		Thallium	76.1
General Chemistry, ±20%	Blank Spike	None	na

Table 4-151

OUT OF TOLERANCE SPIKE SAMPLE RECOVERY FOR STABILIZATION TCLP TEST

Cement Stabilization TCLP			
Analysis Category	Type of Spike	Analyte	Percent Recovery (%)
Radiological, ±30%			

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TABLE 4-152

PCT TRIPLICATE ANALYSIS COMPARISON

Vitrification PCT Triplicate Analysis				
Sample Number	Analyte	Average Concentration	Standard Deviation of Measurements	Percent Relative Standard Deviation
075100-10670604	Boron	4603.3	815.3	17.7
	Potassium	27266.6	1965.5	7.21
	Silicon	54066.7	6557.7	12.1
	Sodium	493000	19924.9	4.04
075101-10670804	Boron	6556.7	2769.6	42.2
	Potassium	2560	408.4	16.0
	Silicon	61900	22954.1	37.1
	Sodium	399733.3	312936.4	78.3
075102-10671004	Boron	1842.7	1129.7	61.3
	Potassium	1590	195.2	12.3
	Silicon	21066.7	9325.4	44.3
	Sodium	287333.3	110495.8	38.5
075103-10671204	Boron	575	442.1	76.9
	Potassium	2046.3	2274.1	111.1
	Silicon	15633.3	5776.1	37.0
	Sodium	96966.7	75495.7	77.9
075100-10674204	Boron	2601.3	2738.5	105.3
	Potassium	2003.3	1192.7	59.5
	Silicon	29500	24651.4	83.6
	Sodium	305333.3	245663	80.5
075101-10674404	Boron	323	339.6	105.1
	Potassium	3172.7	2103.8	66.3
	Silicon	17333.3	5085.6	29.3
	Sodium	58033.3	80511.9	138.7
000000-10675804 Catholic University Reference Glass	Boron	13266.7	723.4	5.45
	Potassium	9270	1388.3	15.0
	Silicon	46200	3019.9	6.54
	Sodium	37100	1253	3.38

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TABLE 4-153

DATA PERCENT COMPLETENESS

Task	Analysis Category	Total Number of Measurements	Number of Valid Measurements	Percent Complete (%)
Five-Day Static Leach	Radiological	517	482	93.2
	Metals	1175	1175	100
	General Chemistry	329	327	99.4
	Total	2021	1984	98.2
Cement Stabilization TCLP	Radiological	462	427	92.4
	Metals	1052	1028	97.7
	General Chemistry	77 validated 175 unvalidated	67	87.0
	Pesticide/PCB	1134	1134	100
	Semivolatiles	2730	2705	99.1
	Volatiles	1428	1428	100
	Total	6883	6789	98.6
Vitrification TCLP	Radiological	456	442	96.9
	Metals	1125	1125	100
	General Chemistry	302 validated 14 unvalidated	294	97.4
	Total	1883	1861	98.8
Vitrification PCT	Radiological	561	479	85.4
	Metals	1275	1273	99.8
	General Chemistry	189	151	79.9
	Total	2025	1903	94.0
Project Totals		12812	12537	97.9

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SECTION 5.0

This Section lists the Contaminants of Potential Concern (CPSs) as identified in the Operable Unit 1 Remedial Investigation Report, October 1993.

TABLE 5-1

RADIOLOGICAL CPCs IN SURFACE SOIL (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	31/60	6.00	1.00	1.00	0/7	ND[a]			1.00
Neptunium-237	1/60	0.500	0.100	0.500	0/7	ND			0.500
Plutonium-238	11/60	4.10	0.400	0.400	0/7	ND			0.400
Plutonium-239/240	10/60	0.800	0.100	0.100	0/7	ND			0.100
Radium-226					5/7	1.20	1.00	1.00	1.00
Radium-228					5/7	1.80	1.20	1.20	1.20
Strontium-90	3/60	1.70	0.400	1.70	2/7	0.600	0.400	0.600	1.70
Technetium-99	18/60	93.0	8.70	8.70	1/7	0.900	0.600	0.900	8.70
Thorium-228	50/60	48.0	5.50	5.50	7/7	2.20	1.60	1.60	5.50
Thorium-230	59/60	972	74.9	74.9	7/7	6.10	3.90	3.90	74.9
Thorium-232	48/60	38.0	4.30	4.30	7/7	1.30	1.10	1.10	4.30
Uranium-234	60/60	298	60.1	60.1	7/7	5.30	4.20	4.20	60.1
Uranium-235	60/60	51.0	6.80	6.80	1/7	0.800	0.50	0.800	6.80
Uranium-238	60/60	1500	245	245	7/7	16.1	11.5	11.5	245

[a]ND - Not detected.

TABLE 5-2

CHEMICAL CPCs IN SURFACE SOIL

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
Aroclor-1254					3/16	1400	310	1400	1400
Inorganics (mg/kg)									
Antimony					16/16	32.5	27.2	27.2	27.2
Arsenic					16/16	6.40	4.90	4.90	4.90
Barium					16/16	92.3	56.9	56.9	56.9
Beryllium					16/16	1.00	0.800	0.800	0.800
Cadmium					16/16	7.70	5.80	5.80	5.80
Chromium					16/16	18.8	14.3	14.3	14.3
Cobalt					16/16	17.0	10.4	10.4	10.4
Copper					16/16	20.1	17.0	17.0	17.0
Lead					16/16	34.3	15.9	15.9	15.9
Manganese					16/16	759	574	574	574
Molybdenum					15/16	5.70	4.30	4.30	4.30
Nickel					16/16	50.2	29.4	29.4	29.4
Silver					16/16	10.3	8.90	8.90	8.90
Uranium					5/5	62.0	52.2	52.2	52.2
Vanadium					16/16	26.9	19.6	19.6	19.6
Zinc					16/16	79.9	46.7	46.7	46.7

TABLE 5-3

RADIOLOGICAL CPCs IN WASTE PIT 1 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	1/5	1.10	0.800	1.10	0/6	ND[a]			1.10
Radium-226					5/6	99.6	86.7	86.7	86.7
Radium-228					5/6	41.0	35.1	35.1	35.1
Strontium-90	0/5	ND			5/6	7.69	4.70	4.70	4.70
Technetium-99	1/5	15.0	9.70	15.0	1/6	1.10	0.800	1.10	15.0
Thorium-228	5/5	52.0	37.8	37.8	1/4	131	433	131	131
Thorium-230	5/5	3600	2800	2800	3/4	5460	6660	5460	5460
Thorium-232	5/5	55.0	39.8	39.8	1/4	131	246	131	131
Uranium-234	5/5	1180	902	902	4/4	830	795	795	902
Uranium-235	5/5	151	108	108	5/5	259	179	179	179
Uranium-238	5/5	6980	4660	4660	5/5	16200	10400	10400	10400

[a]ND - Not detected

TABLE 5-4

CHEMICAL CPCs IN WASTE PIT 1 - SOLID CONTENTS

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin					5/6	1.20	0.770	0.770	0.770
1,2,3,4,6,7,8-Heptachlorodibenzofuran					5/6	1.20	0.800	0.800	0.800
1,2,3,4,7,8-Hexachlorodibenzofuran					3/6	0.830	0.660	0.830	0.830
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin					4/6	0.770	0.520	0.520	0.520
1,2,3,6,7,8-Hexachlorodibenzofuran					3/6	0.290	0.230	0.290	0.290
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin					3/6	0.530	0.340	0.530	0.530
1,2,3,7,8-Pentachlorodibenzofuran					5/6	1.20	0.730	0.730	0.730
2,3,4,6,7,8-Hexachlorodibenzofuran					3/6	0.410	0.320	0.410	0.410
2,3,4,7,8-Pentachlorodibenzofuran					4/6	1.20	0.750	0.750	0.750
2,3,7,8-Tetrachlorodibenzofuran					5/6	14.0	7.64	7.64	7.64
Heptachlorodibenzo-p-dioxin					5/6	2.30	1.45	1.45	1.45
Heptachlorodibenzofuran					5/6	2.70	1.75	1.75	1.75
Hexachlorodibenzo-p-dioxin					5/6	4.90	3.21	3.21	3.21
Hexachlorodibenzofuran					4/6	2.90	2.26	2.26	2.26
Octachlorodibenzo-p-dioxin					5/6	0.74	0.540	0.540	0.540
Octachlorodibenzofuran					3/6	0.760	0.460	0.760	0.760
Pentachlorodibenzofuran					5/6	7.90	4.69	4.69	4.69
Tetrachlorodibenzofuran					6/6	35.0	20.7	20.7	20.7
4,4-DDT	1/6	1600	934	1600	0/5	ND[a]			1600
Aroclor-1221					1/5	4600	4120	4120	4600

TABLE 5-4 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Aroclor-1248	1/6	3500	2540	3500	5/6	10000	7070	7070	7070
Aroclor-1254	6/6	11500	9980	9978	5/5	10000	9250	9250	9980
Aroclor-1260	2/6	7800	6110	7800	0/5	ND			7800
Benzo(a)anthracene	3/6	180	245	180	0/8	ND			180
Benzo(a)pyrene	1/6	140	257	140	0/7	ND			140
Benzo(b)fluoranthene	5/6	330	307	307	0/8	ND			307
Benzo(k)fluoranthene	1/6	140	257	140	0/8	ND			140
Chrysene	5/6	540	451	451	0/8	ND			451
Dichlorodifluoromethane					1/2	29600	107900	29600	29600
Fluoranthene	6/6	430	340	340	2/8	1000	532	1000	1000
Phenanthrene	6/6	2400	1880	1880	5/8	2100	1140	1140	1880
Tetrachloroethene	1/5	120	120	120	6/9	650	252	252	252
Tributyl phosphate					3/3	25000	32600	25000	25000
Inorganics (mg/kg)									
Antimony	1/6	0.400	0.963	0.400	6/6	125	88.9	88.9	88.9
Arsenic	6/6	15.0	11.3	11.3	5/6	1.70	1.70	1.70	11.3
Barium	6/6	395	374	374	6/6	439	405	405	405
Beryllium	5/6	2.20	1.81	1.81	6/6	12.5	8.21	8.21	8.21
Boron					4/5	1650	1220	1220	1220
Cadmium	5/6	5.00	3.32	3.32	6/6	18.5	16.2	16.2	16.2
Chromium	6/6	40.0	30.1	30.1	6/6	347	226	226	226

TABLE 5-4 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cobalt	3/6	28.0	16.7	28.0	6/6	46.8	33.8	33.8	33.8
Copper	1/6	20.0	47.2	20.0	6/6	113	80.0	80.0	80.0
Cyanide	0/6	ND			3/6	0.730	0.450	0.730	0.730
Lead	1/6	17.0	28.7	17.0	5/5	53.4	36.6	36.6	36.6
Manganese	6/6	2910	2130	2130	6/6	3720	2037	2037	2030
Mercury	1/6	0.300	0.182	0.300	0/6	ND			0.300
Molybdenum					6/6	32.7	25.7	25.7	25.7
Nickel	6/6	65.0	41.8	41.8	6/6	57.4	47.1	47.1	47.1
Silver	4/6	33.0	17.8	17.8	6/6	189	122	122	122
Thallium	1/6	0.300	0.220	0.300	1/6	0.460	0.350	0.460	0.460
Uranium					6/6	48500	35000	35000	35000
Vanadium	6/6	67.0	48.3	48.3	6/6	142	95.7	95.7	95.7
Zinc	4/6	58.0	36.7	36.7	6/6	24.9	19.31	19.31	36.7

[a]ND - Not detected

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TABLE 5-5

RADIOLOGICAL CPCs IN WASTE PIT 2 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	2/5	3.60	2.50	3.60	2/4	0.500	0.700	0.500	3.60
Plutonium-238	2/5	0.100	0.100	0.100	0/4	ND*			0.100
Plutonium-239/240	2/5	0.600	0.400	0.600	0/4	ND			0.600
Radium-226					4/4	951	850	850	850
Radium-228					4/4	437	382	382	382
Ruthenium-106	0/5	ND			2/4	4.70	6.00	4.70	4.70
Strontium-90	0/5	ND			3/4	3.99	4.40	3.99	3.99
Technetium-99	3/5	618	390	618	1/4	1.64	1.40	1.64	618
Thorium-228	5/5	164	121	121	2/2	697	912	697	697
Thorium-230	5/5	3980	2990	2990	2/2	18400	60300	18400	18400
Thorium-232	5/5	88.0	69.5	69.5	1/2	268	528	268	268
Uranium-234	5/5	18200	11500	11500	2/2	1651	5370	1651	11500
Uranium-235	5/5	8780	5520	5520	2/2	130	426	130	5520
Uranium-238	5/5	17900	11900	11900	2/2	1860	6064	1860	11900

*ND - Not detected

TABLE 5-6

CHEMICAL CPCs IN WASTE PIT 2 - SOLID CONTENTS

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (µg/kg)									
1,2,3,4,6,7,8-Heptachlorodibenzofuran					1/4	1.00	0.866	1.00	1.00
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin					2/4	3.80	3.30	3.80	3.80
1,2,3,4,7,8-Hexachlorodibenzofuran					1/4	0.260	0.256	0.260	0.260
Heptachlorodibenzofuran					3/4	5.90	5.12	5.90	5.90
Heptachlorodibenzo-p-dioxin					3/4	8.10	7.05	8.10	8.10
Hexachlorodibenzofuran					2/4	2.70	2.28	2.70	2.70
Hexachlorodibenzo-p-dioxin					1/4	0.320	0.367	0.320	0.320
Octachlorodibenzofuran					3/4	4.90	4.30	4.90	4.90
Octachlorodibenzo-p-dioxin					3/4	45.9	40.3	45.9	45.9
Pentachlorodibenzofuran					1/4	0.550	0.481	0.550	0.550
2-Methylnaphthalene	2/5	7000	4500	7000	3/7	7800	4980	7800	7800
4-Nitroaniline	1/5	4900	4210	4900	0/7	ND*			4900
4-Nitrophenol	0/5	ND			1/7	190	6150	190	190
4,4'-DDT	2/5	1400	1040	1400					1400
Acenaphthene	2/5	1200	876	1200	3/7	31000	20000	31000	31000
Acenaphthylene	1/5	43000	27100	43000	1/7	110	1280	110	43000
Anthracene	4/5	120000	75600	75600	3/7	56000	30800	56000	75600
Aroclor-1248	1/5	321	1750	321	2/4	4900	4320	4900	4900
Aroclor-1254	1/5	323	3360	323	0/4	ND			323
Benzene	0/4	ND			1/11	4.00	8.90	4.00	4.00
Benzo(a)anthracene	5/5	130000	82000	82000	3/7	100000	62200	100000	100000

TABLE 5-6 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Benzo(a)pyrene	4/5	120000	75700	75700	3/7	68000	43700	68000	75700
Benzo(b)fluoranthene	5/5	10000	7410	7410	3/7	130000	55600	130000	130000
Benzo(g,h,i)perylene	3/5	42000	26500	42000	3/7	42000	27300	42000	42000
Benzo(k)fluoranthene	4/5	75000	47300	47300	3/7	44000	25600	44000	47300
Chrysene	5/6	130000	65900	65900	2/7	86000	46200	86000	86000
Dibenzofuran	3/5	36000	22700	36000	3/7	21000	13700	21000	36000
Dibenzo(a,h)anthracene	2/5	16000	10200	16000	3/7	20000	11000	20000	20000
Fluoranthene	5/5	490000	309000	309000	5/7	280000	158000	158000	309000
Fluorene	3/5	62000	39100	62000	3/7	37000	23200	37000	62000
Indeno(1,2,3-cd)pyrene	3/5	46000	29100	46000	3/7	37000	23500	37000	46000
Naphthalene	3/5	16000	10300	16000	3/7	23000	14300	23000	23000
Pentachlorophenol	0/5	ND			2/7	1600	5530	1600	1600
Phenanthrene	4/4	18000	15200	15200	5/7	280000	156000	156000	156000
Pyrene	5/5	250000	158000	158000	5/7	230000	132000	132000	158000
Tetrachloroethene	0/4	ND			1/11	45.0	17.0	45.0	45.0
Tributyl phosphate					4/4	39000	41700	39000	39000
Vinyl chloride	1/4	670	622	670	6/11	1900	724	724	724
Inorganics (mg/kg)									
Antimony	2/5	1.20	0.995	1.20	4/4	55.4	58.8	55.4	55.4
Arsenic	5/5	10.0	7.51	7.51	4/4	423	380	380	380
Barium	5/5	208	174	174	4/4	1920	1960	1920	1920
Beryllium	5/5	8.90	6.40	6.40	4/4	26.9	26.8	26.8	26.8
Boron					4/4	238	248	238	238

TABLE 5-6 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cadmium	5/5	9.60	7.92	7.92	4/4	12.8	13.5	12.8	12.8
Chromium	5/5	91.0	67.4	67.4	4/4	282	294	282	282
Cobalt	5/5	451	295	295	4/4	1470	1320	1320	1320
Copper	5/5	329	222	222	4/4	1340	1260	1260	1260
Cyanide	0/5	ND			4/4	2.90	2.64	2.64	2.64
Lead	5/5	190	140	140	4/4	758	848	758	758
Manganese	5/5	917	846	846	4/4	2850	2660	2660	2660
Mercury	4/5	0.700	0.581	0.581	4/4	2.60	2.81	2.60	2.60
Molybdenum					4/4	215	193	193	193
Nickel	5/5	609	404	404	4/4	1740	1580	1580	1580
Selenium	3/5	10.0	6.67	10.0	4/4	131	114	114	114
Silver	3/5	23.0	17.1	23.0	4/4	42.5	41.0	41.0	41.0
Thallium	0/5	ND			1/4	2.40	2.10	2.40	2.40
Vanadium	5/5	106	82.5	82.5	4/4	594	529	529	529
Zinc	5/5	3250	2070	2070	4/4	488	468	468	2070

*ND - Not detected

TABLE 5-7

RADIOLOGICAL CPCs IN WASTE PIT 3 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Neptunium-237	3/7	2.10	1.10	2.10					2.10
Plutonium-238	3/7	1.00	0.500	1.00	1/5	0.980	0.700	0.980	1.00
Plutonium-239/240	3/7	14.0	6.00	14.0	2/5	1.59	1.40	1.59	14.0
Radium-226					6/6	451	306	306	306
Radium-228					6/6	241	186	186	186
Strontium-90	1/7	5.20	2.60	5.20	4/6	4.91	2.80	2.80	5.20
Technetium-99	6/7	1110	521	521	6/6	33	22.7	22.7	521
Thorium-228	7/7	40.0	21.6	21.6	3/5	554	526	554	554
Thorium-230	7/7	11700	8320	8320	6/6	11400	8570	8570	8570
Thorium-232	7/7	59.0	30.7	30.7	3/5	396	334	396	396
Uranium-234	7/7	475	327	327	4/4	991	1110	991	991
Uranium-235	7/7	21.0	16.6	16.6	1/1	51.8		51.8	51.8
Uranium-235/236					4/4	89.2	73.0	73.0	73.0
Uranium-238	7/7	1380	762	762	6/6	1740	1290	1290	1290

TABLE 5-8

CHEMICAL CPCs IN WASTE PIT 3 - SOLID CONTENTS

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin					5/6	1.70	1.12	1.12	1.12
1,2,3,4,6,7,8-Heptachlorodibenzofuran					3/6	0.210	0.164	0.210	0.210
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin					1/6	0.048	0.256	0.048	0.048
Heptachlorodibenzo-p-dioxin					5/6	3.20	2.10	2.10	2.10
Heptachlorodibenzofuran					5/6	0.950	0.687	0.687	0.687
Hexachlorodibenzo-p-dioxin					1/6	0.260	0.180	0.260	0.260
Hexachlorodibenzofuran					4/6	0.350	0.267	0.267	0.267
Octachlorodibenzo-p-dioxin					6/6	19.4	12.7	12.7	12.7
Octachlorodibenzofuran					5/6	1.10	0.745	0.745	0.745
Tetrachlorodibenzofuran					1/6	0.200	0.117	0.200	0.200
Aroclor-1248	0/5	ND[a]			4/6	4800	2730	2730	2730
Aroclor-1254	1/5	140	331	140	5/6	3400	2080	2080	2080
Benzo(a)anthracene	1/7	60.0	394	60.0	1/7	360	471	360	360
Benzo(a)pyrene	0/7	ND			1/7	280	467	280	280
Benzo(b)fluoranthene	1/7	110	391	110	1/7	560	510	560	560
Benzo(g,h,i)perylene	0/7	ND			1/7	160	470	160	160
Chrysene	1/7	75.0	393	75.0	1/7	370	472	370	370
Indeno(1,2,3-cd)pyrene	0/7	ND			1/7	130	472	130	130
Pentachlorophenol	2/6	1300	1470	1300	5/5	1000	783	783	1300

TABLE 5-8 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Inorganics (mg/kg)									
Antimony	2/7	18.0	10.0	18.0	4/6	63.5	52.5	52.5	52.5
Arsenic	7/7	3050	1800	1800	6/6	37200	21300	21300	21300
Barium	7/7	14400	8080	8080	6/6	3570	2540	2540	8080
Beryllium	7/7	24.0	14.4	14.4	6/6	10.7	8.64	8.64	14.4
Boron					4/6	236	155	155	155
Cadmium	7/7	13.0	8.46	8.46	6/6	38.6	25.9	25.9	25.9
Chromium	7/7	152	110	110	6/6	234	186	186	186
Cobalt	7/7	21.0	17.5	17.5	6/6	50.7	36.0	36.0	36.0
Copper	4/7	2330	1670	1670	6/6	2010	1740	1740	1740
Cyanide	0/6	ND			4/6	1.70	1.61	1.61	1.61
Lead	5/7	613	358	358	6/6	837	670	670	670
Manganese	7/7	10600	5120	5120	6/6	20200	16700	16700	16700
Mercury	5/7	4.00	2.00	2.00	5/6	5.10	3.19	3.19	3.19
Molybdenum					6/6	284	241	241	241
Nickel	7/7	504	266	266	6/6	292	206	206	266
Selenium	5/7	90.0	49.5	49.5	5/6	6.00	4.29	4.29	49.5
Silver	4/7	8.10	6.62	6.62	6/6	41.8	37.4	37.4	37.4
Thallium	3/7	12.0	6.40	12.0	4/6	4.10	3.15	3.15	12.0
Tin					1/5	191	134	191	191
Uranium					6/6	5940	4560	4560	4560

TABLE 5-8 (Continued)

PARAMETER	CIS DATA				RI/FS DATA				CPC CONCENTRATION
	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	
Vanadium	7/7	9700	5200	5200	6/6	2200	1890	1890	5200
Zinc	3/7	311	168	311	6/6	325	211	211	311

[a]ND - Not detected

TABLE 5-9

RADIOLOGICAL CPCs IN WASTE PIT 4 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Neptunium-237	1/4	0.400	0.400	0.400					0.400
Plutonium-238	2/4	0.500	0.500	0.500					0.500
Plutonium-239/240	1/4	0.400	0.300	0.400					0.400
Radium-226					5/6	50.1	36.6	36.6	36.6
Radium-228					6/6	141	99.7	99.7	99.7
Strontium-90	0/4	ND[a]			5/6	144	99.4	99.4	99.4
Technetium-99	4/4	225	197	197	5/6	9.43	6.60	6.60	197
Thorium-228	4/4	395	335	335	4/4	2470	2320	2320	2320
Thorium-230	4/4	566	620	566	6/6	1820	1520	1520	1520
Thorium-232	4/4	92.0	80.2	80.2	4/4	838	708	708	708
Uranium-234	4/4	2320	1990	1990	3/3	4100	6060	4100	4100
Uranium-235	4/4	426	368	368	1/1	26.6		26.6	368
Uranium-235/236					4/4	934	898	898	898
Uranium-238	4/4	15800	13400	13400	4/4	41900	44500	41900	41900

[a]ND - Not detected

TABLE 5-10

CHEMICAL CPCs IN WASTE PIT 4 - SOLID CONTENTS

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
1,2,3,4,7,8,9-Heptachlorodibenzofuran					3/6	2.40	1.59	2.40	2.40
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin					1/6	0.060	0.689	0.060	0.060
1,2,3,4,7,8-Hexachlorodibenzofuran					5/6	2.90	1.80	1.80	1.80
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin					2/6	0.160	0.564	0.160	0.160
1,2,3,6,7,8-Hexachlorodibenzofuran					5/6	1.10	0.830	0.830	0.830
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin					2/6	0.220	0.476	0.220	0.220
1,2,3,7,8,9-Hexachlorodibenzofuran					3/6	0.750	1.04	0.750	0.750
1,2,3,7,8-Pentachlorodibenzofuran					5/6	2.10	1.39	1.39	1.39
2,3,4,6,7,8-Hexachlorodibenzofuran					4/6	1.20	0.814	0.814	0.814
2,3,4,7,8-Pentachlorodibenzofuran					5/6	2.70	1.74	1.74	1.74
2,3,7,8-Tetrachlorodibenzofuran					5/6	9.90	6.97	6.97	6.97
Heptachlorodibenzo-p-dioxin					5/6	4.00	3.16	3.16	3.16
Heptachlorodibenzofuran					5/6	4.40	3.18	3.18	3.18
Hexachlorodibenzo-p-dioxin					4/6	2.70	1.85	1.85	1.85
Hexachlorodibenzofuran					5/6	8.50	5.39	5.39	5.39
Octachlorodibenzo-p-dioxin					5/6	9.00	6.52	6.52	6.52
Octachlorodibenzofuran					4/6	4.90	3.66	3.66	3.66
Pentachlorodibenzofuran					5/6	15.3	9.42	9.42	9.42
Tetrachlorodibenzo-p-dioxin					2/6	0.470	0.316	0.470	0.470
Tetrachlorodibenzofuran					6/6	34.1	24.1	24.1	24.1

TABLE 5-10 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
4-Nitrophenol	1/4	2300	2110	2300	0/9	ND			2300
Acenaphthene	2/4	1200	1040	1200	2/9	1900	904	1900	1900
Anthracene	3/4	2500	2160	2500	2/9	2700	1180	2700	2700
Aroclor-1242	2/4	1030	904	1030	0/6	ND[a]			1030
Aroclor-1248	2/4	854	808	854	4/6	7500	5920	5920	5920
Aroclor-1254	4/4	1010	942	942	3/6	6800	4190	6800	6800
Benzene	0/4	ND			1/11	14.0	5.83	14.0	14.0
Benzo(a)anthracene	4/4	4100	3530	3530	2/9	4700	2000	4700	4700
Benzo(a)pyrene	3/4	4500	3840	4500	2/9	2900	1310	2900	4500
Benzo(b)fluoranthene	3/4	3800	3240	3800	2/9	5200	2360	5200	5200
Benzo(g,h,i)perylene	2/4	170	242	170	1/9	990	691	990	990
Benzo(k)fluoranthene	3/4	3700	3170	3700	0/9	ND			3700
Chrysene	4/4	4500	3860	3860	2/9	3300	1580	3300	3860
Dibenzofuran	3/4	1400	1200	1400	2/9	1200	638	1200	1400
Dibenzo(a,h)anthracene	1/4	65.0	273	65.0	0/9	ND			65.0
Fluoranthene	4/4	9900	8570	8570	2/9	11000	4210	11000	11000
Fluorene	3/4	2200	1880	2200	2/9	2000	951	2000	2200
Indeno(1,2,3-cd)pyrene	3/4	180	224	180	1/9	990	691	990	990
Naphthalene	3/4	1100	950	1100	2/9	740	450	740	1100
Phenanthrene	3/4	9400	8130	9400	2/9	12000	4750	12000	12000
Pyrene	4/4	6600	5710	5710	2/9	9000	3475	9000	9000

TABLE 5-10 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Tetrachloroethene	2/4	30000	25200	30000	6/10	240	82.5	82.5	30000
Tributyl phosphate					2/2	72000	136000	72000	72000
Vinyl chloride	0/4	ND			2/11	14.0	8.90	14.0	14.0
Inorganics (mg/kg)									
Antimony	1/5	0.500	0.375	0.500	4/5	317	222	222	222
Arsenic	1/5	4.60	2.99	4.60	5/5	6.50	5.16	5.16	5.16
Barium	5/5	6670	4580	4580	5/5	3720	3130	3130	4580
Beryllium	5/5	13.0	8.35	8.35	3/5	50.6	36.7	50.6	50.6
Boron					5/5	1010	658	658	658
Cadmium	4/5	29.0	18.6	18.6	5/5	34.8	24.5	24.5	24.5
Chromium	5/5	94.0	63.7	63.7	5/5	1500	1050	1050	1050
Cobalt	3/5	84.0	54.5	84.0	4/5	183	129	129	129
Copper	5/5	188	130	130	5/5	482	352	352	352
Cyanide	1/5	0.700	0.551	0.700	2/5	0.240	0.304	0.240	0.551
Lead	5/5	63.0	55.3	55.3	5/5	63.2	53.6	53.6	55.3
Manganese	5/5	3600	3340	3340	5/5	5620	4750	4750	4750
Mercury	3/5	0.600	0.487	0.600	3/5	0.620	0.454	0.620	0.620
Molybdenum					5/5	95.6	69.8	69.8	69.8
Nickel	5/5	50.0	38.2	38.2	5/5	223	167	167	167
Selenium	0/4	ND			1/5	0.370	0.316	0.370	0.370
Silver	4/5	444	279	279	5/5	755	531	531	531

TABLE 5-10 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Tin	4/4	87.0	82.8	82.8	4/5	133	114	114	114
Uranium					6/6	116000	94400	94400	94400
Vanadium	4/5	235	153	153	5/5	558	394	394	394
Zinc	4/5	84.0	63.4	63.4	5/5	200	143	143	143

[a]ND - Not detected

TABLE 5-11

RADIOLOGICAL CPCs IN WASTE PIT 5 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	2/6	76.0	52.8	76.0	9/9	78.0	40.2	40.2	76.0
Neptunium-237	5/6	19.0	15.1	15.1	2/2	46.0	80.5	46.0	46.0
Plutonium-238	5/6	4.40	3.60	3.60	3/9	0.300	0.100	0.300	3.60
Plutonium-239/240	5/6	13.0	9.70	9.70	5/9	3.72	1.20	1.20	9.70
Radium-226					9/9	150	112	112	112
Radium-228					8/9	39.0	26.7	26.7	26.7
Ruthenium-106	0/6	ND[a]			2/9	1.60	1.40	1.60	1.60
Strontium-90	6/6	31.0	20.1	20.1	8/9	15.0	6.80	6.80	20.1
Technetium-99	6/6	2990	2070	2070	9/9	3020	2020	2020	2070
Thorium-228	6/6	44.0	42.9	42.9	9/9	38.0	19.9	19.9	42.9
Thorium-230	6/6	8480	6810	6810	9/9	2600	900	900	6810
Thorium-232	6/6	55.0	45.1	45.1	7/9	10.0	4.70	4.70	45.1
Uranium-234	6/6	1250	929	929	9/9	860	713	713	929
Uranium-235	6/6	79.0	53.9	53.9	4/9	39.0	24.6	24.6	53.9
Uranium-238	6/6	1230	903	903	9/9	960	746	746	903

[a]ND - Not detected

TABLE 5-12

CHEMICAL CPCs IN WASTE PIT 5 - SOLID CONTENTS

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
Aroclor-1248	2/6	550	1080	550					550
Aroclor-1254	2/6	750	2010	750					750
Inorganics (mg/kg)									
Antimony	4/5	64.0	51.7	51.7	9/9	88.1	47.5	47.5	51.7
Arsenic	4/5	2800	2150	2150	7/9	715	542	542	2150
Barium	5/5	36900	30200	30200	9/9	18100	13200	13200	30200
Beryllium	5/5	18.0	14.8	14.8	9/9	22.4	14.2	14.2	14.8
Cadmium	4/5	17.0	11.6	11.6	9/9	4.70	3.32	3.32	11.6
Chromium	5/5	141	116	116	9/9	98.0	78.9	78.9	116
Cobalt	4/5	44.0	35.5	35.5	9/9	17.1	12.1	12.1	35.5
Copper	4/5	18200	11800	11800	9/9	6450	4110	4110	11800
Cyanide	1/3	0.500	0.958	0.500	0/9	ND[a]			0.500
Lead	4/5	168	174	168	9/9	134	105	105	168
Manganese	5/5	3300	3050	3050	9/9	486	466	466	3050
Mercury	5/5	1.80	1.59	1.59	9/9	1.50	1.04	1.04	1.59
Molybdenum					9/9	1350	666	666	666
Nickel	5/5	202	150	150	9/9	178	119	119	150
Selenium	4/5	18.0	13.8	13.8	0/9	ND			13.8
Silver	3/5	9.40	7.81	9.40	5/9	22.2	14.1	14.1	14.1
Thallium	4/5	11.0	9.94	9.94	4/9	52.0	34.5	34.5	34.5

TABLE 5-12 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Tin	1/1	30.0		30.0	9/9	92.8	48.0	48.0	48.0
Uranium					9/9	3700	2760	2760	2760
Vanadium	5/5	5380	4920	4920	9/9	4530	2760	2760	4920
Zinc	3/5	180	166	180	9/9	278	206	206	206

'ND - Not detected

TABLE 5-13

RADIOLOGICAL CPCs IN WASTE PIT 5 - SURFACE WATER (pCi/L)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	2/2	90.0	194	90.0					90.0
Strontium-90	2/2	41.0	59.6	41.0					41.0
Technetium-99	2/2	320	533	320					320
Thorium-230	2/2	0.100	0.100	0.100					0.100
Uranium-234	2/2	420	415	420					420
Uranium-235	2/2	19.0	18.5	19.0					19.0
Uranium-238	2/2	400	385	400					400

TABLE 5-14

CHEMICAL CPCs IN WASTE PIT 5 - SURFACE WATER (µg/L)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics									
Benzene	1/2	11.0	33.6	11.0					11.0
Inorganics									
Antimony	2/2	4.50	6.10	4.50					4.50
Arsenic	2/2	2.10		2.10					2.10
Barium	2/2	108	119	108					108
Copper	2/2	21.0	23.7	21.0					21.0
Cyanide	2/2	87.0	140	87.0					87.0
Lead	2/2	2.90	6.60	2.90					2.90
Nickel	2/2	21.0	26.3	21.0					21.0
Selenium	1/2	2.10	5.40	2.10					2.10
Vanadium	2/2	47.0	49.7	47.0					47.0
Zinc	2/2	114	167	114					114

TABLE 5-15

RADIOLOGICAL CPCs IN WASTE PIT 6 - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	3/4	31.0	31.2	31.0	8/8	14.0	10.8	10.8	31.0
Neptunium-237	4/4	3.60	3.40	3.40					3.40
Plutonium-238	4/4	1.40	1.30	1.30	6/8	1.00	0.800	0.800	1.30
Plutonium-239/240	4/4	15.0	14.3	14.3	8/8	14.0	11.3	11.3	14.3
Radium-226					8/8	4.90	4.40	4.40	4.40
Radium-228					8/8	191	96.3	96.3	96.3
Strontium-90	4/4	5.10	5.50	5.10	6/8	4.80	3.70	3.70	5.10
Technetium-99	4/4	164	167	164	5/8	45.0	31.1	31.1	164
Thorium-228	4/4	1.20	1.10	1.10	8/8	1.70	1.50	1.50	1.50
Thorium-230	4/4	44.0	47.6	44.0	8/8	62.0	45.9	45.9	45.9
Thorium-232	4/4	1.20	1.10	1.10	8/8	1.00	0.700	0.700	1.10
Uranium-234	4/4	5330	5060	5060	8/8	4060	3120	3120	5060
Uranium-235	4/4	1750	1840	1750	8/8	337	267	267	1750
Uranium-238	4/4	18700	20500	18700	8/8	28700	20600	20600	20600

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TABLE 5-16

CHEMICAL CPCs IN WASTE PIT 6 - SOLID CONTENTS

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
Aroclor-1254	1/1	81.0		81.0					81.0
Tetrachloroethene	4/4	29000	31100	29000					29000
Inorganics (mg/kg)									
Arsenic	1/1	7.60		7.60	9/9	76.7	54.9	54.9	54.9
Barium	1/1	95.0		95.0	9/9	71.7	58.6	58.6	95.0
Beryllium	1/1	5.70		5.70	9/9	2.10	1.42	1.42	5.70
Cadmium	1/1	5.70		5.70	1/9	1.30	2.65	1.30	5.70
Chromium	1/1	30.0		30.0	3/9	7.00	22.7	7.00	30.0
Cobalt	1/1	26.0		26.0	5/9	4.60	5.79	4.60	26.0
Copper	1/1	222		222	3/9	10.8	15.5	10.8	222
Lead	1/1	60.0		60.0	9/9	113	79.6	79.6	79.6
Manganese	1/1	35.0		35.0	9/9	312	221	221	221
Nickel	1/1	51.0		51.0	9/9	22.7	18.9	18.9	51.0
Silver	1/1	158		158	7/9	9.20	6.19	6.19	158
Thallium	0/1	ND[a]			6/9	108	71.0	71.0	71.0
Tin					7/9	21.5	13.8	13.8	13.8
Uranium					8/8	27700	19300	19300	19300

TABLE 5-16 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Vanadium	1/1	100		100	0/9	ND			100
Zinc	1/1	48.0		48.0	9/9	61.0	44.7	44.7	48.0

*ND - Not detected

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TABLE 5-17

RADIOLOGICAL CPCs IN WASTE PIT 6 - SURFACE WATER (pCi/L)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Radium-228	5/5	31.3	25.7	25.7					25.7
Technetium-99	5/5	3500	2750	2750					2750
Thorium-230	2/5	0.300	0.300	0.300					0.300
Uranium-234	5/5	77.0	85.2	77.0					77.0
Uranium-235	5/5	9.30	9.90	9.30					9.30
Uranium-238	5/5	460	499	460					460

TABLE 5-18

CHEMICAL CPCs IN WASTE PIT 6 - SURFACE WATER (g/L)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Antimony	1/5	1.70	1.30	1.70					1.70
Cyanide	1/5	10.0	8.10	10.0					10.0
Lead	1/5	2.90	2.00	2.90					2.90
Zinc	2/5	114	72.8	114					114

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TABLE 5-19

RADIOLOGICAL CPCs IN BURN PIT - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Neptunium-237	2/6	0.600	0.500	0.600					0.600
Plutonium-238	1/6	0.500	0.300	0.500	0/4	ND[a]			0.500
Plutonium-239/240	1/6	0.400	0.200	0.400	0/4	ND			0.400
Radium-226					4/4	39.2	34.2	34.2	34.2
Radium-228					4/4	10.4	11.2	10.4	10.4
Strontium-90	0/6	ND			1/4	0.500		0.500	0.500
Technetium-99	4/6	64.0	52.3	52.3	4/4	3.29	3.00	3.00	52.3
Thorium-228	6/6	19.0	12.9	12.9	3/4	12.4	378	12.4	12.9
Thorium-230	6/6	218	127	127	4/4	4530	3810	3810	3810
Thorium-232	6/6	21.0	13.2	13.2	3/4	14.4	173	14.4	14.4
Uranium-234	6/6	415	253	253	4/4	1710	1560	1560	1560
Uranium-235	6/6	27.0	16.1	16.1	4/4	102	101	101	101
Uranium-238	6/6	454	299	299	4/4	2000	1800	1800	1800

[a]ND - Not detected

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TABLE 5-20

CHEMICAL CPCs IN THE BURN PIT - SOLID CONTENTS (mg/kg)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin					2/4	0.520	0.556	0.520	0.520
Heptachlorodibenzo-p-dioxin					2/4	0.980	1.080	0.980	0.980
Octachlorodibenzo-p-dioxin					2/4	4.00	4.50	4.00	4.00
Octachlorodibenzofuran					1/4	0.130	0.191	0.130	0.130
Acenaphthene	0/6	ND[a]			1/5	1100	810	810	810
Anthracene	0/7	ND			1/5	3100	2050	3100	3100
Aroclor-1254	5/7	2700	1560	1560	3/4	7700	6690	7700	7700
Benzo(a)anthracene	4/7	170	209	170	2/5	6300	4030	6300	6300
Benzo(a)pyrene	1/7	160	246	160	2/5	3900	2530	3900	3900
Benzo(b)fluoranthene	4/7	170	210	170	1/5	9600	6120	9600	9600
Benzo(g,h,i)perylene	1/7	85.0	256	85.0	2/5	2900	1900	2900	2900
Benzo(k)fluoranthene	1/7	200	242	200	1/5	340	1660	340	340
Chrysene	3/7	83.0	221	83.0	2/5	7000	4470	7000	7000
Dibenzofuran	0/7	ND			1/5	900	689	900	900
Fluoranthene	3/7	210	243	210	2/5	16000	10100	16000	16000
Fluorene	0/7	ND			2/5	1700	1170	1700	1700
Indeno(1,2,3-cd)pyrene	1/6	78.0	257	78.0	2/5	2200	1460	2200	2200
Pentachlorophenol	2/7	2600	1780	2600	0/5	ND			2600
Phenanthrene	4/7	190	232	190	3/5	15000	9480	15000	15000
Pyrene	3/7	140	231	140	3/5	14000	8870	14000	14000
Tetrachloroethene	2/6	260	194	260	0/4	ND			260

TABLE 5-20 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Vinyl chloride	0/6	ND			1/4	3.00	8.59	3.00	3.00
Inorganics (mg/kg)									
Antimony	1/7	0.600	0.664	0.600	2/4	17.8	18.0	17.8	17.8
Arsenic	5/7	21.0	11.8	11.8	4/4	39.2	34.7	34.7	34.7
Barium	5/7	7100	3050	3050	4/4	299	327	299	3050
Beryllium	5/7	16.0	7.14	7.14	4/4	1.90	2.01	1.90	7.14
Boron					2/3	48.2	61.3	48.2	48.2
Cadmium	7/7	35.0	15.4	15.4	4/4	5.40	5.61	5.40	15.4
Chromium	7/7	88.0	43.4	43.4	4/4	91.2	92.9	91.2	91.2
Cobalt	6/7	104	48.4	48.4	4/4	111	98.9	98.9	98.9
Copper	4/7	166	80.3	80.3	4/4	259	281	259	259
Cyanide	0/7	ND			2/4	0.210	0.199	0.210	0.210
Lead	5/7	53.0	32.4	32.4	4/4	279	310	279	279
Manganese	7/7	1720	859	859	4/4	962	944	944	944
Mercury	2/7	0.200	0.120	0.200	3/4	1.20	1.12	1.20	1.20
Molybdenum					4/4	24.8	24.9	24.8	24.8
Nickel	6/7	60.0	31.4	31.4	4/4	206	187	187	187
Selenium	1/6	0.500	0.347	0.500	4/4	2.00	1.91	1.91	1.91
Silver	2/6	506	255	506	4/4	21.6	23.5	21.6	506
Thallium	3/7	0.500	0.409	0.500	0/4	ND			0.500
Uranium					4/4	4460	4030	4030	4030

TABLE 5-20 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Vanadium	4/7	290	129	129	4/4	43.3	43.3	46.3	129
Zinc	7/7	75.0	57.8	57.8	4/4	505	523	505	505

*ND - Not Detected

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TABLE 5-21

RADIOLOGICAL CPCs IN THE CLEARWELL - SOLID CONTENTS (pCi/g)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Cesium-137	4/4	450	406	406	6/6	71.4	62.9	62.9	406
Neptunium-237	3/4	2.20	2.10	2.20	4/6	1.80	1.70	1.70	2.20
Plutonium-238	0/4				5/6	0.490	0.400	0.400	0.400
Plutonium-239/240	0/4				5/6	0.540	0.400	0.400	0.400
Radium-226					6/6	170	118	118	118
Radium-228					6/6	26.4	24.1	24.1	24.1
Strontium-90	4/4	26.0	22.3	22.3	2/6	12.8	7.20	12.8	22.3
Technetium-99	2/4	278	254	278	6/6	695	523	523	523
Thorium-228	4/4	56.0	54.9	54.9	6/6	28.1	26.8	26.8	54.9
Thorium-230	4/4	5600	4760	4760	6/6	314	233	233	4760
Thorium-232	4/4	39.0	36.9	36.9	6/6	9.69	7.70	7.70	36.9
Uranium-234	4/4	376	364	364	6/6	1050	797	797	797
Uranium-235	4/4	49.0	48.3	48.3	6/6	373	349	349	349
Uranium-238	4/4	670	683	683	6/6	1640	1360	1360	1360

TABLE 5-22

CHEMICAL CPCs IN THE CLEARWELL - SOLID CONTENTS

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Organics (g/kg)									
2,4,5-Trichlorophenol	1/4	6200	5980	6200					6200
Anthracene	1/4	450	711	450					450
Aroclor-1242	1/4	121	168	121					121
Aroclor-1248	1/4	308	284	308					308
Aroclor-1254	4/4	737	643	643					643
Benzo(a)anthracene	2/4	890	917	890					890
Benzo(a)pyrene	1/4	670	772	670					670
Benzo(b)fluoranthene	1/4	710	792	710					710
Benzo(g,h,i)perylene	1/4	230	725	230					230
Benzo(k)fluoranthene	1/4	750	814	750					750
Chrysene	3/4	1000	1000	1000					1000
Fluoranthene	1/4	3100	2700	3100					3100
Indeno(1,2,3 cd)pyrene	1/4	270	719	270					270
Phenanthrene	4/4	2100	1790	1790					1790
Pyrene	3/4	1400	1300	1400					1400

TABLE 5-22 (Continued)

PARAMETER	CIS DATA FREQ	CIS DATA MAX DET	CIS DATA UCL (95%)	CIS DATA REPRESENTATIVE CONCENTRATION	RI/FS DATA FREQ	RI/FS DATA MAX DET	RI/FS DATA UCL (95%)	RI/FS DATA REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Inorganics (mg/kg)									
Antimony	2/4	32.0	27.0	32.0	4/6	10.9	9.41	9.41	32.0
Arsenic	4/4	18.0	16.6	16.6	5/6	59.1	54.0	54.0	54.0
Barium	4/4	6910	6140	6140	6/6	1790	1610	1610	6140
Beryllium	4/4	9.10	7.78	7.78	6/6	2.90	2.34	2.34	7.78
Cadmium	2/4	7.20	7.27	7.20	6/6	2.90	2.73	2.73	7.20
Chromium	4/4	76.0	70.7	70.7	6/6	196	153	153	153
Cobalt	2/4	23.0	23.8	23.0	6/6	25.7	21.4	21.4	23.0
Copper	4/4	1120	1050	1050	6/6	3320	2420	2420	2420
Cyanide	1/4	9.20	7.85	9.20	4/6	1.47	1.09	1.09	9.20
Lead	4/4	83.0	75.6	75.6	6/6	588	433	433	433
Manganese	4/4	1660	1660	1660	6/6	19800	13200	13200	13200
Mercury	4/4	4.40	4.80	4.40	6/6	1.60	1.41	1.41	4.40
Molybdenum					6/6	40.9	36.5	36.5	36.5
Nickel	4/4	67.0	64.8	64.8	6/6	228	167	167	167
Selenium	1/4	3.70	3.19	3.70	4/6	0.850	0.617	0.617	3.70
Silver	1/4	3.30	3.18	3.30	5/6	12.7	9.84	9.84	9.84
Thallium	1/4	2.10	1.82	2.10	4/6	1.60	1.26	1.26	2.10
Thorium					6/6	88.9	70.5	70.5	70.05
Tin					5/6	24.1	18.1	18.1	18.1
Uranium					6/6	2780	2090	2090	2090
Vanadium	4/4	2600	2200	2200	6/6	285	232	232	2200
Zinc	4/4	194	177	177	6/6	314	246	246	246

TABLE 5-23

RADIOLOGICAL CPCs IN THE CLEARWELL - SURFACE WATER (pCi/L)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Radium-226	2/2	1.10		1.10					1.10
Technetium-99	2/2	4030	9480	4030					4030
Thorium-230	1/2	0.400	1.20	0.400					0.400
Uranium-234	2/2	1900	2170	1900					1900
Uranium-235	2/2	120	147	120					120
Uranium-238	2/2	6200	8330	6200					6200

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TABLE 5-24

CHEMICAL CPCs IN THE CLEARWELL - SURFACE WATER (µg/L)

	CIS DATA				RI/FS DATA				
PARAMETER	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	FREQ	MAX DET	UCL (95%)	REPRESENTATIVE CONCENTRATION	CPC CONCENTRATION
Arsenic	2/2	4.20	6.60	4.20					4.20
Copper	2/2	19.0	32.3	19.0					19.0
Cyanide	1/2	87.0	305	87.0					87.0
Selenium	1/2	3.00	8.70	3.00					3.00
Silver	2/2	14.0	22.0	14.0					14.0
Vanadium	2/2	513	1810	513					513
Zinc	2/2	47.0	153	47.0					47.0

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