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STATUS UPDATE AND REQUEST FOR EXTENSION FOR THE HF TANK CAR CLOSURE PLAN INFORMATION AND DATA

03/18/94

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DOE-FN/OEPA
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LETTER

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Department of Energy
Fernald Environmental Management Project
P.O. Box 398705
Cincinnati, Ohio 45239-8705
(513) 738-6357

MAR 18 1994

DOE-1248-94

Mr. Phil Harris
Hazardous and Solid Waste Division
Ohio Environmental Protection Agency
40 South Main Street
Dayton, Ohio 45402-2086

Dear Mr. Harris,

STATUS UPDATE AND REQUEST FOR EXTENSION FOR THE HF TANK CAR CLOSURE PLAN INFORMATION AND DATA

Reference: Letter, (DOE-0654-94), Walter J. Quaider to Robin Fisher, "Request for Extension, RE: NOD Responses for HF Tank Car Closure Plan Information and Data," dated December 22, 1993.

This letter, with enclosure, is being submitted to provide a summary of the bench scale testing being conducted for neutralization of the dilute hydrofluoric acid (DHF) currently being stored in the HF Tank Car. This letter also requests an extension until July 29, 1994 for submittal of the revised Closure Plan Information and Data (CPID).

As discussed in the reference letter, the intent of the bench scale test was to compare and evaluate the following four methods for DHF neutralization:

Method 1. Lime Slurry - Elementary Neutralization

Method 2. Activated Alumina/Ion Exchange Neutralization

Method 3. Soda Ash Addition Neutralization

Method 4. Nitric Acid Addition/Lime Slurry Neutralization

Methods 2, 3, and 4 were eliminated from bench scale testing based on health and safety concerns and the needs for additional processing equipment and procedures. Based on bench scale tests, the lime slurry neutralization was demonstrated to be viable and was selected for further bench scale testing to evaluate operational parameters for lime neutralization. The lime neutralization methods being evaluated include lime slurry neutralization and direct neutralization by adding lime to a diluted acid solution. A summary of the ongoing bench scale testing is provided in the enclosure.

Bench scale testing was not completed by January 31, 1994 as projected in the reference letter. The test plan was revised in January, 1994 and testing under the revised test plan was initiated February 9, 1994. The bench scale testing described in the enclosure will be completed by April 30, 1994. As the data becomes available, the bench scale test results will be evaluated to determine if any further testing is required to define the parameters and performance requirements that need to be considered in designing, evaluating, and selecting a lime neutralization system. Once the lime neutralization system performance requirements are defined, the identification and evaluation of alternative designs will be conducted. As part of identifying and comparing alternative lime neutralization system designs, the need for specific bench scale tests to evaluate specific variations to the process system parameters and operating requirements will be assessed.

If additional bench scale testing is required the appropriate amendments to the test plan will be completed before additional testing is conducted. At present, it is anticipated that all bench scale testing necessary to provide the basic performance requirements for the neutralization process will be completed by May 30, 1994. This includes the tests described in the enclosure and any additional tests identified. Evaluation of the bench scale testing data, identification and evaluation of alternatives, and selection of the final lime neutralization system design should be completed by June 30, 1994. At that time, a status update and summary will be provided to the Ohio Environmental Protection Agency.

A revised CPID will be submitted by July 29, 1994 and will include a description of the neutralization system selected for DHF neutralization. The revised CPID will also include a schedule for construction of the lime neutralization treatment system, start up and testing of the system, neutralization of the DHF, and decontamination of the HF Tank Car.

In addition to the activities described above, the preparations for moving the rail car over secondary containment are nearing completion. Weather permitting, the final rail repairs and rail line testing could be completed to enable the movement of the HF Tank Car as early as March 25, 1994. The HF Tank Car move should be completed by April 30, 1994.

If you or your staff have questions concerning this letter, please contact is Mr. John Sattler at (513) 648-3145.

Sincerely,

Walter J. Quaider

Walter J. Quaider
Assistant Manager
Technical Support

Enclosures: As Stated

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cc w/enc:

G. E. Mitchell, OEPA-Dayton
J. A. Saric, USEPA Region V
K. A. Hayes, EM-424 TREV

cc w/o enc:

D. R. Schregardus, OEPA-Columbus
M. McDermontt, DOJ
J. Van Kley, Ohio AGO
R. Meyer, OEPA-Columbus
P. D. Pardi, OEPA-Dayton
J. Reising, DOE-FN
R. J. Janke, DOE-FN
D. Maynor, DOE-FN
K. L. Alkema, FERMCO/65-2
P. F. Clay, FERMCO/52-2
J. T. Curtis, FERMCO/8
J. E. King, FERMCO/52-3
D. Ofte, FERMCO/1
J. W. Thiesing, FERMCO/1
Administrative Record

Enclosure
Summary of Bench Scale Testing Results Completed
March 15, 1994

The HF Tank Car has been identified as a Hazardous Waste Management Unit (HWMU) and neutralization of the DHF is required for closure. The HF Tank Car contains approximately 4400 gallons of DHF with a concentration of 28.7 weight percent hydrofluoric acid. The screening of alternatives and bench scale tests (to confirm that lime slurry neutralization method is feasible) have been completed for evaluation and comparison of four neutralization treatment methods. Lime neutralization has been selected as the preferred treatment method to neutralize the dilute hydrofluoric acid (DHF) currently being stored in the HF Tank Car.

This enclosure describes the testing results which have been obtained to date and the additional testing planned for the near future to define process operating requirements for lime neutralization of the DHF. The final process operating requirements will be used for identification, evaluation and design of the treatment facilities needed to accomplish treatment of the DHF and management of the treatment residues as a low-level waste.

Screening of Alternatives and Initial Test Runs

The objectives of the initial screening of the four methods and bench scale were to:

- Develop Safe Testing Procedures
- Evaluate the Process Feasibility of the Four Alternative Methods
- Identify Base Case Testing Conditions
- Initial Characterization of the Treatment Wastes

Evaluate the Process Feasibility of the Four Processing Methods - The four process methods considered for neutralizing and treating the DHF were:

Method 1. Lime Slurry - Elementary Neutralization

Method 2. Activated Alumina/Ion Exchange Neutralization

Method 3. Soda Ash Addition Neutralization

Method 4. Nitric Acid Addition/Lime Slurry Neutralization

Based on evaluations of these four methods, the lime slurry neutralization (Method 1) was identified as the preferred alternative for treatment of the DHF in the rail car. Lime slurry neutralization was determined to be a better alternative than Methods 2 and 3 because of the relatively lower solubility of the calcium fluoride precipitate formed by lime neutralization. The potential for environmental releases and the relative toxicity of fluoride compounds precipitated during DHF neutralization is directly related to the solubility of the fluoride compounds formed. The lime slurry (Method 1) dissolves to form calcium hydroxide which reacts with the DHF and precipitates calcium fluoride. To achieve DHF neutralization using Method 2, activated alumina (AA) dissolves to form aluminum hydroxide which reacts with DHF and precipitates aluminum fluoride. The use of soda ash (Method 3) forms sodium hydroxide which reacts with the DHF and precipitates sodium fluoride. The toxicity of these fluoride compounds increases as the solubility increases. Calcium fluoride, the least soluble, is considered mildly toxic by ingestion. Aluminum fluoride (approximately 300 times more soluble than calcium fluoride) is a moderately toxic subcutaneous poison and severe eye irritant. Sodium fluoride (approximately 2,600 times more soluble than calcium fluoride) is used as rat poison and insecticide, is considered an experimental poison via ingestion and skin contact and is a corrosive irritant to skin, eye and mucous membranes. To minimize fluoride releases to the environment, additional treatment for removal and\or stabilization of soluble fluoride compounds would also be required if Methods 2 or 3 were used.

Method 4 was eliminated because 1) it presumes that additional fluoride treatment is required to reduce fluoride in the aqueous portion of the neutralization wastes to allow discharge to a wastewater treatment system and 2) if fluoride treatment is needed, there are proven treatment methods to remove soluble fluorides from wastewaters (e.g., ion exchange and reverse osmosis) that are safer and less complicated. Use of Method 4 would require additional equipment and processing to prepare a calcium nitrate solution from lime and nitric acid. The calcium nitrate solution with the DHF precipitates calcium fluoride prior to elementary neutralization. Because Method 4 uses nitric acid, the volume of acid to be neutralized is increased and the resulting waste volume is also increased. Increased handling and processing of greater volumes of acids and use of incompatible acids (i.e., nitric acid can react violently with hydrofluoric acid) increases risks to worker safety and health and the environment. Additional equipment and procedures would be required to segregate and isolate the nitric from hydrofluoric acid, control potential nitrogen oxide (NOX) emissions and evaluate possible treatment requirements to address previously non-existing concerns for nitrate compounds in the neutralization wastes.

Although assumed in Method 4, the need for additional fluoride treatment, if any, will be determined through characterization of the residues from bench scale testing of lime slurry neutralization. In addition, further fluoride treatment may also be minimized or eliminated through selection of a lime slurry neutralization process design alternative which either reduces the volume and thereby the mass loading of fluorides (e.g., recycling the filtrate\supernate to prepare a new batch of lime slurry) and\or eliminates wastewater discharges (e.g., solidification of recycled wastewaters after neutralization is completed).

After the lime slurry neutralization method was selected, the scope of the bench scale testing was modified to provide a more detailed evaluation of lime neutralization processes. A total of 18 lime slurry neutralization tests were performed under differing conditions. Based on those results, two methods for lime neutralization are being evaluated. First is addition of DHF to a lime slurry. The second method involves adding lime to a diluted DHF solution. to evaluate base case test conditions necessary for completion of the testing various process parameters.

Develop Safe Testing Procedures - The DHF is an extremely hazardous material and it also exhibits a small degree of radiological activity due to the presence of uranium. Therefore, procedures had to be established and appropriate testing equipment had to be obtained and installed and a in a radiologically-controlled laboratory testing area. After installing the equipment in an appropriate laboratory, a series of 18 test runs were performed to evaluate the lime slurry neutralization method and identify unforeseen problems.

The testing method used for the lime slurry neutralization test runs began by placing a specific volume of 5 weight percent lime slurry in an container using an agitator to mix the slurry. Instruments were added to continuously monitor pH and temperature. To begin the neutralization, DHF was added at a controlled rate to the agitated slurry while monitoring pH and temperature. The addition of DHF was stopped when the pH of the container had decreased to a value of 6 or below. The container was then stirred for an additional 5 minutes. Following this, the agitation was stopped and the solids in the container were allowed to settle for a period of 60 minutes. The position of the solid/liquid interface was noted at time intervals of 0, 30 and 60 minutes after mixing was stopped. Following settling, the container was remixed and the neutralized solids were transferred to a laboratory vacuum filter. The filter medium consisted of a laboratory filter paper pre-coated with a solution of "Dicalite". The entire slurry was passed through the filter and the filtered solids and filtrate were retained for further characterization testing.

The parameters that were varied between the 18 test runs were batch size and DHF addition rate. The parameters that were monitored were temperature rise, solids settling, solids filterability, filtrate fluoride level, and filtrate pH. The quantities of solid and liquid residues from these treatments were also measured. The results of these tests are being used to establish the base case test condition to be used in evaluating other process parameters for lime slurry neutralization.

The 18 test runs resulted in 12 trials at different DHF addition rates. The volume of the lime slurry batches were increased as needed to test higher rates of DHF addition and varied from 100 ml to 1,200 ml. The remaining 6 test runs were repeats of unsuccessful trials or duplications of a trial to repeat and evaluate the results using the same test conditions. A summary of 6 of the 12 trials is provided as Table 1. The other 6 trials were not reported because they did not provide complete data due to problems that were encountered during the performance of the test. The trials and test runs that were not reported in Table 1 were used as guidance to avoid similar problems in future tests. The major problems encountered were excessively fast DHF addition rate, equipment failure, inadequate mixing, and procedural errors.

Identify Base Case Testing Conditions - The first 18 test runs provided some insight into the process parameters and limits that will constrain the remaining testing for neutralization of DHF with lime. A review of the result of these 18 tests Indicated lime slurry neutralization is a viable method. However, it was noted that a stoichiometric excess of lime of approximately 100 percent has been required in initial testing to neutralize the DHF and difficulties have been encountered in efforts to repeat the original test conditions. The functional difficulty appears to be reproducing the conditions under which the precipitates that form can be separated (i.e., filtered or settled out) from the neutralized slurry.

In an effort to improve precipitation and reduce the stoichiometric excess of calcium required for neutralization, a series of tests are being conducted to evaluate the impact of reversing the addition of lime and acid to the water to obtain a neutralized slurry of calcium fluoride and water. Based on additional research, calcium fluoride crystal formation should be enhanced by adding the acid to the water then adding the lime to the acid\water solution. Improved precipitation should result from an increase in the available dissolved calcium during the early stages of neutralization and an initial slower formation of crystals before the acid concentration is reduced by neutralization. The initial increase of dissolved calcium should enhance the reaction with the calcium and reduce the total amount of calcium required to neutralize the acid. The slower crystal formation in the initial stages of neutralization would provide nucleation particles that would enhance formation of larger crystals in the precipitate which would increase settling and filterability of the precipitates.

Further testing of the lime solutions used in the 18 test runs identified differences between 5 weight percent lime slurry batches used. An assay of remaining residues of the first batch of 5 weight percent lime slurry contained 57.6% by weight calcium carbonate and 31.2% by weight calcium hydroxide. In contrast, The 5 weight percent lime slurry prepared with the supply of bagged lime provided to complete the testing contains 8.2% by weight calcium carbonate and 84.9% by weight calcium hydroxide. Additional tests are being conducted to determine the appropriate mix of carbonates to hydroxides necessary to reproduce the previous test conditions.

Once the ongoing tests are completed, the results will be compared to determine the best order of lime and acid additions to the water to completed DHF neutralization. The test conditions that yield the best results will be used as the base test conditions for evaluation of other parameters that can effect the neutralization process and define the operational requirements for the lime neutralization process.

Characterize the treatment wastes - The solid and liquid residues from all neutralization tests are being characterized by fluoride content, settling rate, filterability, weight, volume, and pH. These results will provide guidance on the types of solid wastes which will be produced during the remaining treatment tests. The characterization results are summarized in Table 1. Table 2 provides preliminary data characterizing the DHF and lime being used in the bench scale testing.

Additional Testing Planned

A variety of process parameters have been identified which have an operational affect on the lime neutralization process. The general procedure for evaluating these parameters is to use a base case as a point of comparison between the variables to be tested. As previously discussed, the base case for lime neutralization is currently being established the prefered order of DHF and lime additions to obtain a neutralized slurry of calcium fluoride and lime and ensure repeatability of results. The following process parameters will be tested against the base case:

1) Lime Quantity - The quantity of lime required to neutralize a particular quantity of DHF will be determined. The stoichiometric volume of lime to acid determined for the base case condition will provide the optimum ratio for comparison.

   The variables that affect the DHF/lime ratio will be studied by monitoring the total quantity of DHF required to reach the desired pH during variation of the other variables discussed below. This is an important issue for minimizing the total volume of low-level waste produced during the closure of the HF Tank Car HWMU (i.e., the solids precipitates and lime from the neutralization reaction).

2) Lime Concentration - The ratio of calcium carbonate to calcium hydroxide concentrations will be tested at double and half the ratio used in the base test condition. If the base case selected involves adding DHF to a lime slurry, weight percent concentrations of 10% and 25% lime will also be tested.

   The total volume of neutralized slurry solids can be reduced by optimizing the size of the crystals in the precipitates and minimizing the quantity of lime necessary to neutralize the DHF. Precipitates with larger particle sizes are easier to separate from the water and should result in reduced moisture content in the filtered\settled solids from the neutralized slurry. The volume of solid residues can also be reduced by minimizing the amount of lime relative to the stoichiometric amount needed to neutralize the DHF.

3) Temperature Rise - The temperature during the neutralization reaction will be monitored as other variables described below are varied to identify the magnitude of the temperature increase and the corresponding heat release which will develop. This will provide data for calorimetric calculations which will be used in the design process to ensure that excessive heat will not lead to an unplanned release during the full-scale treatment process.

4) Agitation Time - An agitation time of 15 minutes will be used following DHF or lime additions as a base case condition. The agitation time is the time that the reaction container will be mixed following the addition of all of the lime and DHF. If the neutralized slurry pH is not 6 after 15 minutes of agitation, additional DHF or lime (depending upon the order of addition selected for the base case condition) will be added be added and the reaction container will be mixed for an additional 15 minutes. A reduced agitation time will also be tested to evaluate changes that will occur as a result. The agitation time might be expected to have an effect on the total quantity of lime required for neutralization, the final particle size, and the final quantity of solids produced.

5) Neutralized Slurry Viscosity - The viscosity of the neutralized slurry will be measured for the test cases that are close to the final operational conditions to enhance evaluation of design alternatives.

The viscosity measurements will be used to determine the pumpability and handling characteristics of the neutralized slurry. This information will be used in the final design to ensure that the necessary equipment will be available to prevent handling mishaps.

6) Frothing/Spattering - Characteristics of the reaction solution such frothing, spattering, bubbling, etc. will be noted during testing. This information will be used to identify and avoid conditions that could result in excessively violent reactions during full scale treatment.

7) DHF Concentration - Reduced DHF concentrations of 10 and 20 weight percent will be tested to determine the effect on settling and filterability which are indications of precipitate particle size.

8) Fluoride Removal Effectiveness - Fluoride concentrations will be monitored in the filtrate using a calibrated ion-specific probe. As an additional test for suspended fluoride, the filtrate will also be diluted 10x with room-temperature deionized water and stirred for one hour at room temperature before repeating the test for fluoride. It is expected that small suspended fluoride particles in solution will be dissolved during the dilution and will increase the dissolved fluoride detected by the ion-specific probe. The use of deionized water rather than an acidification agent better reflects conditions of the final process and eliminates the need for additional handling steps to acidify and digest the filtrate. The final samples will be verified by analyses of samples in another laboratory using accepted EPA methodology for suspended fluoride.

9) Addition Rate - The addition rate for the DHF or lime (depending on the order of addition in the base case condition) will be increase to evaluate the effect on other process parameters. The anticipated maximum addition rate is 3 ml\min. of DHF or a calculated equivalent amount of lime.

10) Agitator Speed - Additional neutralization tests at varied agitator speeds will be performed to monitor changes in process parameters with respect to a base case. The agitation speed might be expected to have an effect on the total quantity of lime required for neutralization, the final particle size, and the final quantity of solids produced.

11) Dewatering Time in Vacuum Filter - Filtration time will be measured to observe relative effects on filterability. The filtration time measured is the time between the beginning of filtration and the point when all free liquid has been removed from the filter and no further droplets are dropping from the filter.

12) Filter Cake Density - The density of the filtered solids will be estimated by measuring the weight and measuring the cake thickness and filter diameter. The density of the filter cake will be used to quantify the waste volume and to estimate the size of the filtration equipment required to filter the neutralization slurry.

13) Filter Cake Quantity - The weight of the filtered solids will be measured. The weight of filtered solids will be used to determine the

quantity of dewatered solids obtained.

14) Solids Settling Rate - The solids settling will be measured at 0, 30 and 60 minute intervals after the cessation of agitation. The degree of solids settling provides an indication of the particle size and density in the neutralized slurry. This information will be useful in the final design of the treatment system. It will also be used to define the need for mixing equipment to keep the solids in suspension during storage.

15) Stabilization Agent Quantity - Stabilization agent quantity will be evaluated for the neutralized slurry to determine if stabilization is a viable disposal option.

16) Stabilized Waste Quantity - The weight and volume of stabilized waste will be measured for the cases tested with stabilization agents above. The weight and volume of stabilized waste will provide information to estimate the total quantity of waste that would be produced if stabilization were required for the neutralized slurry solids to meet disposal acceptance criteria.

Following the completion of the testing, samples of the neutralization residues will be collected for laboratory analyses to verify that the concentrations of total metals (including the 8 RCRA metals on TCLP list plus nickel and copper), total uranium, and fluoride concentrations are within waste treatment and disposal acceptance criteria.

Final Design Parameters

The data obtained from the testing will be used to determine the final design operating conditions. These conditions will be used as the design parameters and operational constraints in identifying processing system components, evaluating alternative process systems and selecting the final system design to treat the DHF using lime slurry neutralization.

TABLE 1: SUMMARY OF 6 TESTS CONDITIONS (TRIALS) FOR DHF NEUTRALIZATION IN A LIME SLURRY

Neutralization Data	Units	Test No. and Date					
		1 22-Feb-94	2 24-Feb-94	3 1-Mar-94	4 2-Mar-94	5 3-Mar-94	6 4-Mar-94
Lime Slurry Volume	ml	100	100	600	1200	1200	1200
DHF Volume	ml	7	8	23	48	95.5	60.5
DHF Addition Rate	ml\min.	0.6	1.1	7.7	6.9	4.3	4.7
Temperature Rise	°C	5	9	10	9	17	10
Waste Characterization							
Initial Solids\Liquid Interface Ht.	cm.	5.5	5	7.5	9.4	10	7.8
Solids\Liquid Interface - 30 min.	cm.	0.9	0.6	3.8	4.6	10	4
Solids\Liquid Interface - 60 min.	cm.	1.1	0.7	3.2	3.8	10	4
Filtration Time	min.	16	15	31	clogged	clogged	57
Filtered Solids Weight	grams	14.06	18.78	87.52	"	"	149.43
Filtrate Weight	grams	92.74	91.43	545.21	"	"	1,116.98
Filtrate pH	pH	7.86	5.38	8.38	"	"	7.81
Filtrate Fluoride Concentration	mg/l	17.6	36.4	14.7	"	"	13.7

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TABLE 2: PRELIMINARY ANALYSES OF TEST FEED MATERIALS

Analyses	Units	Test Materials Used	
		Bagged Lime	DHF
Total Arsenic	μg\l	1.0	2,140
Total Barium	μg\l	40.0	<200
Total Cadmium	μg\l	1.0	<17.9
Total Chromium	μg\l	4.4	1,204
Total Copper	μg\l	8.0	6,092
Total Lead	μg\l	1.2	<300
Total Mercury	μg\l	0.2	0.05
Total Nickel	μg\l	8.0	11,500
Total Selenium	μg\l	1.0	<5.0
Total Silver	μg\l	3.1	<10.0
Total Uranium	mg\l	12.3	54.7
Isotopic Uranium$_{235}$	mg\l	ND	0.699
Normality	gram eq. wt./l	NA	13.7