

**REVISED TEST PLAN**  
Containing Sampling and Analysis Plan

December 5, 2002

**In Situ Chemical Stabilization of Metals and Radionuclides Through Enhanced Anaerobic Reductive Precipitation:**

*For Bench Scale Testing Using Samples from the Fernald Environmental Management Project,  
Cincinnati, Ohio*

**Work Performed Under Contract:  
DE-AC26-01NT41304**

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**Submitted To:**

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National Energy Technology Laboratory  
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## 1.0 Technology Background and Experience

In-situ Reactive Zone (IRZ) also known as Enhanced Anaerobic Reductive Precipitation (EARP) technology is used for the precipitation of selected dissolved metals and dissolved radionuclides of interest to DOE in groundwater. ARCADIS has been successfully exploiting molasses, whey, high fructose corn syrup (HFCS), and other food grade carbohydrate additives as electron donors since 1995 through the application of its IRZ technology. Since the initial pilot-scale evaluation in 1995, ARCADIS has been retained to implement IRZ as either a field-pilot evaluation or at full-scale at more than 110 contaminated sites in 20 states and in 2 foreign countries in a variety of geologies and with a variety of remedial objectives. These sites have included both enhanced metals precipitation applications and enhanced reductive dechlorination of various chlorinated hydrocarbons.

The IRZ technology relies on enhancing the biologically mediated reactions by supplying an energy substrate or electron donor to the groundwater system and driving the groundwater oxidation-reduction potential (ORP) to a lower, more strongly reduced state. This is accomplished by amending the groundwater system with an electron donor in the form an aqueous solution of a food-grade carbohydrate, such as molasses, cheese whey, or high fructose corn syrup. Molasses and cheese whey are cost-effective and innocuous amendments that have been accepted by both many state and federal regulatory agencies.

Indigenous heterotrophic microorganisms readily degrade the electron donor aerobically in the presence of dissolved oxygen. This metabolic degradation process utilizes available dissolved oxygen (DO) contained in groundwater, as well as other alternative electron acceptors such as nitrate, iron, and manganese, and as a result, drives the system to a more anaerobic and reduced state. The bacterial community present in the aquifer prior to electron donor addition adapts to the changed biogeochemical aquifer conditions. In the enhanced subsurface environment, the bacterial population adjusts; facultative species begin to use alternative electron acceptors in the absence of oxygen and populations of obligately anaerobic species increase in size. A bacterial community capable of fermenting carbohydrate molecules found in molasses or cheese whey develops. Fermentation end products like volatile fatty acids, alcohols, and hydrogen are generated as the endpoints of carbohydrate fermentation. Figure 1 (figures are in attached Appendix B) shows the utilization of an injected carbohydrate and provides its chemical fate during microbiological processing in an IRZ.

Hydrolysis and fermentation of carbohydrate ultimately result in the production of acetate and hydrogen, which serve as the most desirable sources of energy for bacteria using sulfate and carbon dioxide (CO<sub>2</sub>) as electron acceptors. Methanogens use CO<sub>2</sub> as an electron acceptor and are the most noted metabolic group of obligately anaerobic bacteria responsible for reductive dechlorination, which is the transformation of volatile organic compounds (VOC) into less chlorinated intermediates and finally to ethene, CO<sub>2</sub>, and water.

The microorganisms using sulfate as a terminal electron acceptor are called sulfate-reducing bacteria (SRB). SRBs are widespread in aquatic and terrestrial environments such as waterlogged soils that become anaerobic due to active microbial respiration processes (Brock and Madigan, 1988). SRBs produce sulfide as a waste product. The precipitation of certain metals as insoluble complexes within the contaminated aquifer requires or is aided by sulfide (mercury, cadmium, lead, zinc, arsenic, uranium). Other dissolved metal species, like chromium, precipitate chemically in the anoxic environment created by bacterial consumption of dissolved oxygen. Regardless of whether metals precipitation occurs as a result of the creation of an anaerobic aquifer or as a result of a chemical reaction with biologically produced sulfide, the solubility of the resulting metal salt must be carefully studied over varying pH and ORP conditions. This solubility investigation is imperative to insure that the metal will not re-dissolve if the aquifer's pH or ORP condition is altered in the future following the remedial action.

The compounds this technology has been successfully applied for in the field include organics such as TCE, DCE, VC, CT, CF, chlorinated propanes, PCP, and pesticides, and metals and radionuclides such as Cr+6, Ni, Pb, Cd, Zinc, Hg, and U.

The mechanism of this process for metals precipitation is well understood. Following creation of the necessary reducing conditions in the groundwater, two reactions generally occur that will reduce the mobility of the metals. First, any dissolved metals present in higher oxidation states (for example, hexavalent chromium [Cr<sup>+6</sup>]) will be reduced (in the case of chromium, to trivalent chromium [Cr<sup>+3</sup>]). Second, the dissolved metals (in the more reduced forms) will react with reduced anions present in groundwater such as oxides, carbonates, and sulfides.

An important feature of the in situ metals precipitation technology is its irreversibility. Over the natural pH range encountered in the groundwater system at the most contaminated sites, these heavy metal precipitates have extremely low thermodynamic and kinetic solubilities. This results in a very low probability that the precipitates, once formed, will re-dissolve into the groundwater under natural conditions. Only under extreme changes to the pH or redox conditions in the groundwater could the precipitate resolubilize to any significant extent. These conditions would generally include either very low (less than 4) or very high (greater than 10) pH, or a strongly oxidizing environment (such as that caused by the continuous injection of oxidizing chemicals such as hydrogen peroxide or ozone). These conditions would not be present under any natural scenario. Once the desired aquifer microbiology has been attained, carefully timed subsequent additions of the electron donor amendment are utilized to support the altered aquifer microbiology until remediation of the contaminants present is complete. The IRZ performance following carbohydrate enhancement is measured by monitoring for the target contaminants and relative concentrations of degradation products, as well as other indicator parameters in groundwater such as dissolved oxygen, ORP, and changes in concentrations of electron acceptors within the treatment area.

If the metal contaminant in question at a given site precipitates as a sulfide salt, it is particularly important to monitor the formation of sulfide in the reactive zone over time. The potential for sulfide formation relies on four IRZ factors within the reactive zone. These four factors are important IRZ operation parameters and are summarized below:

- (a) SRBs are obligately anaerobic and thus require negative redox conditions (-150 to -200 mv).
- (b) SRBs require available sulfate, or in some cases, can use elemental sulfur. Sulfate is provided as a normal component of the molasses that is added to form the IRZ.
- (c) SRBs require an acceptable electron donor to be metabolically active. Acceptable electron donors for SRBs include fatty acids, organic acids, alcohols, and hydrogen (Brock and Madigan, 1988). Suitable SRB substrates are a product of bacterial fermentation of the molasses that is periodically dosed into the treatment zone (See Figure 1).
- (d) The concentration of other naturally occurring dissolved metal ions that may compete with the contaminant(s) for sulfide is an important factor that affects the total mass of sulfide required to attain regulatory requirements for contaminant concentration(s). The most important naturally occurring metallic elements in this category are iron and manganese. Both dissolved iron and manganese have the potential to compete with metallic contaminants for sulfide. Thus the IRZ as engineered must provide sulfide to meet the system's demands for iron sulfide and manganese sulfide in addition to the sulfide salts of the metallic contaminants. However the presence of iron and manganese can also be a benefit since it allows coprecipitation processes to take place, similar to those often used in ex-situ water treatment.

Negative redox conditions are required for SRBs to exist and be metabolically active at the site. Given the presence of a viable population, the SRBs reduce sulfate to sulfide while oxidizing suitable electron donors. If any of these three variables is absent or available in an unreliable manner within the IRZ, sulfide production may not meet the technical requirements for adequate precipitation.

At a typical IRZ implementation for metals whose precipitation is sulfide dependent, both (a) and (b) above are routinely monitored at the site. The availability of substrates for SRBs is typically not monitored at sites whose performance is deemed acceptable. Substrate availability analyses are occasionally specified by ARCADIS as a trouble-shooting measure to better understand and potentially correct the performance of an IRZ.

The geochemistry of the specific heavy metals and radionuclides of primary interest to DOE has recently been reviewed in depth by ARCADIS. The result of this review suggests that this approach will be successful in treating Uranium and Technetium-99 under many conditions commonly found *in situ*. We will now discuss in detail the mechanism for this process for five specific CoCs: Cd, Cr, Hg, U, and Tc.

### 1.1 Cadmium Mechanism

Dissolved cadmium, when present in groundwater, is thought to react with either sulfide or carbonate present in the aquifer to form the stable cadmium carbonate or cadmium sulfide precipitates as follows:

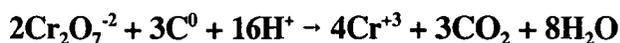
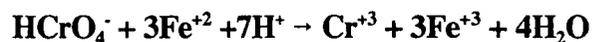


As discussed above, excess sulfide will be present in the groundwater as a result of the microbial reduction of sulfate occurring naturally in the groundwater at contaminated sites or as a component of the injected molasses solution. Carbonate is naturally present in groundwater and will also be formed as a result of the formation of carbon dioxide from the microbial degradation of the carbohydrates in the molasses solution.

### 1.2 Chromium Mechanism

Of the two primary oxidation states for chromium, the hexavalent (VI) is by far of the greatest concern. These compounds have reported mutagenic, teratogenic, and carcinogenic concerns. Hexavalent chromium is primarily found as the highly mobile anions  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ . In contrast, the +3 state has relatively low toxicity and may be immobilized under moderately alkaline to slightly acidic conditions (Figure 2).

Fortunately, Cr(VI) is easily reduced. Palmer and Puls and Suthersan report reduction by both ferrous iron and organic carbon via the following reactions. They state that the ferrous iron in pyrite is capable of reducing chromium.



Jardine (1999) provides arguments for reduction by surface bound organic matter.

The EARP technology provides all of these reductive routes to the detoxification of Cr(VI). As noted previously, EARP provides a reducing environment, organic carbon, and sulfide ions. The conditions created by EARP are sufficient to reduce ferric iron, which is usually present in most aerobic geochemical systems, to ferrous.

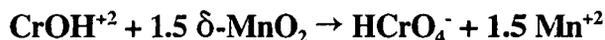
Once the Cr is reduced several solid minerals can form. As Margolis (1962) and Swift and Schaefer (1962) note any chromium sulfide which attempts to form is hydrolyzed in the presence of water to form  $\text{Cr}(\text{OH})_3$ . Figure 2 suggests the stable species is  $\text{Cr}_2\text{O}_3$ . Suthersan agrees with the  $\text{Cr}(\text{OH})_3$  end product. Cotton and Wilkinson (1966) clarify this apparent inconsistency, noting, "...the hydrous oxide,  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . The latter, commonly called chromic hydroxide, although its water content is variable..." Palmer and Puls argue for the formation of a non-stoichiometric solid solution of the form  $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ . They state that the concentration of Cr(III) in equilibrium with this solid solution

is expected to be  $<10^{-6}$  molar within the pH range of 5 to 12. Swift and Schaefer report a solubility product constant for the hydroxide of  $10^{-30}$ .

ARCADIS has experience in the remediation of Cr(VI) contaminated sites using the EARP technology at numerous sites. Results reported by Vance (Internet Paper) are based on one such site (Figure 3). Remediation started with pump and treat technology, which after seven years reached its asymptotic limit. When EARP replaced it, chromium concentrations dropped by two orders of magnitude in a matter of months.

Palmer and Puls review the oxidation of Cr(III) back to Cr(VI). They note there are only two natural species that can perform this oxidation, dissolved oxygen and manganese dioxide. A review of the literature concluded that dissolved oxygen was not a significant agent in this oxidation.

In contrast, manganese dioxide has been demonstrated to oxidize Cr(III) via the reaction:



However, note that the above reaction depends on solid-dissolved species interaction. Based on the low solubility constant reported, the above should happen at a very slow rate post-remediation. Also note that manganese dioxide may not survive the EARP treatment. According to the Eh-pH diagram for the system Mn-O-H,  $\text{MnO}_2$  requires oxidative, basic conditions. As EARP drives the system anaerobic and reductive, the  $\text{Mn}^{+2}$  ion is the stable species. In the presence of sulfide, manganese sulfide,  $\text{MnS}$ , should form, thus further reducing the possibility of  $\text{Cr}^{\text{III}}$  oxidizing and resolubilizing.

As shown in Figure 16, ARCADIS has collected field data at full scale to support the contention that the chromium, once precipitated, does not resolubilize at an appreciable rate.

### ***1.3 Mercury Mechanism***

The best reaction for stabilization of mercury is its reaction with hydrogen sulfide to form the highly insoluble compound,  $\text{HgS}$ , cinnabar, which is the primary ore used to produce mercury. It has a solubility of  $4.5 \times 10^{-25}$  mole/liter and a solubility product constant,  $K_{\text{sp}}$ , of  $2.0 \times 10^{-49}$  (Conner 1990). This suggests that precipitation of mercury by Enhanced Anaerobic Reductive Precipitation (EARP) should be effective.

Figure 4, presents the Eh-pH diagram for the system Hg-O-H-S-Cl. As can be seen, mercury may be expected to be present as elemental mercury or mercuric oxide under initial conditions with typical levels of dissolved oxygen. As the system is driven anaerobic to Eh levels of -200 to -300 mV, the stable species becomes mercuric sulfide.

The above presumes that hydrogen sulfide is present in the system so this reaction can occur, but we know from both theory and field experience that the reduction of available sulfate will occur as the system attains these Eh levels. The prevalent sulfur form will be hydrogen sulfide with some partitioning to  $\text{HS}^-$ , depending upon pH.

Barnett's evidence (Barnett et al., 1997) shows the above proposed mercury immobilization technique has been observed to occur in the field. Analysis of mercury-contaminated soils from a flood plain demonstrated immobilization of mercury as the sulfide. In this work, they found the mineral formed was metacinnabar.

Barnett does not present any data on the long-term stability of the formed mercuric sulfide. They note that, "Ongoing experimental measurements of the oxidation rate of metacinnabar indicate that HgS is one of the slowest weathered minerals in soil."

However, Ravichandran argues that humic acids provide a mechanism for the potential dissolution of mercuric sulfide under both oxic and anoxic conditions (Ravichandran et al., 1998). On the other hand, they found no dissolution in the absence of stirring. In the absence of stirring, fresh active sites are not exposed. Thus, this need not be considered a significant mechanism for dissolution under natural conditions.

In 1994, ARCADIS commercial bench-scale study of mercury-impacted groundwater demonstrated that amendment with molasses produced, gradually over the course of a 6-month study, an anaerobic microbial community capable of reducing sulfate to sulfide. Thorough mercury analyses of samples collected in each of the three monitoring events suggests that the sulfides reacted with mercury to form precipitates.

#### *1.4 Uranium Mechanism*

Uranium is a naturally occurring radionuclide. Uranium is naturally available as  $^{238}\text{U}$ , the most abundant isotope, plus  $^{235}\text{U}$ . Minor quantities of  $^{234}\text{U}$  are present as a breakdown product of  $^{238}\text{U}$ .

Under ordinary aerobic conditions, uranium exists in the +6 state. In the absence of carbon, the  $\text{UO}_2^{+2}$  ion is found in acid to slightly basic conditions. Under strongly basic conditions, the mixed oxidation state complex  $\text{U}_3\text{O}_8$  exists. In the presence of carbon, the uranyl ion exists only under clearly acidic conditions. Above a pH of about 5, carbonates prevail. The solid uranyl carbonate exists over a fairly narrow pH range of 5 to 6+ with uranyl carbonate anions existing from near neutral to strongly basic conditions. Throughout this range, uranium remains in the +6 oxidation state.

As EARP begins to drop the Eh, the mixed oxide,  $\text{U}_3\text{O}_8$ , is established over a fairly narrow Eh-pH range. As the process continues and the system begins to go reductive, uranium is reduced to the +4 oxidation state and the solid oxide,  $\text{UO}_2$ , is the stable species. In the presence of naturally occurring iron and reduced sulfur, as described earlier, coprecipitation will occur with pyrite.  $\text{UO}_2$  is the naturally occurring mineral uraninite. This is the pure uranium mineral found in pitchblende. As such, it can be expected to remain stable.

As discussed above in the +4 oxidation state, uranium normally precipitates as  $\text{UO}_2$ . Some evidence for the sorption of  $\text{UO}_2$  to sulfide mineral surfaces exists (Wersin et al., 1992).

When Si is a significant species, either with or without carbon, the Eh-pH diagram is significantly changed. However, there is an immobile mineral form, coffinite ( $USiO_4$ ), that has a large stability field under reducing conditions, and neutral to acidic conditions, suggesting that EARP can be effective in treating U in the presence of Si as well. An Eh-pH diagram for Uranium is provided as Figure 5.

Uranium precipitation and its efficacy as a remedial alternative has been the subject of several recent laboratory research programs. Research programs conducted by University of New Mexico/Los Alamos National Laboratory and University of Tennessee/Pacific Northwest National Laboratory/Horticulture Research International/AEA Technology Environment have resulted in journal articles published in 2000 and 2001 respectively. These papers show two mechanisms (chemical and biological) for the reduction of soluble uranium and its precipitation as the mineral uraninite. In the first, chemical mechanism, as the IRZ technology begins to drop the Eh, the mixed oxide,  $U_3O_8$ , is established over a fairly narrow Eh-pH range. As the process continues and the system begins to go reductive, uranium is reduced to the +4 oxidation state and the solid oxide,  $UO_2$  or uraninite is formed. The second mechanism is microbiologically driven and arises from the research of Lovley et. al, Abdelouas et al., and Chang et al., which, taken together describe the biological reduction of U(VI) to U(IV) by sulfate reducing bacteria (SRB) and its subsequent precipitation as uraninite. In addition, the work of Abdelouas et al., contributes a better understanding of the distribution of uranium reducing bacteria, which is favorable for the applicability of this technology since they find that these bacteria are widespread or even ubiquitous. Senko et. al (2002) predicts on thermodynamic grounds that Uranium reduction will occur under conditions more reducing than are required to reduce nitrate but less reducing than are required for sulfate reduction. Ganesh (1997) summarizes the effects of various organic and inorganic ligands on the rate of the biological reduction process. Although one case was found where a particular pure culture was unable to reduce a particular uranium organic ligand complex in general this process proceeded over useable time lines (10s of hours) for almost all cultures and organic complexes studied.

More fundamental work has also been done to examine the details of the biological reduction of Uranium by particular organisms. For example Payne and coworkers examined the role of various proteins in the biological reduction of Uranium by *Desulfovibrio desulfuricans* with hydrogen, lactate or pyruvate as electron donors (Payne 2002). Holmes (2002) discusses the relative role of iron reducing and sulfate reducing organisms in the direct reduction of uranium. They also report reduction of Uranium with acetate as the electron donor. They emphasize the role of *Geobacteraceae* in the reduction of Uranium.

### ***1.5 Uranium Experience and Precipitate Longevity***

ARCADIS conducted a laboratory evaluation in 1997 of U precipitation in the presence of sulfate reduction for the Department of Energy-Office of Environmental Management. This laboratory study concluded that U was precipitated as  $UO_2$ .  $UO_2$  may be subject to resolubilization under positive redox conditions. However this can be prevented/managed as discussed below. The more recent laboratory studies of other researchers have concluded that U precipitates in the presence of

sulfide as uranium sulfide or is utilized as a terminal electron acceptor and thus reduced from the soluble, toxic U(VI) to the insoluble U(IV) (Chang et al., 2001). In the +4 oxidation state, uranium precipitates as  $UO_2$ . Some evidence for the sorption of  $UO_2$  to sulfide mineral surfaces exists (Wersin et al., 1992).

Currently, ARCADIS possesses only short- to mid-term field experience with the application of its IRZ technology for the precipitation of dissolved uranium. The first ARCADIS uranium precipitation field scale project is being performed on a commercial basis for a government contractor facility, in Erwin, Tennessee (see [http://www.epa.gov/epaoswer/hazwaste/ca/success/r4s\\_nucl.pdf](http://www.epa.gov/epaoswer/hazwaste/ca/success/r4s_nucl.pdf) for more information). The results of this study that demonstrate uranium precipitation are shown in figure 15. A successful field-pilot study has been conducted and ARCADIS has been requested to provide a design for a full-scale treatment system that will start-up soon. The implementation of the IRZ remedy at the NFS site is being cooperatively overseen by USEPA, Region 4 and the Tennessee Department of Environment & Conservation (USEPA Region 4 and TDEC contacts available upon request). The NFS field-pilot project was initiated in August 2000 and continued through January 2001.

Successful bench scale results from a biological reduction process with some similarities to EARP have been published for Uranium precipitation from various Western U.S. groundwaters (Abdelouas 1998, Abdelouas, 2000). These authors were able to reduce uranium to below treatment standards. The process used by these authors was similar to EARP in that it relied on a naturally occurring mixed culture. It differed in that the substrate was a pure substance ethanol rather than the complex food grade substrates ARCADIS prefers to employ. Furthermore a trimetaphosphate addition was used as a nutrient, which we do not normally find to be necessary. Finally the ethanol dose was kept low - based on stoichiometry of the uranium. We find that the best results are achieved when greater than stoichiometric doses are employed to allow for the numerous inevitable side reactions and formation of biomass. Abdelouas's results do confirm that the precipitated product, at least in their system, is uraninite, albeit in their system, a calcium containing solid solution of uranite. Starting concentrations of U as high as 235 mg/l and as low as 0.250 mg/l were successfully treated.

In order for this in-situ technology to be successful long-term the precipitated uranium must not be redissolved at an unacceptable rate once groundwater geochemical conditions return to their pretreatment state (which is often is aerobic and near neutral pH). The literature shows that, irrespective of which mechanism is responsible for uraninite precipitation, in the presence of available iron and sulfur (usually in the form of sulfate), iron sulfide minerals such as pyrite ( $FeS_2$ ) and mackinawite ( $FeS_{0.9}$ ) are likely to be precipitated at the same time and in close proximity to the uraninite. These iron sulfide minerals protect the uranite from reoxidation (Abdelouas 1999). Use of molasses as the carbon source (electron donor) would be expected to increase the amount of iron sulfide precipitated. The literature reveals that commercially important uraninite deposits are often found to contain significant quantities of sulfide as well. Gross describes ore samples that "had a yellow oxidized coating 1/4 to 1/2 inch thick rimming a black interior of unoxidized pitchblende and sulfides." Abdelouas (1999) reviews several studies of natural uranium ore deposits and states that

pyrite oxidation is the protective reaction at the Pocos de Caldas mine in Brazil. The protection is provided by siderite ( $\text{FeCO}_3$ ) and ferrihydrite ( $\text{Fe}(\text{OH})_3$ ) at the uranium deposit at Oklo (Gabon).

Abedelouas (1999) verifies that this protective mechanism minimizes the flux of uranium from the redissolution of biologically precipitated uranium in column experiments using groundwater and bedrock from the Tuba City AZ site. Their column experiments differ from the ones to be conducted by ARCADIS using Fernald materials in several ways:

- they use ethanol as the carbon source with trimetaphosphate as a supplemental nutrient
- they appear to be operating the columns in a static mode during the precipitation portion of the test and then in a flow through mode with oxidized groundwater subsequently. Thus they observe a flushing out of biomass and attached Uranium in the initial pore volume following the introduction of the oxygenated water.

However their experiments do verify that small masses of uranite (corresponding to groundwater concentrations of uranium "on the order of a few milligrams per liter or less") are protected from reoxidation and thus dissolution at a level greater than groundwater protection standards for a simulated time of several hundred years. Note that at many DOE sites, for example Fernald, the concentration of uranium in groundwater requiring remediation is even less than this - a fraction of a milligram per liter.

The results of Senko (2002) do suggest that the reduced uranium can be reoxidized and remobilized especially in the presence of nitrate. However the conditions studied by Senko were already highly reducing before the addition of mobile uranium and electron donor. This would make the coprecipitation of iron with the uranium less likely.

Thus, ARCADIS now believes that, though potential for the slow redissolution of uraninite exists, the presence of iron sulfide minerals that is precipitated in close proximity to uraninite will act to shelter the uraninite from re-oxidation. Indeed, Brock et al. provides a table of sulfide minerals listed in order of increasing resistance to oxidation which displays  $\text{FeS}$  as the most oxidizable sulfide mineral listed.  $\text{FeS}$  is likely to be produced during the implementation of the IRZ technology at sites where iron is naturally available. The implementation of the IRZ technology is likely to both increase concentrations of soluble ferrous iron due to the negative redox, slightly acidic conditions that it induces and to provide free sulfide for reaction with the ferrous iron in solution through the action of stimulated populations of SRB. The precipitation of  $\text{FeS}$  along with uraninite is likely to occur within the stoichiometric constraints of ferrous iron and sulfide availability. Once the  $\text{FeS}$  is precipitated in close proximity to precipitated uraninite, experimental bench scale and observational field evidence suggests it will shelter uraninite from re-oxidation (Albedous 2002). The length of time that precipitated  $\text{FeS}$  will shelter uraninite is stoichiometrically dependent on the amount of dissolved oxygen that groundwater flow exposes the  $\text{FeS}$  to over time making the longevity of uranium precipitated as uraninite a site specific phenomenon that should be investigated further for each site. Note, however, that the existence of natural commercial uranite deposits suggest that uranite is reasonably stable over geologic time

scales of billions of years (Albedous 2002). Albedous has also conducted an acceleration test discussed above and shown "that mackinawite can protect uranite for hundreds of years" (Albedous, 1999 as cited in Albedous 2002).

There is yet another group of mechanisms by which iron can protect precipitated uranium from resolubilization. Lack and coworkers (2002) has shown that fresh amorphous Fe(III)oxide is a very strong sorbent for a variety of metals including uranium. This amorphous Fe(III) oxide is "a precursor of many natural forms of crystalline Fe(III) oxides" that adsorbs or incorporates into its structure many trace metals. They write that "selective anaerobic bio-oxidation of Fe(II)...may be an effective means of capping off and completing the attenuation of HMR (heavy metals and radionuclides) in a reducing environment, allowing the system to naturally revert to an oxic state while preventing remobilization of previously reduced and isolated HMR....by precipitating Fe(III)(hydr)oxides over immobilized HMR in situ, forming an insoluble barrier that crystallizes with time....adsorbing any leached HMR locally"

Finally, it is important to realize that for the technology to meet regulatory standards, it need not prevent any resolubilization for all time. Rather, it must, and we believe will, allow resolubilization at a slow enough rate (flux) that the groundwater concentrations downgradient will remain below regulatory standards.

EARP has been accepted regulatorially in numerous states and EPA regions under the CERCLA and RCRA programs for other metals, most commonly Chromium. As discussed above EPA has published the first EARP field application for uranium as a RCRA success story. We believe there are several reasons why this technology as applied to Uranium is environmentally beneficial and sustainable:

A) the concentrations of Uranium in soil after this precipitation process will in many cases not add markedly to the naturally occurring concentration. Note that the earth's crust contains 2.4 ppm Uranium on average and that granites typically contain up to 15 ppm (Merian)!

B) analogous processes have been frequently accepted for nonradionuclide metals, since essentially they are returning the metals to their natural state - as ores.

C) there are likely to be no cost-effective and technically practical remedial alternatives.

### ***1.6 Technetium-99 (<sup>99</sup>Tc) Mechanism***

The isotope <sup>99</sup>Tc is a product of nuclear fission reactions. <sup>99</sup>Tc has a half-life of  $2.13 \times 10^5$  years. Reference to the Eh-pH diagram for the system Tc-S-O-H (Figure 6) shows that the anion  $TcO_4^-$  is the stable species under ordinary aerobic conditions. As EARP technology is implemented and the system moves towards anaerobic, reductive conditions, this ion is reduced first to  $TcO_2$  and then to the mixed oxidation state oxide,  $Tc_3O_4$ . Finally, as reductive conditions stabilize and sulfides are generated, the stable compound  $TcS_2$  becomes the dominant species. In the absence of sulfide,  $Tc_3O_4$  is reduced to the hydroxide,  $Tc(OH)_2$ .  $TcS_2$  is known to be stable in the presence of sulfide as

Brookins states, "The stability of the  $TcS_2$  species is well documented under sulfur-present conditions in laboratory experiments, and may further retard and retain any escaping Tc from breached radioactive waste containers."

Lee reaches an even more emphatic conclusion (Lee et al., 1983) regarding a slightly different technetium sulfide stoichiometry  $Tc_2S_7$  (*italic emphasis added*).

*Pertechnetate oxyanion,  $^{99}TcO_4^-$ , a potentially mobile species in leachate from a breached radioactive waste repository, was removed from a brine solution by precipitation with sulfide, iron, and ferrous sulfide at environmental pHs. Maghemite ( $\gamma-Fe_2O_3$ ) and goethite ( $\alpha-FeOOH$ ) were the dominant minerals in the precipitate obtained from the  $TcO_4^-$  ferrous iron reaction. The observation of small particle size and poor crystallinity of the minerals formed in the presence of Tc suggested that the Tc was incorporated into the mineral structure after reduction to a lower valence state. Amorphous ferrous sulfide, an initial phase precipitating in the  $TcO_4^-$  ferrous iron-sulfide reaction, was transformed to goethite and hematite ( $\alpha-Fe_2O_3$ ) on aging. The black precipitate obtained from the  $TcO_4^-$ -sulfide reaction was poorly crystallized technetium sulfide ( $Tc_2S_7$ ) which was insoluble in both acid and alkaline solution in the absence of strong oxidants. The results suggested that ferrous- and/or sulfide-bearing groundwaters and minerals in host rocks or backfill barriers could reduce the mobility of Tc through the formation of less-soluble Tc-bearing iron and/or sulfide minerals.*

There is even evidence in a 1996 paper by Lemire (Lemire and Jobe) that the Tc(IV) oxides may be more stable than previously supposed:

*Recently, the authors reported a value of  $\Delta_f H^\circ(TcO_2(cr)) = \text{minus } (458 \pm 6) \text{ kJ/mol}$  based on heat of solution measurements. The implications of this value on the database used in the Canadian Nuclear Fuel Waste Management Program for the evaluation of the technetium released by congruent dissolution of used  $UO_2$  fuel have now been assessed. It is probable that the Tc(IV) oxides are more stable than previously predicted and, hence, they are less likely to be oxidized to  $TcO_4^- (aq)$  under moderately reducing conditions. The authors have revised earlier calculations done to predict the solution concentrations of technetium species in a vault as a function of the oxidation conditions in model groundwaters."*

However we will need to verify the performance of this technology in the laboratory for technetium since mobile humic substances can enhance the solubility of technetium oxides (Geraedts et al., 2000).

Overall this analysis suggests that EARP should be highly effective for Tc.

## **2.0 Site Background**

### **2.1 Geology and Hydrogeology**

The FEMP is situated over the New Haven Trough, a large buried valley filled with glacial sand and gravel outwash deposits (braided stream depositional environment) with an axis running northeast southwest. Figure 7 is a bedrock topographic map that defines the valley floor. The floor walls of the New Haven Trough consist of Ordovician age shale and limestone. During the Pleistocene the New Haven trough was carved into the shale and limestone bedrock, filled with sand and gravel, and capped by a layer of Wisconsin age clay-rich glacial overburden. The sand and gravel forms the matrix of the regionally extensive Great Miami Aquifer.

The Great Miami Aquifer is unconfined, anisotropic, and heterogeneous and has been federally designated a sole-source aquifer by the U.S. EPA. As recorded from core collected during the drilling of Monitoring Well 4398, the lithology consists of approximately 24 feet of silty clay and approximately 167 feet of sand and gravel. The sand and gravel forms the aquifer matrix. The silt clay lies on top of the aquifer. Bedrock is approximately 191 feet below the ground surface. An idealized cross section is Figure 8.

The part of the plume that is targeted for demonstration is called the South Field. Hydraulic conductivity in the South Field area is approximately 523 feet/day. The seepage velocity is approximately 1.1 foot/day, based on 30% porosity. The average gradient is approx. 0.0008. The uranium concentration cleanup level is 30 ppb. Uranium concentrations in the South Field range up to approx. 600 ppb. The South Field is aerobic (pH approx. 6.8, and Redox approx. 300 to 500 mV), but just to the East conditions turn slightly anaerobic, and a redox front may be present. Redox potentials in the aquifer just East of the plume have been measured in the 200 mV range. It appears that Redox conditions in the aquifer become more reduced with depth and with distance from recharge points. The principal cation found in groundwater from the aquifer is calcium, the principal anion is bicarbonate. Figure 9 includes a piper diagram from a monitoring well in the South Field that is representative of the general water chemistry.

### **2.2 Site Background - Previous Investigations**

The nature and extent of groundwater contamination from operations at the FEMP has been investigated, and the risk to human health and the environment from these contaminants has been evaluated in the Operable Unit 5 Remedial Investigation Report (DOE 1995d). As documented in that report, the primary groundwater contamination at the FEMP is uranium. Approximately 230 acres of the Great Miami Aquifer are contaminated above the 20  $\mu\text{g/L}$  groundwater total uranium FRL in use at that time. Contamination of the groundwater resulted from infiltration through locations where the glacial overburden is eroded, and the sand and gravel of the aquifer are in direct contact with uranium-contaminated surface water from the FEMP.

After the nature and extent of groundwater contamination was defined, various remediation technologies were evaluated in the Feasibility Study Report of Operable Unit 5 (DOE 1995). This

report recommended a pump-and-treat remedy with re-injection for the groundwater contaminated with uranium. The remedy consists of 28 groundwater extraction wells pumping at a combined rate of 4,000 gpm, located on and off property.

This groundwater remediation strategy focuses primarily on the removal of uranium, but also has been designed to limit the further expansion of the plume, achieve removal of all targeted contaminants to concentrations below designated FRLs, and prevent undesirable groundwater drawdown impacts beyond the FEMP property.

A groundwater re-injection demonstration was conducted at the FEMP from September 2, 1998, to September 2, 1999. The ensuing Demonstration Test Report (DOE 2000c) was issued to EPA and OEPA in May 2000. The Test Report details the demonstration and recommends its incorporation into the FEMP's aquifer restoration strategy.

The enhanced groundwater remedy also included extraction wells in on-site areas of the aquifer contamination. Groundwater modeling studies conducted in support of the enhanced groundwater remedy suggested that, with the early installation of additional extraction wells and re-injection technology, the length of the remedy could potentially be reduced to 10 years.

During 1998, significant portions of the enhanced groundwater remedy were completed. By the end of June 1998, construction was complete on the pipeline distribution network and associated electronic controls for the three groundwater restoration modules: South Plume Optimization Module, South Field (Phase I) Extraction Module, and Re-injection Demonstration Module. By September 1998, all three modules were on line and, in combination with the South Plume Module, were pumping 3,500 gpm from the aquifer and re-injecting 1,000 gpm.

During 2000, active remediation of the great Miami Aquifer continued at the following groundwater restoration modules: South Plume/South Plume Optimization Module, South Field (Phase I) Extraction Module, and Re-injection Module. As identified in the 1999 Integrated Site Environmental Report (DOE 2000b), Extraction Wells 32446 and 32447 were installed during the fourth quarter of 1999 to supplement the South Field (Phase I) Extraction Module. These two wells began pumping in February 2000.

The 10 extraction wells of the South Field (Phase I) Extraction Module (Extraction Wells 31550, 31560, 31561, 31562, 31563, 31564, 31565, 31566, 31567, and 32276) began operating on July 13, 1998. As a result of groundwater remedy performance monitoring, Extraction Wells 32446 and 32447 were installed during the fourth quarter of 1999 as part of the south field (Phase I) Extraction Module. The wells began pumping in February 2000.

Data collected during 2000 are showing that the souther plume is being captured by the existing system and that further movement of uranium to the south of the extraction wells is being prevented. However, some monitoring wells in the eastern portion of the South Field (Phase I) Extraction Module area have steady or increasing total uranium concentrations. Options for increasing the flushing of the aquifer in the eastern portion of the South Field area are scheduled to

be evaluated in 2001. A diagram showing the location of the pump and treat system is provided (Figure 10)

A map of the Uranium plume is provided in Figure 11. An Uranium concentration cross section in the area of interest is also provided in Figure 12. A temporal trend for the Uranium at wells 62408 and 62433 near our target area is provided as Table 1 and Figure 13. Concentrations in these wells are stable or increasing.

**Table 1. Temporal Trend for the Uranium at Wells 62408 and 62433**

| <i>Date</i> | <i>Well 62433</i> | <i>Well 62408</i> | <i>Well 62408</i> |
|-------------|-------------------|-------------------|-------------------|
|             | <i>Unfiltered</i> | <i>Unfiltered</i> | <i>Filtered</i>   |
| 14-Sep-99   | 331.9             | 86.5              |                   |
| 27-Dec-99   | 450.5             | 152.3             |                   |
| 07-Mar-00   |                   | 139.3             |                   |
| 08-Mar-00   | 399.4             |                   |                   |
| 05-Jun-00   | 417.3             | 136.7             |                   |
| 06-Sep-00   | 415               | 157               |                   |
| 26-Dec-00   | 571.4             | 156.4             |                   |
| 06-Mar-01   | 845               | 159.3             | 148.3             |
| 05-Jun-01   | 676.6             |                   |                   |
| 11-Jun-01   |                   | 121.4             | 125.8             |
| 04-Sep-01   | 650               |                   |                   |
| 05-Sep-01   |                   | 127               | 133               |
| 08-Oct-01   | 612               |                   |                   |

### **2.3 Analysis of EARP Technology Applicability to Fernald Site**

Several factors suggest to us that this is a suitable site for an EARP demonstration:

- the system is initially aerobic but there is some indication that Uranium has a sharp concentration decrease front that corresponds roughly to an observed redox decrease front.

This suggests that if reducing conditions could be achieved across the plume that Uranium could be precipitated in-situ

- the system is highly permeable so delivery of dissolved phase reagents should be easy (although large volumes of reagent may be needed)
- Uranium is the sole driver for remediation and there is a strong theoretical and experiential basis for believing EARP can treat uranium effectively as discussed above.

### 3.0 Objective

The primary objective of the bench-scale testing portion of this project is to confirm the efficacy of ARCADIS' IRZ/EARP technology for precipitating uranium from contaminated groundwater from the South Field Plume at the Fernald Environmental Management Project, Cincinnati, Ohio and therefore to provide evidence of its applicability to problems at numerous DOE sites.

In addition, there are two secondary objectives associated with the bench-scale portion of this project. Foremost is our intention that the bench-scale testing provide information that can be used to confirm engineering criteria for optimal IRZ scale-up at this site. Information from the bench-scale testing such as the molasses dosing concentrations required to achieve anaerobic conditions and the retention time within the test column that is required for optimal precipitation of target contaminants will permit optimization of IRZ scale-up if the project is transitioned to the field pilot stage.

Lastly, ARCADIS intends to subject the soil to chemical speciation before and after the laboratory scale EARP treatment. Chemical speciation refers to identification of the molecular form or chemical composition of a constituent of interest as it may exist under a specified set of environmental conditions. Speciation refers primarily to a solid phase analysis method used to identify the host mineral or amorphous compound that contains a target element, but it can also refer to determination of the redox state and coordination chemistry of a metal in solution.

Currently, the literature is somewhat contradictory with regard to the form in which U precipitates. Lovley et al., provides evidence that U serves as an alternate electron acceptor and is thus reduced from U(VI) to U(IV) and precipitated as  $UO_2$  (uraninite or pitchblend). Conversely, ARCADIS and Chang et al., believe that the formation of uranium sulfide minerals during IRZ application is also feasible.

ARCADIS intends to subcontract a grouping of sophisticated analyses to speciate precipitated uranium compounds. Thus, it is a secondary goal of this project to determine whether dissolved U is precipitated as an oxide or sulfide, or whether both compounds are precipitated during bench-scale simulation of IRZ treatment. Once the predominant precipitated compound is known, its fate under natural aquifer pH and Eh conditions can be confirmed more conclusively. In addition, it is hoped that the size of individual particles of precipitated contaminants can be determined so as to

permit an evaluation of the potential for colloidal transport subsequent to precipitation. A more thorough discussion of speciation analyses can be found in Appendix A.

### 3.1 Success Criteria: Non-Site Specific

Success, either of bench-scale or full-scale testing, will be defined as the permanent immobilization of the metals of interest such that:

- (1) The rate of any dissolution reactions under any reasonably foreseeable environmental condition, (i.e. pH 4-9 + ORP - 400 + 400 MV) will be such that the maximum ground water concentration of a long-lived radionuclide or hazardous metal concentration at a sentinel well or receptor well will be < 30% of the established or proposed regulatory limit for that constituent and <10% of the pretreatment value.
- (2) The expected dissolution time for 90% of the constituent of concern, if it is a short-lived radionuclide (under expected ORP + pH conditions), will be at least five times longer than the half-life of that hazardous radionuclide. This criteria should ensure that these short-lived radionuclides will have a sufficient time to decay into less hazardous forms before release.

Success will further require that this treatment be achieved at a cost projected (on a life-cycle, net present value basis) at 50% or less of the cost of competing or conventional remedial approaches (i.e. pump and treat).

In order to achieve this ultimate success, the following alterations of the biogeochemical conditions in situ will typically need to be induced and maintained during the active treatment phase of an EARP application.

- pH - > 4.5 s.u. in the injection wells; > 5.0 s.u. in the monitoring wells
- DO - < 1.0 mg/L in both monitoring and injection wells
- ORP - > -400 mv and < -250 mv in the injection wells; < -200 mv in the monitoring wells. For demonstration sites where reducing environments are identified in the groundwater prior to initiation of reagent injections, a target goal of lowering the ORP by 200 mv in the injection wells and 100 mv in the monitoring wells will be employed
- TOC - >500 mg/L and < 5,000 mg/L in the injection wells and > 50 mg/L in the monitoring wells
- Conductance - order of magnitude increase in the injection wells; 20 to 50 % increase in monitoring wells

In order to demonstrate success, sufficient time must be allowed after the cessation of carbon source injection to allow the carbon to be consumed, and the Eh, pH, DO, and conductivity to either revert

to pretreatment values or to stabilize at a value that does not change even with further oxygen recharge. Only if the radionuclides or hazardous metals remain stable under those conditions can the technology be deemed to be completely successful.

### **3.2 Quantitative Site Specific Objectives**

The quantitative dissolved phase clean-up objective for Uranium at this site is 30 ppb. Ideally this demonstration would show that a somewhat lower dissolved phase concentration could be achieved to provide some margin of safety. Achieving this treatment goal requires approximately 95% reduction in the groundwater U concentration as measured at well #62433 and 80% reduction at well #62408 for example.

### **4.0 Materials and Methods**

This section includes not only the information normally provided as part of a test plan, but also the details of sampling and analysis required to constitute a Sampling and Analysis Plan in one integrated document for easy reference.

#### **4.1 Field Sampling**

The intent of the saturated soil collection event is to obtain representative unconsolidated material for the Phase I Treatability Study. Given the very course nature of this soil it has been determined that the recovery of intact core samples is not practical and that repacked columns will be adequate for our purposes. Soil samples will be collected from within the saturated, unconsolidated portion of the aquifer that is targeted for treatment. Fluor Fernald plans to collect the soil samples on our behalf using a rotasonic drilling rig with sample collection into a plastic sleeve that has been previously been sterilized by ARCADIS. The plastic sleeve sample would be logged and then transferred to autoclaved glass containers. Required would be 8 feet of 4" diameter OR 30 feet of 2" diameter liner from the installation of one borehole into the great Miami Aquifer. As was indicated by Mr. Broberg of Fluor, the ideal area may be on the east side of the South Field Area in an aerobic zone near well 62433, but down gradient of the extraction wells.

The plastic sleeve will be disinfected with isopropanol or ethanol prior to loading into the sampler. After sterilization, the isopropanol or ethanol would be allowed to volatilize before the liner was used. The soil liners will be handled aseptically while being loaded and sampled to the extent feasible (for example the field team will be provided with sterile gloves).

Groundwater will be collected using an appropriate pump installed in the candidate well. The pump flow rate during collection of groundwater for the Treatability Study will reflect the expected productivity of the well. Groundwater will be collected in a disinfected sample container and shipped on ice to the treatability laboratory. Required is 135 liters of contaminated groundwater and 95 liters of uncontaminated groundwater, shipped in autoclaved vessels supplied by ARCADIS. Contaminated groundwater for use in this demonstration was collected from Well 62433 and

uncontaminated water was collected from well 2096 (Karen Voisard, personal communication 3/22/02).

## **4.2 Bench-Scale Treatability Testing**

### **4.2.1 Sample Receipt and Storage**

Impacted soil and groundwater samples will be collected by Fluor Fernald staff during their ongoing drilling program. The samples will be stored within sealed metal, glass, or plastic containers or liners and shipped on ice, for overnight delivery to:

David Demorest  
Envirotest Laboratories, LLC  
420 West First Street  
Casper, WY 82601  
(800) 666-0306  
(307) 266-1676

Sample chain-of-custody forms shall be properly completed and submitted with all samples. Envirotest Laboratories, LLC (Envirotest) will formally take custody of the samples, noting arrival dates on the applicable chain-of-custody forms, and will unload samples promptly, noting the condition in which they were received. All soil and groundwater samples in the custody of Envirotest will be stored under refrigeration at 4 °C:

### **4.2.2. Core Conversion, Soil Homogenization and Repacking**

Because the soil of the aquifer is relatively coarse and loose, it is not feasible to transfer an intact core. Therefore, we will use repacked cores as opposed to intact cores.

Soil will be homogenized quickly (to minimize volatilization) by hand in a stainless steel tray using a stainless steel spoon for at least five minutes after the soil aliquot visually appears homogenous. The experimental apparatus will be assembled as shown in Figure 14. Triplicate soil samples will be taken and analyzed for the parameters in Table 3. A matrix spike/matrix spike duplicate will also be analyzed at that time. Duplicate samples of the contaminated and a single sample of the uncontaminated groundwater to be used, will also be analyzed for the full parameter list (Table 2).

### **4.2.3 Column Operation**

Once two duplicate columns have been made out of the soil core samples, the columns will be operated in an up flow mode to minimize the chance of channeling. Both columns will have contaminated groundwater pumped through them using a peristaltic pump or a combination of a peristaltic pump and timer. One column will have molasses reagent added to the groundwater flow immediately prior to entering the column using a syringe pump. The molasses reagent will be introduced through a tee at the base of the column to achieve a concentration typical of that

achieved in down gradient IRZ monitoring wells (total organic carbon concentration of 200 mg/L). The second column will be an unamended control that does not receive the molasses reagent. Teflon tubing (1/8" O.D.), inert plastic fittings, and metal fittings will be used to plumb the two columns during set-up. Short sections of tygon tubing will be needed for the peristaltic pumps to function properly. The flow rate of impacted groundwater through the columns will be determined based on a desire to mimic as closely as possible the actual site groundwater velocities and will take into account the following stipulations:

- (a) Requirements to obtain sufficient sample volumes for certain liquid phase tests
- (b) The volume of contaminated groundwater required to a quantity that can be reasonably obtained, shipped, and stored
- (c) The flow rates achievable from available, reliable pumps

These practical constraints may require that the flow be recycled through the column during some periods of the study or that timers be used to control intermittent pumping (i.e. pump on for ten seconds per minute). Established flow rates will be monitored weekly at a minimum by timing the collection of a known volume of effluent and converting to milliliters per minute for comparison to the target rate.

#### 4.2.4 Column Study Length and Sampling Frequency

The columns will be 36 inches long with a diameter of 4 inches, which translates in a total volume of 7,413 cubic centimeters. Assuming a porosity of 30%, this provides a void volume of 2,224 cubic centimeters. The groundwater velocity volume is 1.1 ft/day (34 cm/day), leading to a calculated flow rate of 0.566 ml/min. Assuming 120 days of operation with contaminated groundwater (80 days with uncontaminated groundwater), the number of contaminated and uncontaminated pore volumes is 44 and 29 respectively. This translates into the a requirement of 130 liter contaminated, and 90 liter of uncontaminated sample. The soil sample requirements for the study (2 columns) are 14,827 cubic centimeters, or 95.0 feet of 1" liner, 24.2 feet of 2" liner, and 6.0 feet of 4" liner.

To achieve the desired molasses dosing we have calculated that we will need to add 0.0283 ml/min of a 4000 mg/l TOC dilute TOC solution to the treated column only. However this dose will be varied at the direction of the ARCADIS project manager or his designee after review of interim monitoring data. The dilute molasses solution will also be spiked with potassium bromide to achieve a larger concentration of 5-10 mg/l in the total column influent of the treated column only.

The reagent will be supplied continuously for a month or more of operation. ARCADIS anticipates that the columns will be operated with the molasses in the liquid phase of the molasses-dosed column for a total of 2 to 4 months. The exact time period will be chosen to provide at least one month of reaction time after the redox potential stabilizes at the desired Eh and DO levels (Eh = -150 mv to -200 mv; DO = < 1 mg/L). The columns will then be operated for approximately 2

months with the influent switched to an uncontaminated site groundwater. This phase will simulate the "rebound" period after active treatment in which the residual degradable carbon is consumed and dissolved oxygen is recharged. Several effluent samples will be taken during this period to determine if the constituents of concern are truly irreversibly precipitated. Influent pressures will also be monitored weekly using pressure gauges installed on the influent side of the columns between the columns and the pumps as an indication of any changes in soil permeability that may occur as a result of the precipitation reactions. The exact length of time for the rebound period will be chosen to provide at least one month of column operation beyond the point at which the degradable carbon has been consumed/flushed out and the columns have returned to a stable higher DO and Eh.

The parameters to be measured in the effluent of the two columns are listed in Table 2. Effluent parameters (except speciation) will be measured four times in the effluent of each column. The first effluent sampling will occur after the exchange of approximately 3 void volumes of groundwater through each column. After the sampling of this effluent the molasses flow into the treatment column will be initiated and continued until the rebound period. In addition, ARCADIS plans to sample the column effluents one month after study initiation, three months after study initiation, and near the end of the rebound observation period.

Additionally, a total of two influent samples will be taken during the course of the study (the influent for the control and test columns will be the same except for the addition of the molasses solution). Liquid phase analyses for the full monitoring parameter list will also include two blanks during the course of the test program and one matrix spike/matrix spike duplicate. Thus, a total of 14 liquid samples (including QC) for the full analyte list is planned.

An abbreviated list of effluent parameters, noted in Table 1, will be sampled on a more frequent basis (at least four additional times during the study). During each of these rounds an effluent sample will be taken from each column (one influent sample and one blank). On one occasion, an analytical duplicate will be analyzed and on one occasion a matrix spike/matrix spike duplicate will be analyzed. Thus, a total of 19 liquid samples (including QC) for the abbreviated analyte list is planned.

After the treatment appears well established, on one occasion only, a total of four liquid samples will be taken for speciation (and sent to MCL), comprising of one influent and two effluents from the treated column and one effluent from the control column.

Finally, a brief list of system performance monitoring parameter (temperature, DO, ORP, pH, TOC, bromide) will be monitored even more frequently (an additional six times) in the two column effluents and in the influent. We have found that these parameters are the most useful to monitor the establishment of conditions in an IRZ conducive to precipitation. These parameter also help us adjust the dosage of the carbon source. Thus, since these parameter are also part of both the full and abbreviated monitoring rounds, they will be analyzed a total of at least 14 times during the course of the study. No additional QC samples will be generated in these rounds. Thus, a total of 18 liquid sample analyses for the system performance monitoring list is planned.

#### 4.2.5 Column Disassembly and Soil Sampling

At the completion of the study, discrete soil samples will be removed from the influent end, the effluent end, and the midpoint of each column, and analyzed for concentrations of the constituents of concern (Table 3) and sent to MCL for speciation.

#### 4.2.6 Data Analysis and Reporting

Following completion of testing, the effluent groundwater and soil chemistry results will be evaluated to determine if the success criteria listed above are met. It is anticipated that a data analysis strategy will be to plot the concentrations of constituents of concern versus time, effluent volume, and also versus the master geochemical parameters such as DO and redox. Changes in chemical speciation will also be assessed.

#### 4.2.7 Quality Assurance/Quality Control

Most necessary quality assurance and quality control provisions have been discussed in the foregoing sections. Specifically provisions for analytical blanks, duplicates and matrix spikes/matrix spike duplicates are provided in order to assess the precision and accuracy of these analyses. A control column is being utilized to gauge the effectiveness of treatment. Additionally, the cited standard methods, which are incorporated into this document by reference, contain extensive QA/QC procedures including lab blank, calibration and calibration check procedures.

The ARCADIS Durham office, the lead office for this project, has a management-approved QA Program Plan, which sets a QA framework applicable to all projects performed by the office. Furthermore, Envirotest operates under a complete corporate QA manual. Goals for data quality for the various analytical measurements are shown in Table 4.

**Table 2. Parameters Included in Four Full Effluent Monitoring Events and Six Abbreviated Monitoring Events**

| Parameter        | Analytical Method  | Concentration Units Reported In | Parameter Included also In Abbreviated Monitoring Events? |
|------------------|--|---------------------------------|---|
| Temperature      | EPA 170.1  | ° C                             | Yes   |
| ORP              | ASTM D1498   | m.v.                            | Yes   |
| Dissolved Oxygen | EPA 360.1  | mg/L                            | Yes   |
| pH               | EPA 150.1  | s.u.                            | Yes   |
| Conductance      | Standard methods for examination of water & wastewater, 15 <sup>th</sup> edition method 205 & USEPA method 120.1 | millisiemens                    | Yes   |
| Alkalinity       | 310.1  | mg/L                            | No  |
| Nitrate          | 300.0A   | mg/L                            | No  |

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| Parameter                  | Analytical Method                              | Concentration Units Reported In | Parameter Included also In Abbreviated Monitoring Events? |
|----------------------------|--|---------------------------------|---|
| Nitrite                    | 300.0A   | mg/L                            | No  |
| Sulfate                    | 300.0A   | mg/L                            | No  |
| Chloride                   | 300.0A   | mg/L                            | No  |
| Methane, Ethane, Ethene    | Modified RSK-175,<br>Microseeps Method WA 1.02 | µg/L                            | No  |
| Carbon Dioxide             | Microseeps Method WA 2.01                      | mg/L                            | No  |
| Chemical Oxygen Demand     | 410.4 or 410.1                                 | mg/L                            | No  |
| Biochemical Oxygen Demand  | 405.1  | mg/L                            | No  |
| Total Organic Carbon (TOC) | 415.1  | mg/L                            | Yes   |

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| Parameter  | Analytical Method   | Concentration Units Reported In | Parameter Included also In Abbreviated Monitoring Events? |
|--|---|---------------------------------|---|
| Dissolved Total Organic Carbon (DOC)   | 415.1   | mg/L                            | No  |
| Ammonia  | 350.1   | mg/L                            | No  |
| Sulfide  | Color Chart/ Effervescence of H <sub>2</sub> S (Hach Kit 25378-00)                    | mg/L                            | Yes   |
| Total Iron   | 6010B   | µg/L                            | No  |
| Total Manganese  | 6010B   | µg/L                            | No  |
| Dissolved Iron   | 6010B   | µg/L                            | No  |
| Dissolved Manganese  | 6010B   | µg/L                            | No  |
| Total of Dissolved Target Radioisotopic Constituents; i.e. Uranium and Technetium, Total Concentration | Uranium 6020<br>TC99-LSC-ETL RSOP-0033<br>(based on a method developed at Portsmouth) |                                 | Yes   |

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| Parameter  | Analytical Method  | Concentration Units Reported In | Parameter Included also In Abbreviated Monitoring Events? |
|--|--|---------------------------------|---|
| Target Constituents Speciated (select samples only)              | As discussed in Appendix A, may include SEM, TEM, EDS, SAED and/or XRD |                                 | No  |
| Bromide  | 300.0  | mg/L                            | Yes   |
| Dissolved and Total Target Metal Constituents, Chromium and Zinc | 6010   | µg/L                            | Yes   |
| Hexavalent Chromium  | 7196A  | µg/L                            | Yes   |

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**Table 3. Parameters Included In Soil Monitoring Events**

| <i>Parameter</i>  | <i>Analytical Method</i>   | <i>Concentration Units Reported In</i> | <i>Notes</i>  |
|---|--|--|---|
| <i>Total Organic Carbon (TOC)</i>   | 9060   | mg/kg                                  |   |
| <i>Target Radionuclide Constituents; i.e. Uranium and Technetium, Total</i>                           | 6020 ICPMS for U<br>LSC Method ETL RSOP-0033<br>fo Tc                          | mg/kg                                  | Technetium  |
| <i>Target Radionuclide Constituents; i.e. Uranium and Technetium, Speciated (select samples only)</i> | As discussed in appendix text<br>may include SEM, TEM, EDS,<br>SAED and/or XRD |  |   |
| <i>Target Metal Constituents: Chromium and Zinc</i>   | 6010B  | mg/kg                                  |   |
|   |  |  |   |
| <i>Target Constituents: Chlorinated Aliphatic Hydrocarbons</i>  | 8260   | mg/kg                                  |   |
| <i>Grain Size</i>   | ASTM D-422   | % passing                              | Performed only<br>in initial<br>untreated soils,<br>not post<br>treatment |

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Table 4. Accuracy, Precision and Completeness Goals for Analytical Parameters

| <i>Parameter</i>                               | <i>Accuracy (%)</i>                         | <i>Precision (%)</i>                        | <i>Completeness (%)</i> |
|--|---|---|-------------------------|
| <i>Temperature</i>                             | <i>" 2 degree</i>                           | <i>10</i>                                   | <i>90</i>               |
| <i>ORP</i>                                     | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Dissolved Oxygen</i>                        | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>pH</i>                                      | <i>" 0.2 s.u.</i>                           | <i>10</i>                                   | <i>90</i>               |
| <i>Conductance</i>                             | <i>15</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Alkalinity</i>                              | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Nitrate</i>                                 | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Nitrite</i>                                 | <i>15</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Sulfate</i>                                 | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Chloride</i>                                | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Methane, Ethane, Ethene</i>                 | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Carbon Dioxide</i>                          | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Chemical Oxygen Demand</i>                  | <i>20</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Biochemical Oxygen Demand</i>               | <i>15</i>                                   | <i>20</i>                                   | <i>90</i>               |
| <i>Total Organic Carbon (TOC)</i>              | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Dissolved Total Organic Carbon</i>          | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Ammonia</i>                                 | <i>10</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Sulfide</i>                                 | <i>25</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Total Iron</i>                              | <i>Groundwater – 20</i><br><i>Soil – 15</i> | <i>Groundwater – 10</i><br><i>Soil – 10</i> | <i>90</i>               |
| <i>Total Manganese</i>                         | <i>Groundwater – 25</i><br><i>Soil – 20</i> | <i>Groundwater – 10</i><br><i>Soil – 10</i> | <i>90</i>               |
| <i>Dissolved Iron</i>                          | <i>20</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Dissolved Manganese</i>                     | <i>25</i>                                   | <i>10</i>                                   | <i>90</i>               |
| <i>Total Uranium and Technetium</i>            | <i>15</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Bromide</i>                                 | <i>15</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Total and Dissolved Metals, ie Chromium</i> | <i>15</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Hexavalent Chromium</i>                     | <i>15</i>                                   | <i>15</i>                                   | <i>90</i>               |
| <i>Grain Size</i>                              | <i>20</i>                                   | <i>25</i>                                   | <i>90</i>               |
| <i>CAHs</i>                                    | <i>0</i>                                    | <i>*</i>                                    | <i>90</i>               |

\* = Method 8260 provides accuracy information (% recovery) and precision information (% RSD) on a compound and matrix specific basis and asks each laboratory to establish goals for each compound in each matrix.

## 5.0 Time and Personnel Required for the Operation

Our labor hours are based on one site (Fernald). If an additional site was added to the program as proposed, the time to perform work at two sites would be less than double the time of doing one site. The following labor hours (Table 5) are based on ARCADIS' knowledge of the proposed sites and previous experience testing, designing, and implementing IRZ technology demonstrations.

**Table 5. Labor Hours**

|                                      | Task 1.0                          | Task 2.0                       | Task 3.0                                    | Task 4.0                | Task 5.0  | Task 6.0                                |                      |
|--------------------------------------|-----------------------------------|--------------------------------|---|-------------------------|---|---|----------------------|
|                                      | <i>Project Mgt. and Reporting</i> | <i>Field Sample Collection</i> | <i>Soil Sub-sampling &amp; Column Setup</i> | <i>Column Operation</i> | <i>Column Breakdown &amp; Treated Soil Sampling</i> | <i>Data Analysis &amp; Final Report</i> | <i>Project Total</i> |
| <b>Labor Category</b>                | <b>Hours</b>                      | <b>Hours</b>                   | <b>Hours</b>                                | <b>Hours</b>            | <b>Hours</b>  | <b>Hours</b>                            | <b>Hours</b>         |
| <b>ARCADIS Geraghty &amp; Miller</b> |                                   |                                |   |                         |   |   |                      |
| Project Director 2                   | 5                                 | 1                              | 1   | 4                       | 1   | 6                                       | 18                   |
| Sr Prj Mgr/Principal Sci/Eng         | 128                               | 4                              | 2   | 60                      | 8   | 56                                      | 258                  |
| Prj Mgr/Sr Sci/Eng/Des/Arch          | 52                                | -                              | 10  | 40                      | -   | 96                                      | 198                  |
| Project Sci/Eng/Des/Arch             | 166                               | 34                             | -   | -                       | -   | -                                       | 200                  |
| Staff Sci/Eng/Des/Arch               | -                                 | 10                             | -   | -                       | -   | -                                       | 10                   |
| Sci/Eng/Des/Arch II                  | -                                 | -                              | 40  | -                       | 20  | 16                                      | 76                   |
| Tech/CADD/Field Observer             | 16                                | -                              | -   | -                       | -   | 28                                      | 44                   |
| Admn / WP / Clerical                 | 28                                | 4                              | -   | -                       | -   | 30                                      | 62                   |
| Admn / WP / Clerical                 | 85                                | -                              | -   | -                       | -   | 36                                      | 121                  |
| <b>SUBTOTAL</b>                      | <b>480</b>                        | <b>53</b>                      | <b>53</b>                                   | <b>104</b>              | <b>29</b>   | <b>268</b>                              | <b>987</b>           |
| <b>Enviro-Test Laboratories</b>      |                                   |                                |   |                         |   |   |                      |
| Lab Scientist                        |                                   |                                | 40  | 215                     | 20  |   | 275                  |
| <b>SUBTOTAL</b>                      |                                   |                                | <b>40</b>                                   | <b>215</b>              | <b>20</b>   |   | <b>275</b>           |
| <b>GRAND TOTAL</b>                   | <b>480</b>                        | <b>53</b>                      | <b>93</b>                                   | <b>319</b>              | <b>49</b>   | <b>268</b>                              | <b>1262</b>          |

An organization chart and discussion of personnel responsibilities have been provided in the management plan.

## 6.0 Waste Generation

Please refer to the Hazardous Substance Plan for this project.

## 7.0 References Cited

Abdelouas, A., W. Lutze, W. Gong, E. H. Nuttall, B. A. Strietelmeier, and B. J. Travis, "Biological Reduction of Uranium in Groundwater and Subsurface Soil," *The Science of the Total Environment* 250 p. 21-35, 2000.

Brock, T.D. and M.T. Madigan, Biology of Microorganisms, Prentice Hall, Englewood Cliffs, New Jersey, 07632, p. 635 and p. 711, 1988.

Chang, Y.-J., A. D. Peacock, P. E. Long, J. R. Stephen, J. P. McKinley, S. J. MacNaughton, A. K. M. Anwar Hussain, A. M. Saxton, and D. C. White, "Diversity and Characterization of Sulfate-Reducing Bacteria in Groundwater at a Uranium Mill Tailings Site," *Applied and Environmental Microbiology* Vol. 67, No. 7, p. 3149-3160, 2001.

Conner, J.R., "Chemical Fixation and Solidification of Hazardous Wastes," ISBN 0-442-20511-2, Table 4-12, p. 84, 1990.

Ehmann, W.D.; Vance, D.E., *Radiochemistry and Nuclear Methods of Analysis, Appendix A: Statistics for Radiochemistry*, John Wiley & Sons, Inc., NY, 1991.

Geraedts, K., Maes, A., and Vancluysen, J., "Transport Behaviour of Perchnetate and Technetium - Humate Complexes in Gorleben Sand," Louvain Univ., Heverlee (Belgium). Lab. for Colloid Chemistry, pp 239-250, 2000.

Gross, E. B., "A Unique Occurrence of Uranium Minerals, Marshall Pass, Asguache County, Colorado," *The American Mineralogist*, Vol. 50, July-August, P. 909-922, 1965.

Jensen, M. L., "Significance of  $S^{32}/S^{34}$  Ratios on the Origin of Sulfides in Uranium Deposits of the Colorado Plateau," *Geological Society of America*, Volume 68. No. 12, Pt. 2, P. 1752-1753, 1957.

Lee, S. Y.; Bondietti, E. A., "Technetium Behavior in Sulfide and Ferrous Iron Solutions," *Scientific Basis for Nuclear Waste Management, Proceedings of the Sixth International Symposium*, North Holland Publishing, New York, ed. Brookings, D. G., pp. 31-5-22, 1983.

Lemire, R. J. and Jobe, D. J., "Predicted Behavior of Technetium in a Geological Disposal Vault for Used Nuclear Fuel -- Ramifications of a Recent Determination of the Enthalpy of Formation of  $TcO_2(cr)$ ," AECL, Chalk River, Ontario, Canada.

Lieser, K.H.; Bauscher, C., "Technetium in the Hydrosphere and in the Geosphere. II. Influence of pH, of Complexing Agents and of Some Minerals on the Sorption of Technetium," *Radiochim. Acta*, 44/45, 125-128, 1988.

Lovley, D.R., and E. J. P. Phillips. "Reduction of Uranium by *Desulfovibrio Desulfuricans*" *Applied and Environmental Microbiology* Vol. 58, No. 3. p. 850-856, 1992.

Mann, D.; Spence, V.; Berrier, P. (1997), "Determination of 99Tc in K-25 Site Cooling Tower Wood Leachates," presented at 1997 Eichrome Industries Users Seminar, Oak Ridge, TN.

Materials and Chemistry Laboratory, Inc. (1999), "Guideline for the Determination of Tc-99 in Scrap Metal, MCL-GL-011.

Naval Facilities Engineering Command, and U.S. Environmental Protection Agency, "Field Sampling and Analysis Technologies Matrix and Reference Guide, First Edition," EPA/542/B-98/002, Federal Remediation Technologies Roundtable, pp. 4 -7 to 4 -16, March 1998.

"Technetium-99 Analysis using Extraction Chromatography," Method RP550 in Goheen, S.C. et al. (1994), DOE Methods for Evaluating Environmental and Waste Management Samples, DOE/EM-0089T, Rev. 2.

Wildung, R.E.; McFadden, K.M.; Garland, T.R. (1979), "Technetium Sources and Behavior in the Environment," J. Environ. Qual., 8, 156.

Wright, H. D., and W. P. Shulhof, "Uranium Content of Base-Metal Sulfide Minerals as an Indication for the Uranium Concentration in Ore-Forming Solutions," 1956. Geological Society of America, Volume 67. No. 12, Pt. 2, P. 1745-1746.

Abdelouas, A., W. Lutze, W. Gong, E. H. Nuttall, B. A. Strietelmeier, and B. J. Travis, "Biological Reduction of Uranium in Groundwater and Subsurface Soil". 2000. The Science of the Total Environment 250 p. 21-35.

Abdelouas, A. et al, Oxidative Dissolution of Uranite Precipitated on Navajo Sandstone, Journal of Contaminant Hydrology, 1999, 36, 353-75.

Abdelouas, A. et al., Reduction of U(VI) to U(IV) by Indigenous Bacteria in Contaminated Groundwater; Journal of Contaminant Hydrology 1998, 35, 217-33.

Brock, T.D. and M.T. Madigan, Biology of Microorganisms, 1988. Prentice Hall, Englewood Cliffs, New Jersey, 07632, p. 635 and p. 711.

Chang, Y-J., A. D. Peacock, P. E. Long, J. R. Stephen, J. P. McKinley, S. J. MacNaughton, A. K. M. Anwar Hussain, A. M. Saxton, and D. C. White, "Diversity and Characterization of Sulfate-Reducing Bacteria in Groundwater at a Uranium Mill Tailings Site". 2001. Applied and Environmental Microbiology Vol. 67, No. 7, p. 3149-3160.

Ehmann, W.D.; Vance, D.E. (1991), Radiochemistry and Nuclear Methods of Analysis, Appendix A: Statistics for Radiochemistry, John Wiley & Sons, Inc., NY

- Ganesh, R. Reduction of Hexavalent Uranium from Organic Complexes by Sulfate and Iron Reducing Bacteria, Applied and Environmental Microbiology, Nov 1997 p4385-4391, Vol 63 No 11, 1997.
- Geraedts, K., Maes, A., and Vancluysen, J., "Transport Behaviour of Per technetate and Technetium - Humate Complexes in Gorleben Sand," Louvain Univ., Heverlee (Belgium). Lab. for Colloid Chemistry, pp 239-250, 2000.
- Gross, E. B., "A Unique Occurrence of Uranium Minerals, Marshall Pass, Asguache County, Colorado," 1965. The American Mineralogist, Vol. 50, July-August, P. 909-922.
- Jensen, M. L., "Significance of  $S^{32}/S^{34}$  Ratios on the Origin of Sulfides in Uranium Deposits of the Colorado Plateau," 1957. Geological Society of America, Volume 68. No. 12, Pt. 2, P. 1752-1753.
- Lee, S. Y.; Bondietti, E. A., "Technetium Behavior in Sulfide and Ferrous Iron Solutions," Scientific Basis for Nuclear Waste Management, Proceedings of the Sixth International Symposium, North Holland Publishing, New York, ed. Brookings, D. G., pp. 31-5-22, 1983.
- Lemire, R. J. and Jobe, D. J., "Predicted Behavior of Technetium in a Geological Disposal Vault for Used Nuclear Fuel -- Ramifications of a Recent Determination of the Enthalpy of Formation of  $TcO_2(cr)$ ," AECL, Chalk River, Ontario, Canada.
- Lieser, K.H.; Bauscher, C. (1988), "Technetium in the Hydrosphere and in the Geosphere. II. Influence of pH, of Complexing Agents and of Some Minerals on the Sorption of Technetium," Radiochim. Acta, 44/45, 125-128.
- Lovley, D.R., and E. J. P. Phillips. "Reduction of Uranium by *Desulfovibrio desulfuricans*". Applied and Environmental Microbiology Vol. 58, No. 3. p. 850-856. 1992.
- Lack, J.G. et al., Applied and Environmental Microbiology, p 2704-2710; vol 68 no. 6, June 2002.
- Mann, D.; Spence, V.; Berrier, P. (1997), "Determination of  $^{99}Tc$  in K-25 Site Cooling Tower Wood Leachates," presented at 1997 Eichrome Industries Users Seminar, Oak Ridge, TN.
- Materials and Chemistry Laboratory, Inc. (1999), "Guideline for the Determination of Tc-99 in Scrap Metal, MCL-GL-011.
- Merian, Earnest Ed. "Metals and their Compounds in the Environment: Occurance, Analysis and Biological Relevance," VCH Publishers Weinheim, Chapter II.33.
- Naval Facilities Engineering Command, and U.S. Environmental Protection Agency, "Field Sampling and Analysis Technologies Matrix and Reference Guide, First Edition," EPA/542/B-98/002, Federal Remediation Technologies Roundtable, pp. 4 -7 to 4 -16, March 1998.

Payne, Rayford B. Applied and Environmental Microbiology, June 2002, p 3129-3132.

Senko, J.M. et al., "In-situ Evidence for Uranium Immobilization and Remobilization," ES&T 2002, 35, 1491-6.

Goheen, S.C. et al., "Technetium-99 Analysis using Extraction Chromatography," Method RP550, (DOE Methods for Evaluating Environmental and Waste Management Samples, DOE/EM-0089T, Rev. 2, 1994.

Wildung, R.E.; McFadden, K.M.; Garland, T.R. (1979), "Technetium Sources and Behavior in the Environment," J. Environ. Qual., 8, 156.

Wright, H. D., and W. P. Shulhof, "Uranium Content of Base-Metal Sulfide Minerals as an Indication fo the Uranium Concentration in Ore-Forming Solutions," 1956. Geological Society of America, Volume 67. No. 12, Pt. 2, P. 1745-1746.

Lemire, R. J. and Jobe, D. J., "Predicted Behavior of Technetium in a Geological Disposal Vault for Used Nuclear Fuel -- Ramifications of a Recent Determination of the Enthalpy of Formation of  $TcO_2(cr)$ ," AECL, Chalk River, Ontario (Canada).

Geraedts, K., Maes, A., and Vancluysen, J., "Transport Behaviour of Per technetate and Technetium - Humate Complexes in Gorleben Sand," Louvain Univ., Heverlee (Belgium). Lab. for Colloid Chemistry, pp 239-250, 2000.

Lee, S. Y.; Bondietti, E. A., "Technetium Behavior in Sulfide and Ferrous Iron Solutions," Scientific Basis for Nuclear Waste Management, Proceedings of the Sixth International Symposium, North Holland Publishing, New York, ed. Brookings, D. G., pp. 31-5-22, 1983.

Wersin et al., "Abstracts of Papers," American Chemical Society National Meeting, 203GEOC, 1992.

Barnett, M.O. , L.A. Harris, R.R. Turner, R.J. Stevenson, T.J. Henson, R.C. Melton, D.P. Hoffman, "Formation of Mercuric Sulfide in Soil," ES&T, 31:3037-3043, 1997.

Jardine, P.M., S.E. Fendorf, M.A. Mayes, I.L. Larsen, S.C. Brooks, W.B. Bailey, "Fate and Transport of Hexavalent Chromium in Undisturbed Heterogeneous Soil," ES&T, 1999, 33:2939-2944.

Margolis, E.J. , "Qualitative Anion-Cation Analysis," John Wiley & Sons, Inc., LC 62-19150, 1962.

Swift E.H. , W.P. Schaefer, "Qualitative Elemental Analysis," W.H. Freeman & Company, L.C. 61-17384, 1962.

Cotton, F.A. and G. Wilkinson, "Advanced Inorganic Chemistry a Comprehensive Text,"  
Interscience Publishers, LC 66-20662, 1966.

Vance, D.B., "New Applications of Redox Reactions for In-situ Groundwater Remediation,"  
Internet paper <http://www.2the4.net/ThreeRedox.htm>

## APPENDIX A

### Speciation Approach

#### Liquid Samples

Chemical speciation refers to identification of the probable molecular form or chemical composition of a constituent of interest including valence state, as it may exist under a specified set of environmental conditions. The particular chemical form of the elemental constituent may affect such chemical and physical parameters as its volatility, aqueous solubility, bioavailability, toxicity, etc., and thus affect its impact on human and ecological health. These same parameters may determine the way that the constituents will respond to remediation technologies. An example is mercuric sulfide, a relatively nonvolatile, highly stable form of mercury that has a low bioavailability, which represents a much lower health risk than other forms of toxic mercury such as methyl mercury. Similarly, hexavalent chromium is a much greater hazard than trivalent chromium.

In the solution phase, speciation may involve the determination of the constituent of interest, the concentrations of various ligands that may form soluble complexes or insoluble mineral phases with the constituent of interest, anionic or cationic nature of the complex formed, and the measurement of a set of "master parameters" (e.g., pH value, redox condition, dissolved oxygen level, solution temperature, etc.) that control the overall chemical composition of the various probable constituents at equilibrium. Often, these parameters may be entered into a predictive thermodynamic model to estimate the relative predominance of the possible chemical forms of the constituent of interest. Similar predictions may be made for the solid phases that may exist at equilibrium.

The following methods are available for speciation of specific elements in groundwater samples and may also be used in this project:

Tc - In groundwater, Tc can be at least partially speciated using DOE Method RS 551, which utilizes the Empore™ Technetium Rad Disk discussed at [http://www.3m.com/product/index\\_E/index\\_E\\_26.html](http://www.3m.com/product/index_E/index_E_26.html)

U - Has been speciated in aqueous samples by Morris (1996) using a combination of X-ray absorption, optical luminescence, and Raman vibrational spectroscopies. An Ion Chromatography Method with spectrophotometric detection is cited in the Toxicological Profile.

#### Solid Samples

Particle speciation is an analysis method used to identify the host mineral or amorphous compound that contains a target element. The target element of interest, is typically at a minor or trace concentration in the bulk sample. Materials and Chemistry Laboratory, Inc. (MCLinc), who

will perform this work under subcontract to ARCADIS G&M, uses scanning electron microscopy (SEM), transmission electron microscopy (TEM), in conjunction with energy dispersive spectroscopy (EDS), and selected area electron diffraction (SAED) to determine the size, elemental association, matrix association, and composition of particulates. MCLinc also uses x-ray diffraction (XRD) to determine the crystalline phases present in samples.

Often the first task is to employ one of a number of sample preparation techniques, which are used to increase the concentration of the host compound by removing interferences and thereby make identification more exact. If a sample contains a trace amount of, as an example plutonium, a sample preparation scheme that concentrates the host compound such as density separation can enrich the sample by upwards of 100 times. This will allow SEM, TEM, and XRD techniques to identify compounds at levels that were initially below the level of detection.

Subsequent analysis steps may involve the use of SEM with EDS, TEM with EDS and SAED, and XRD. SEM with EDS analysis is capable of analyzing each particle in a sample. This is done by rastering a beam of electrons across a sample and then doing a chemical analysis with EDS of each of these grains or selected grains from that area. EDS looks at the characteristic x-rays that are generated when a substance is struck by electrons. The size of each area observed is dependent on the sample. If the particles are relatively small (between 1 and 5 micrometers) the analysis proceeds faster than if there is a larger variations in grains size (0.5 to 30 micrometers). The typical method is to use SEM with EDS to catalog the particles in a sample and then to determine which one or ones contain the element of interest. If the element of interest has a relatively heavy nucleus (as does, e.g., uranium or mercury), select imaging techniques (such as electron backscatter, where signal contrast is proportional to average atomic number in the field of view) may be used to identify areas of elemental concentration within the sample matrix. Information from SEM with EDS may answer questions such as "is the element of interest (uranium, lead, etc.) generally associated with silica (or aluminum, phosphorous, etc.)," or "are the toxic elements primarily associated with the smaller (potentially respirable or readily dispersible) particles," etc. Finding an element diffusely distributed at a low concentration in association with aluminum and silicon (principle components of soil or clay minerals) may suggest that the element may be sorbed to these components, whereas finding localized high concentrations of elements in definite proportions may suggest the deposition of specific mineral phases. Elemental associations are useful in postulating speciation (e.g., consistently finding mercury in association with sulfur may infer the presence of mercuric sulfide), but ancillary techniques are required to confirm specific chemical forms that may be present.

TEM analysis looks at small particles, like SEM with EDS does, but also has the capability to collect diffraction information on particles. This coupling of EDS and diffraction makes possible the identification of each grain as to type of compound or mineral. The size limits for optimum analysis by TEM are 5 micrometers and smaller.

XRD analysis is based on the collection and interpretation of a diffractogram. Copper x-rays are typically used to irradiate a crushed sample. These x-rays will be diffracted by the crystal structure of the components of the sample. The location and relative intensity of the resulting

peaks on the diffractogram are unique for crystalline material. From this diffractogram, the crystalline phases can be determined provided they are at a detectable level (0.5 to 1 percent). Often, physical separations (e.g., sieving, sedimentation rate in density gradients, etc.) may be used to prepare an enriched sample fraction for subsequent characterization and analysis.

Valence state speciation involves the determination of the valence state of the target element. This analysis can be carried out in an x-ray photoelectron spectrometer (XPS or ESCA). Samples are introduced into the chamber where an x-ray source is used to energize the photoelectrons. These electrons contain signatures of the valence state of their source elements. Profiles of the collected spectra are compared to standard spectra and the valence state or states for elements is determined. The list of elements that can be determined is comprised of lithium through the rest of the Period Chart. Other wet chemistry valence state determinations are also done. An example of this type of analysis would be Davies Grey for the valence state of uranium.

These speciation methods have been applied to a variety of projects by MCL including mercury speciation in stream deposits, permeable barrier characterization, and plutonium speciation in soil.

If concentrations of metals of interest in any solid phase sample are insufficient for these instrumental approaches we will speciate the metals using a multiple extraction technique similar to the method of Tessler et al. (1979). This method classifies the metals present in the sample into approximately 5 broad groups of mineralogical forms based on their behavior when exposed to different solvents.

## References

Morris, David, Patrick G. Allen, John M. Berg, Catherine J. Chisholm-Brause, Steven, D. Conradson, Robert J. Donohoe, Nancy J. Hess, John A. Musgrave, and C. Drew Tait, "Speciation of Uranium in Fernald Soils by Molecular Spectroscopic Methods: Characterization of Untreated Soils," Environ.

U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, "Toxicological Profile for Uranium," 1999.

# Figures

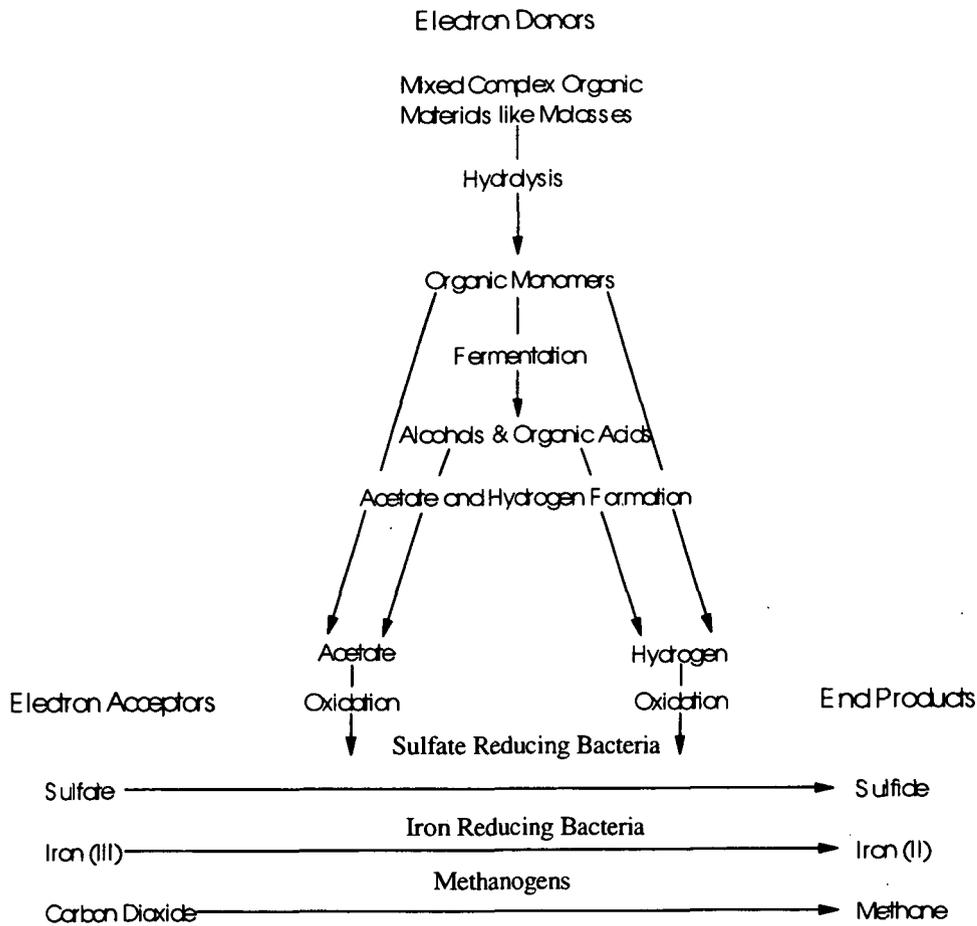


Figure 1. Utilization of Carbohydrates in IRZ

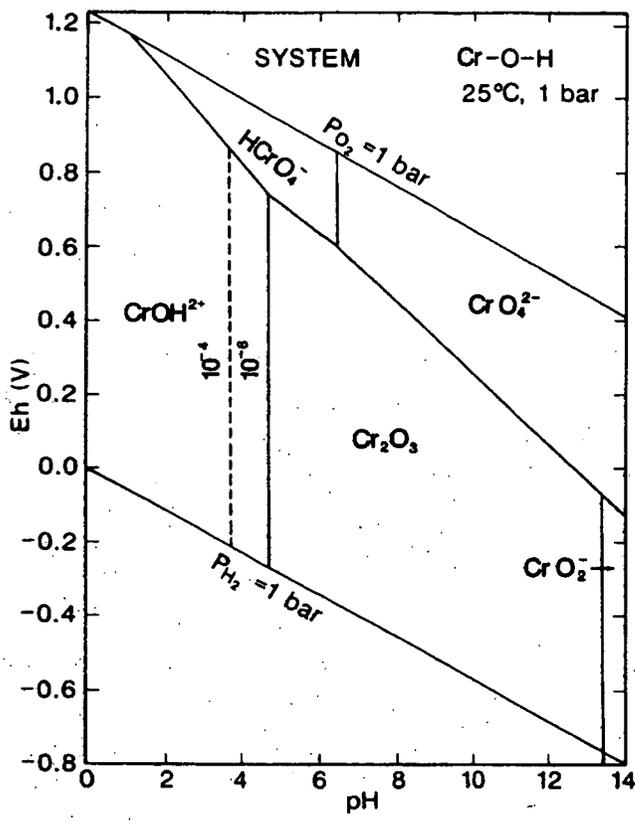


Figure 2. Cr Eh-pH Diagram

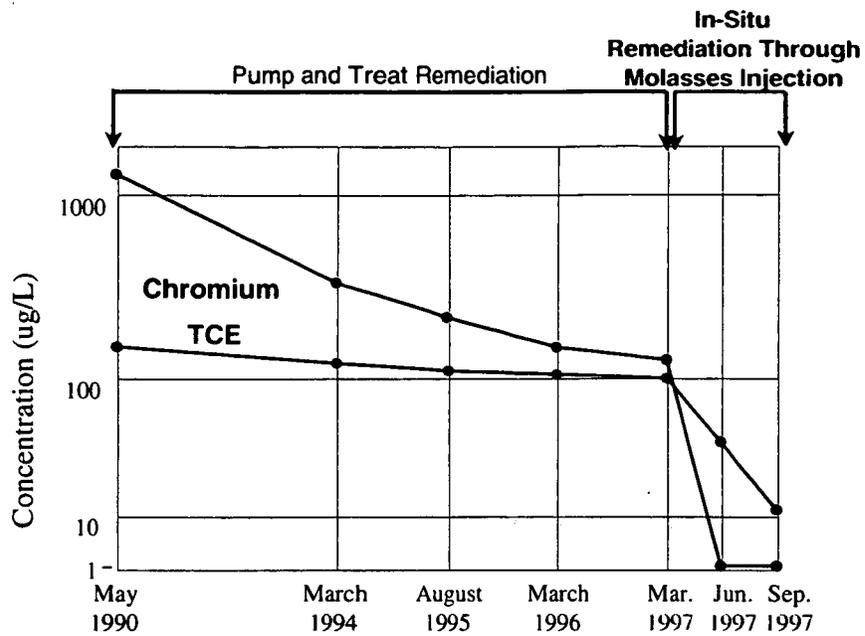


Figure 3. TCE and Chromium Concentrations versus Time (Metal Manufacturing and Plating Facility, Eastern Pennsylvania)

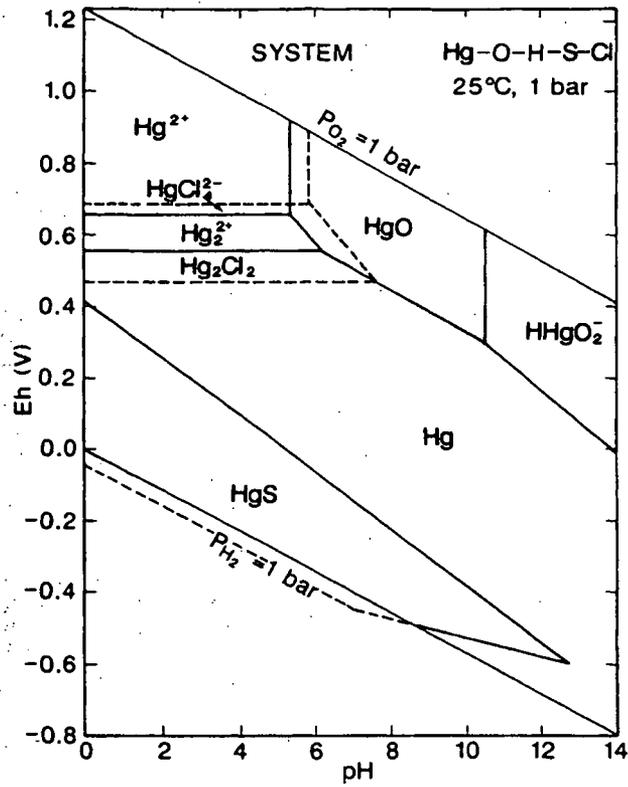


Figure 4. Eh-pH Diagram for the System Hg-O-H-S-Cl

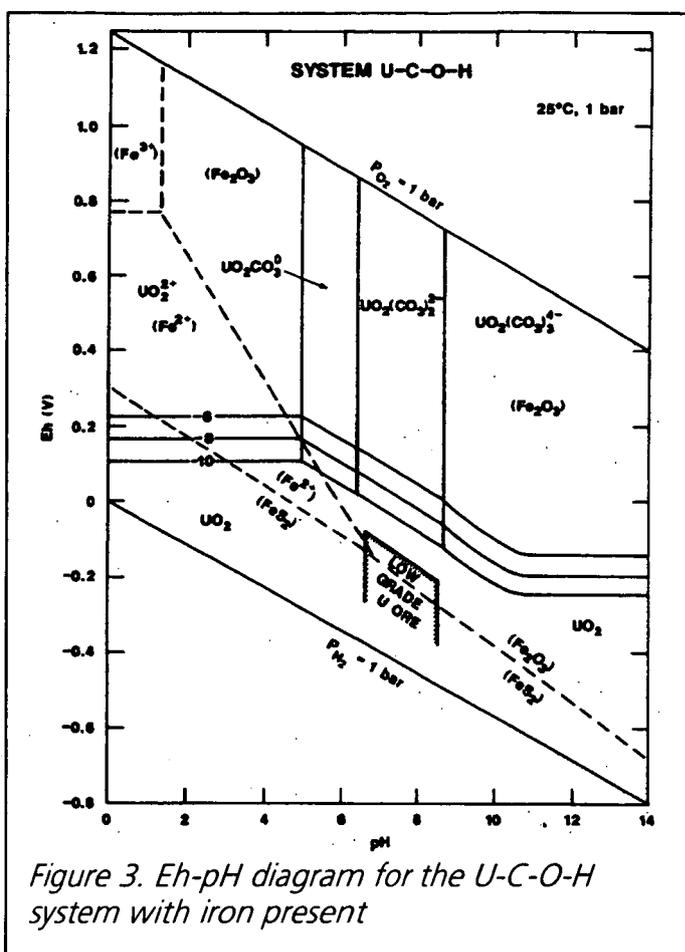


Figure 5. Eh-pH Diagram for Uranium

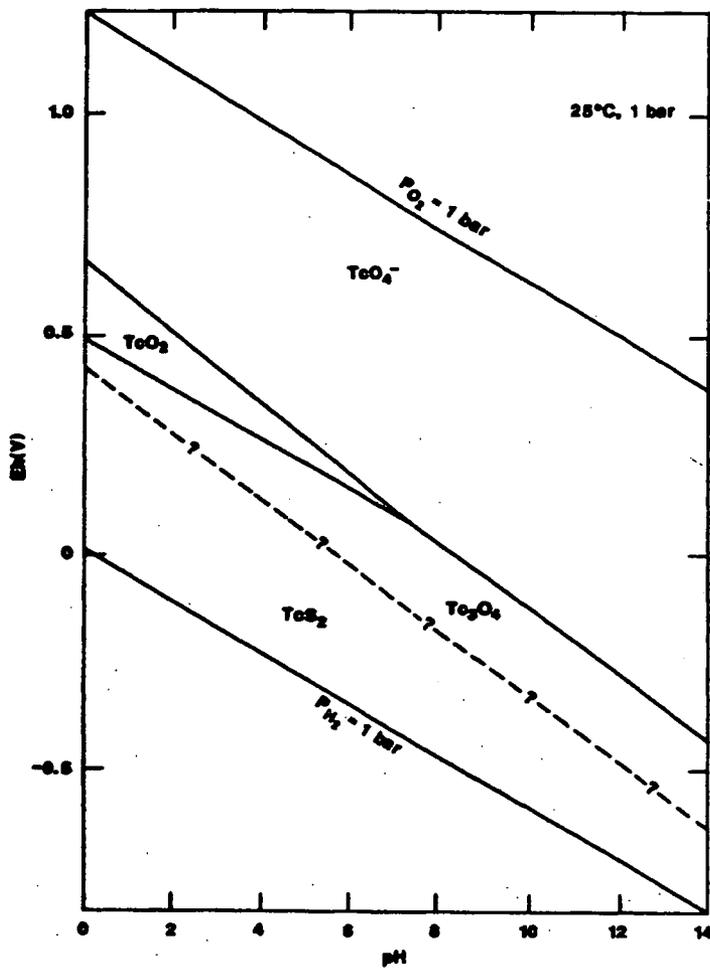
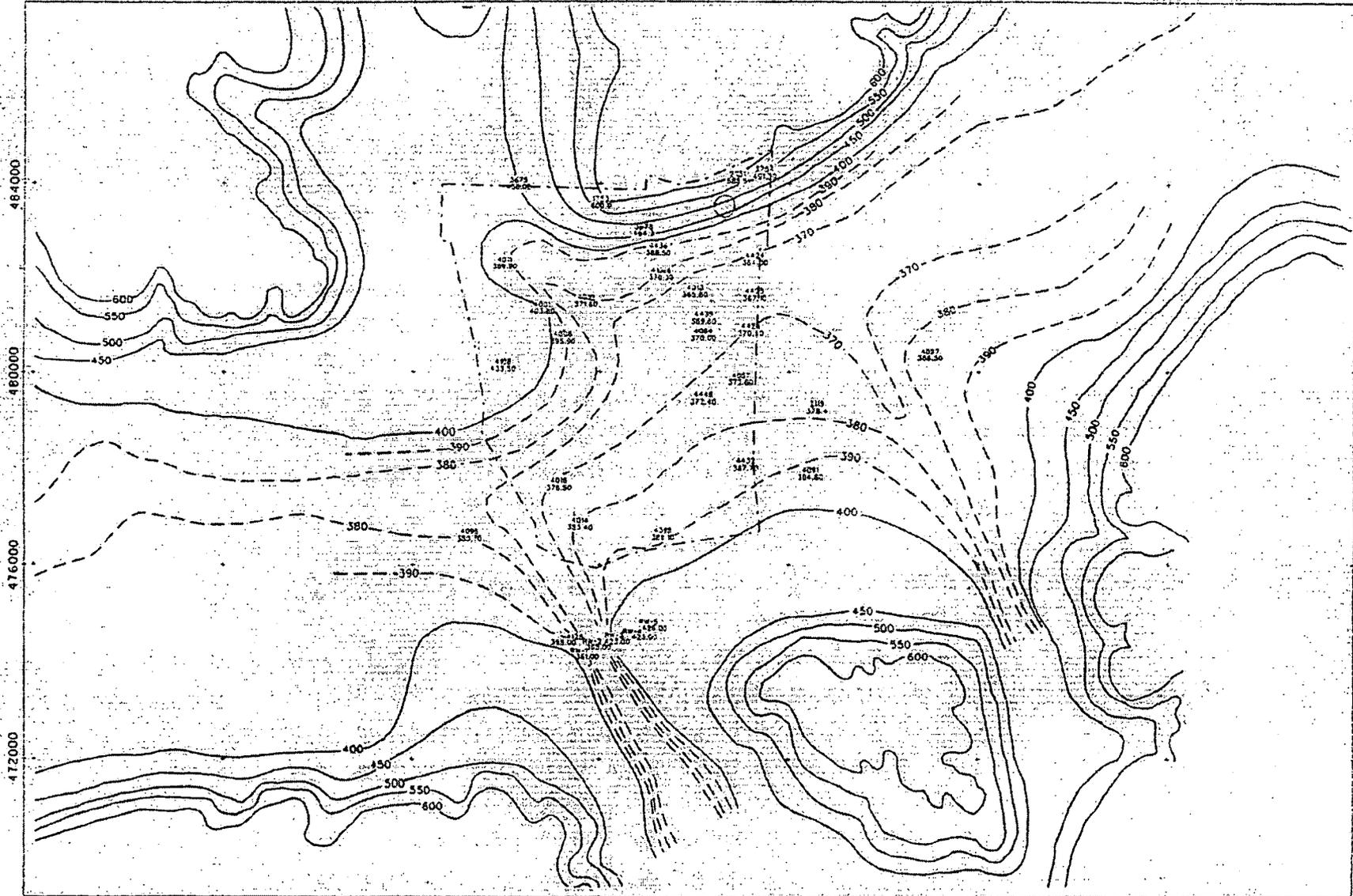


Figure 6. Eh-pH Diagram for the System Tc-S-O-H

1368000 1372000 1376000 1380000 1384000 1388000 1392000

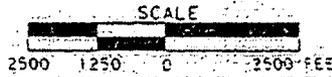


000048

4645

**LEGEND:**

- FEMP BOUNDARY
- - - 10 FOOT BEDROCK CONTOUR (R1/F5 WELL DATA)
- 50 FOOT BEDROCK CONTOUR (WATKINS & SPIEKER, 1971)
- 4296 WELL/BORING NUMBER
- 340.70 BEDROCK ELEVATION



DRAFT  
FINAL

2500 1250 0 2500 FEET  
BEDROCK  
TOPOGRAPHIC SURFACE

Figure 7. Bedrock Topographic Map  
Defining Valley Floor

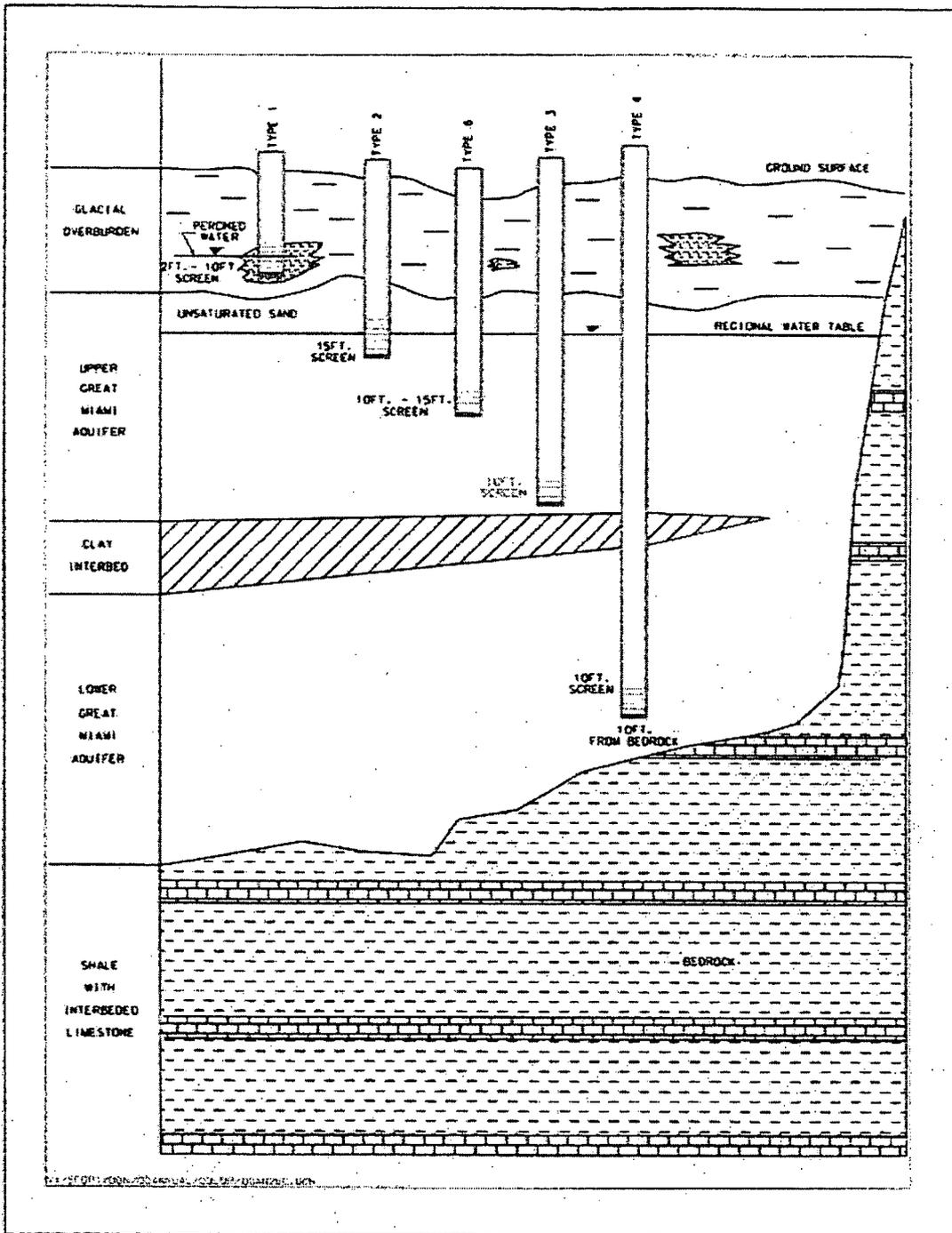


Figure 3-4. Monitoring Well Relative Depths and Screen Locations

Figure 8. Idealized Cross Section

Figure 5-1, Piper Diagram  
Monitoring Well 2015

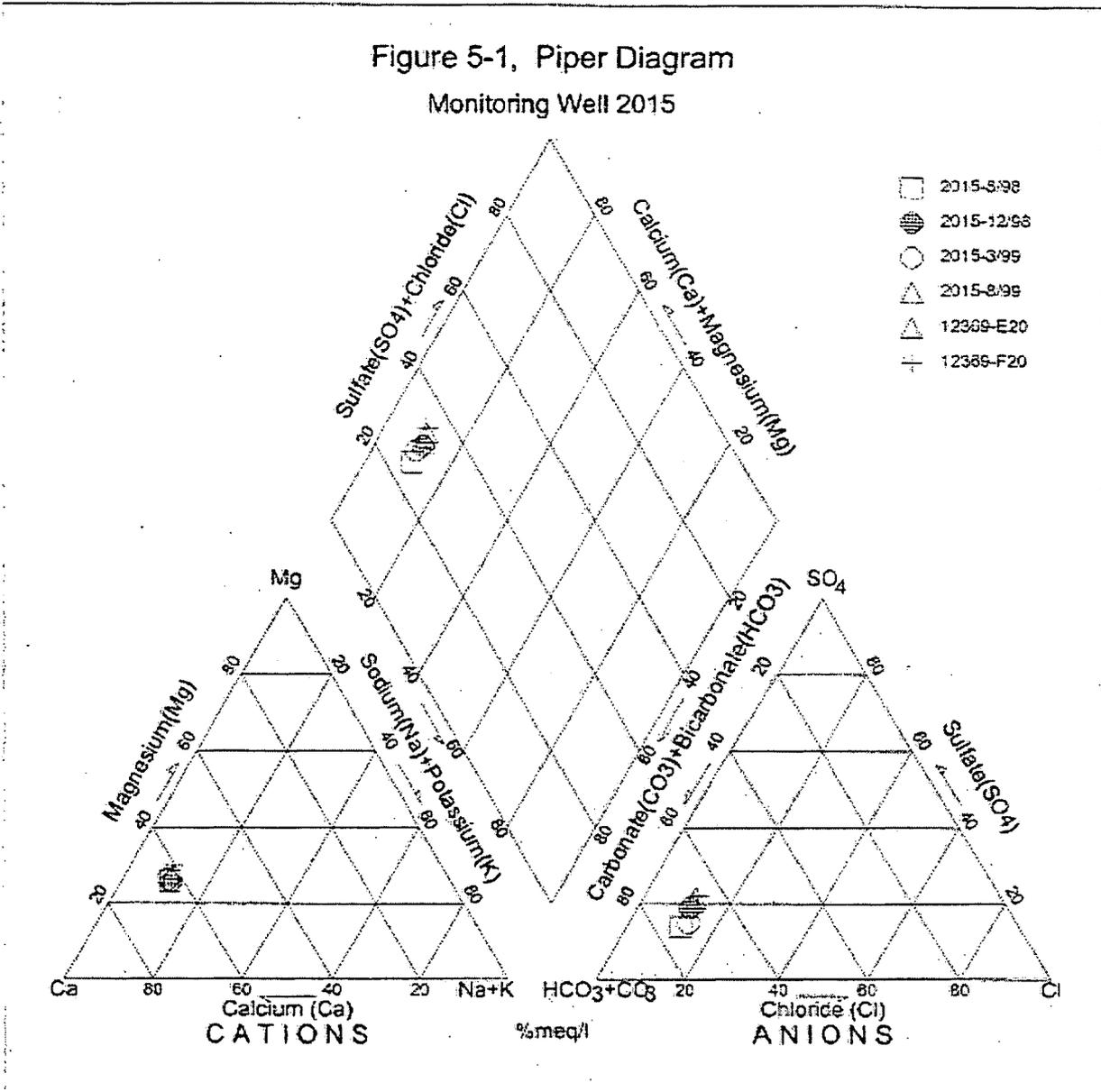
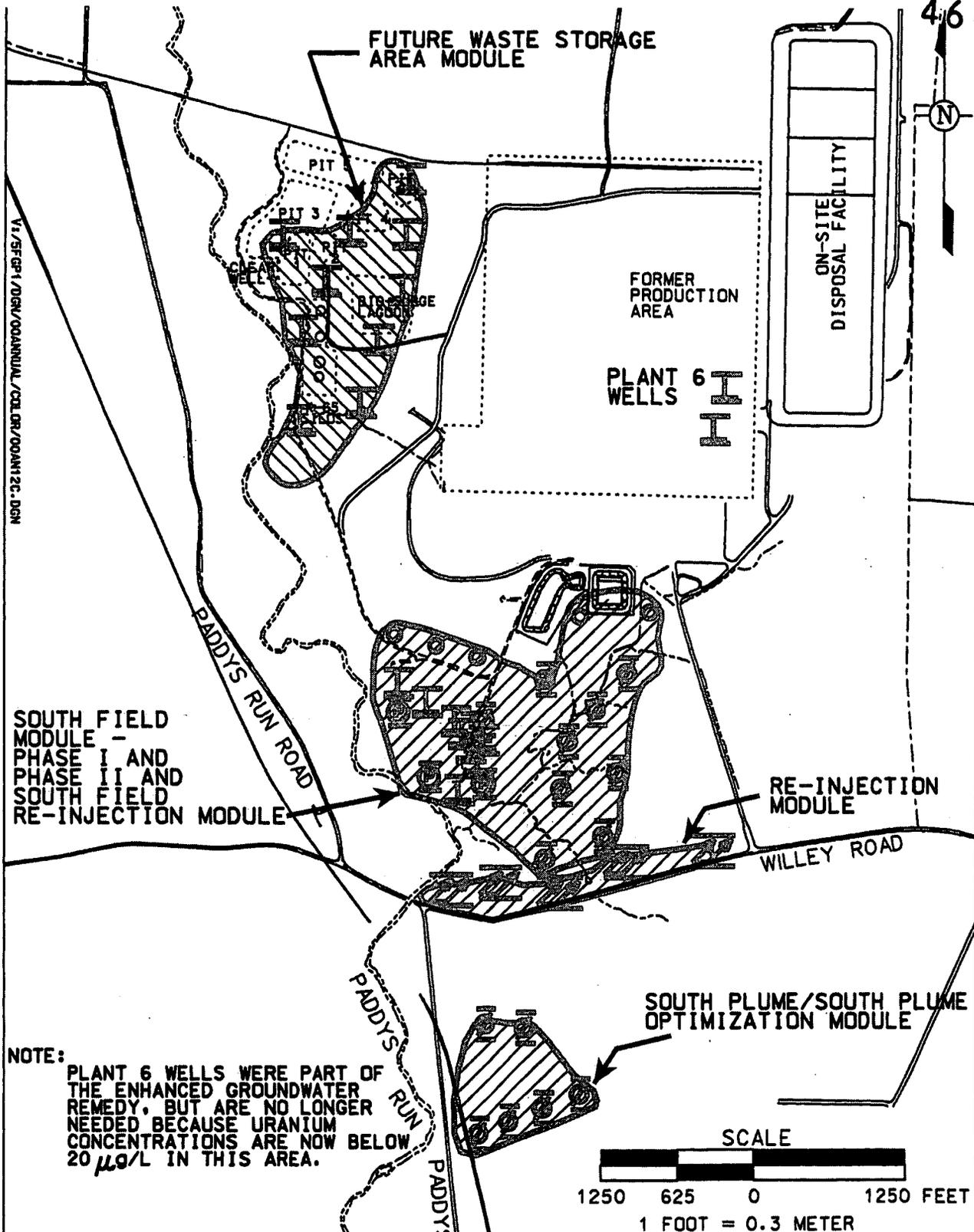


Figure 9: Piper Diagram



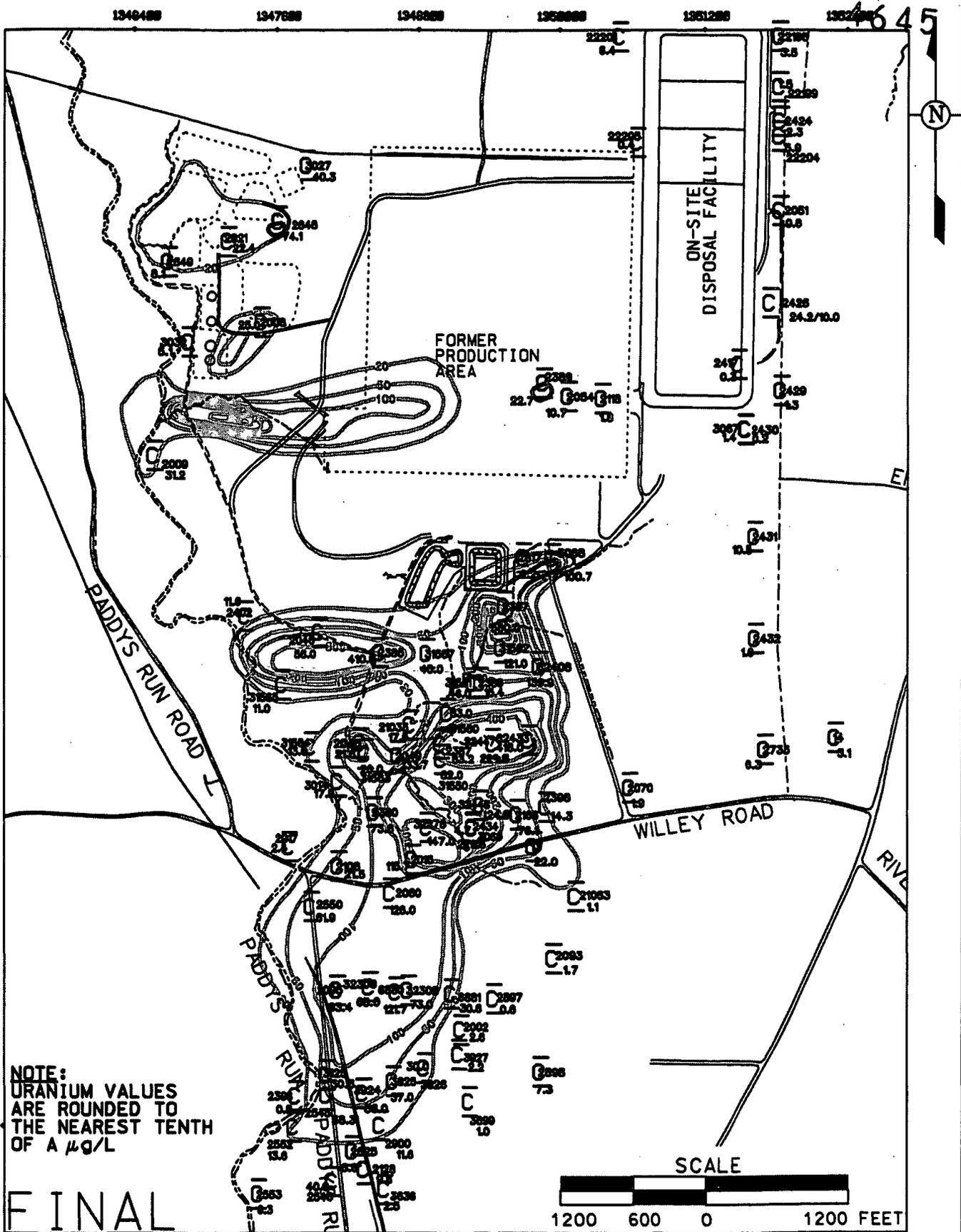
NOTE:  
 PLANT 6 WELLS WERE PART OF THE ENHANCED GROUNDWATER REMEDY, BUT ARE NO LONGER NEEDED BECAUSE URANIUM CONCENTRATIONS ARE NOW BELOW 20  $\mu\text{g}/\text{L}$  IN THIS AREA.

**LEGEND:**

- - - - FEMP BOUNDARY
- ⊕ EXTRACTION WELL
- ⊗ RE-INJECTION WELL
- ⊕⊗ CURRENT EXTRACTION/FUTURE RE-INJECTION WELL
- ▨ FUTURE EXTRACTION WELL
- FUTURE RE-INJECTION WELL
- ▨ CURRENT ACTIVE MODULE AREA
- ▨ FUTURE MODULE AREA
- 20  $\mu\text{g}/\text{L}$  TOTAL URANIUM PLUME FROM FOURTH QUARTER 2000

Figure 10. Location of Pump and Treat System

000051



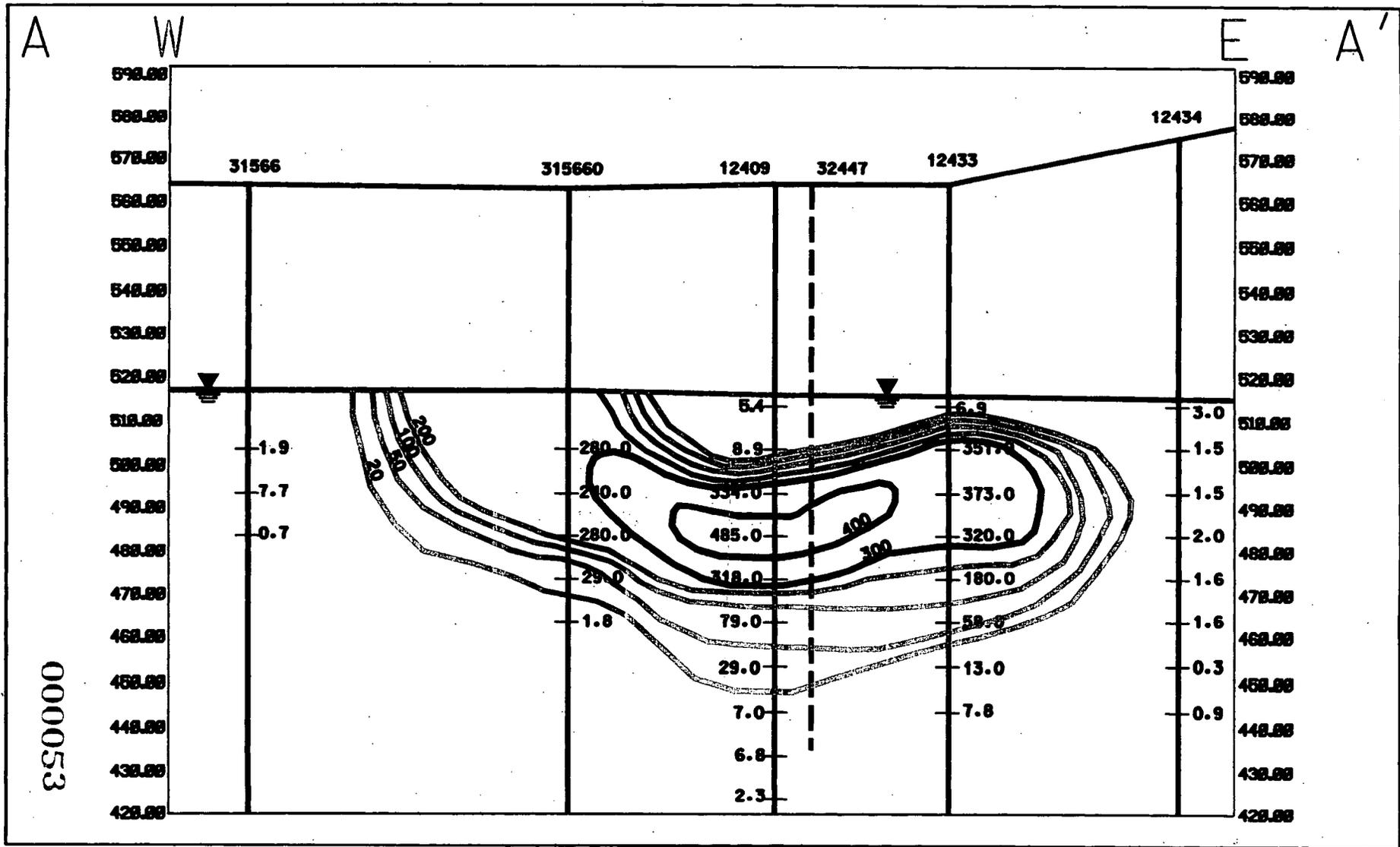
NOTE:  
 URANIUM VALUES  
 ARE ROUNDED TO  
 THE NEAREST TENTH  
 OF A  $\mu\text{g/L}$

FINAL

- LEGEND:**
- MONITORING WELL OR GEOPROBE LOCATION
  - TOTAL URANIUM CONCENTRATION MEASURED IN SECOND QUARTER 2000
  - CONTOUR CHANGES BASED ON NEW MAXIMUM SECOND QUARTER 2000 DATA
  - FEMP BOUNDARY
  - MAX TOTAL URANIUM CONTOUR IN  $\mu\text{g/L}$  FROM BASELINE MODIFIED QUARTERLY
  - 10-YEAR, URANIUM-BASED RESTORATION FOOTPRINT

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Figure 11. Map of Uranium Plume



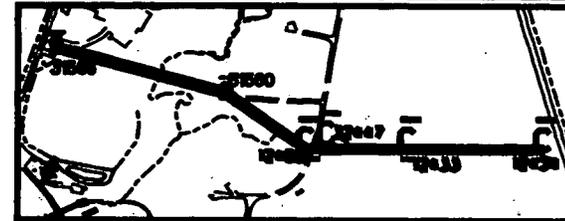
LEGEND:

--- PROPOSED LOCATION FOR WELL 32447

0.7

PROPOSED LOCATION FOR WELL 32447

TOTAL URANIUM IN GROUNDWATER  $\mu\text{g/L}$



000053

DRAFT

STATE PLANAR COORDINATE SYSTEM 1927

DATE

Figure 12. Cross Section of Uranium Plume

4645

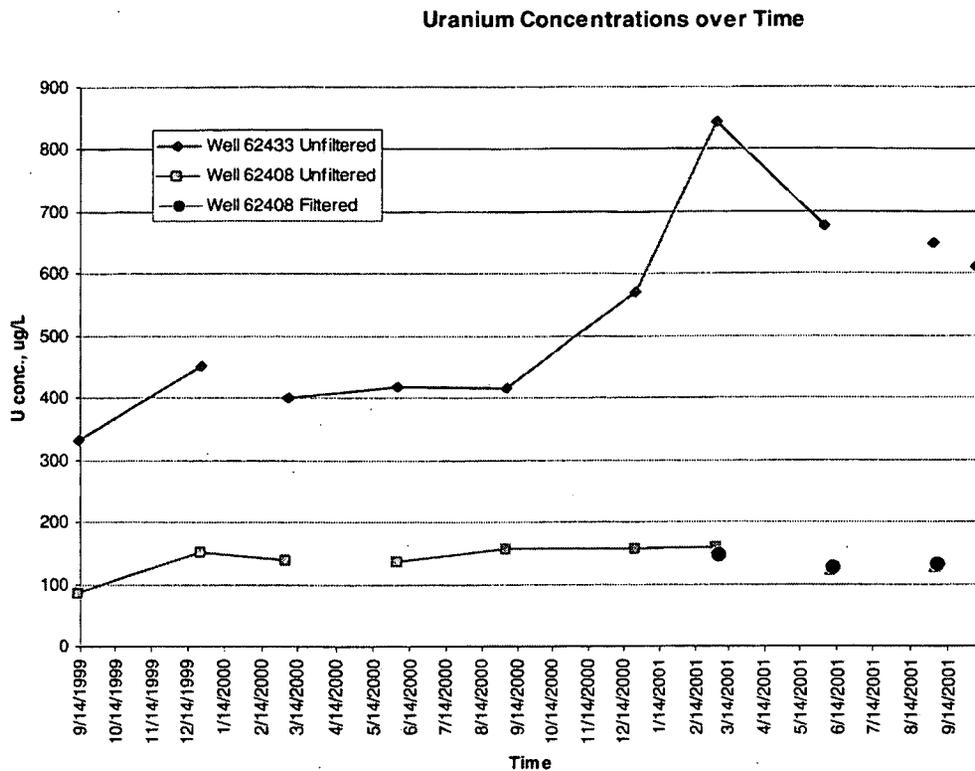


Figure 13. Temporal Trend for the Uranium at Wells 62408 and 62433

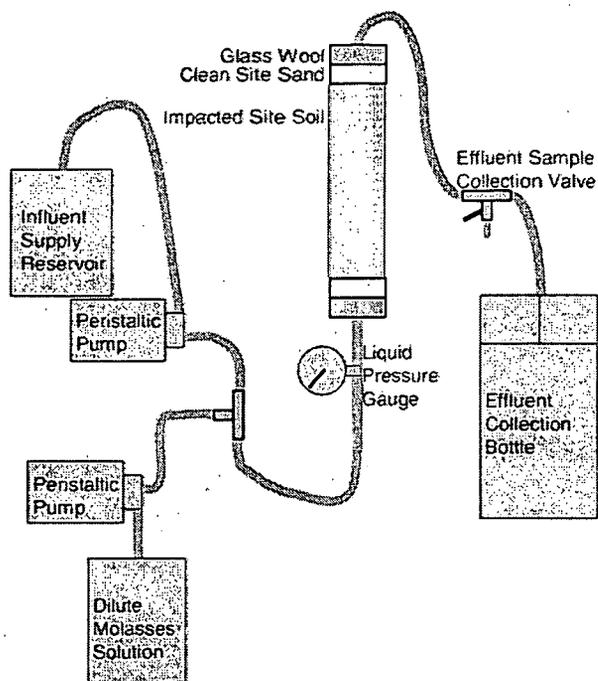


Figure 14. Bench-scale Experimental Setup

Exhibit 8: Uranium Precipitation in Monitor Well 108A from August 2000 to May 2002

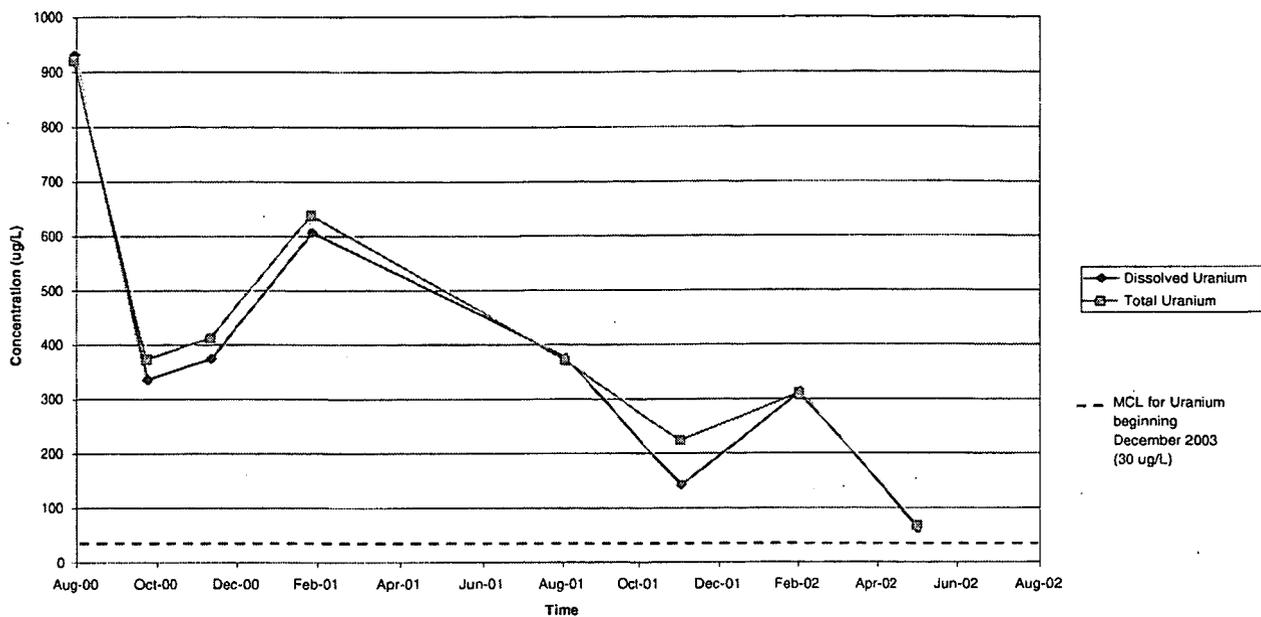


Figure 15: Erwin TN Field Scale Study, Uranium

### Hexavalent Cr Precipitation

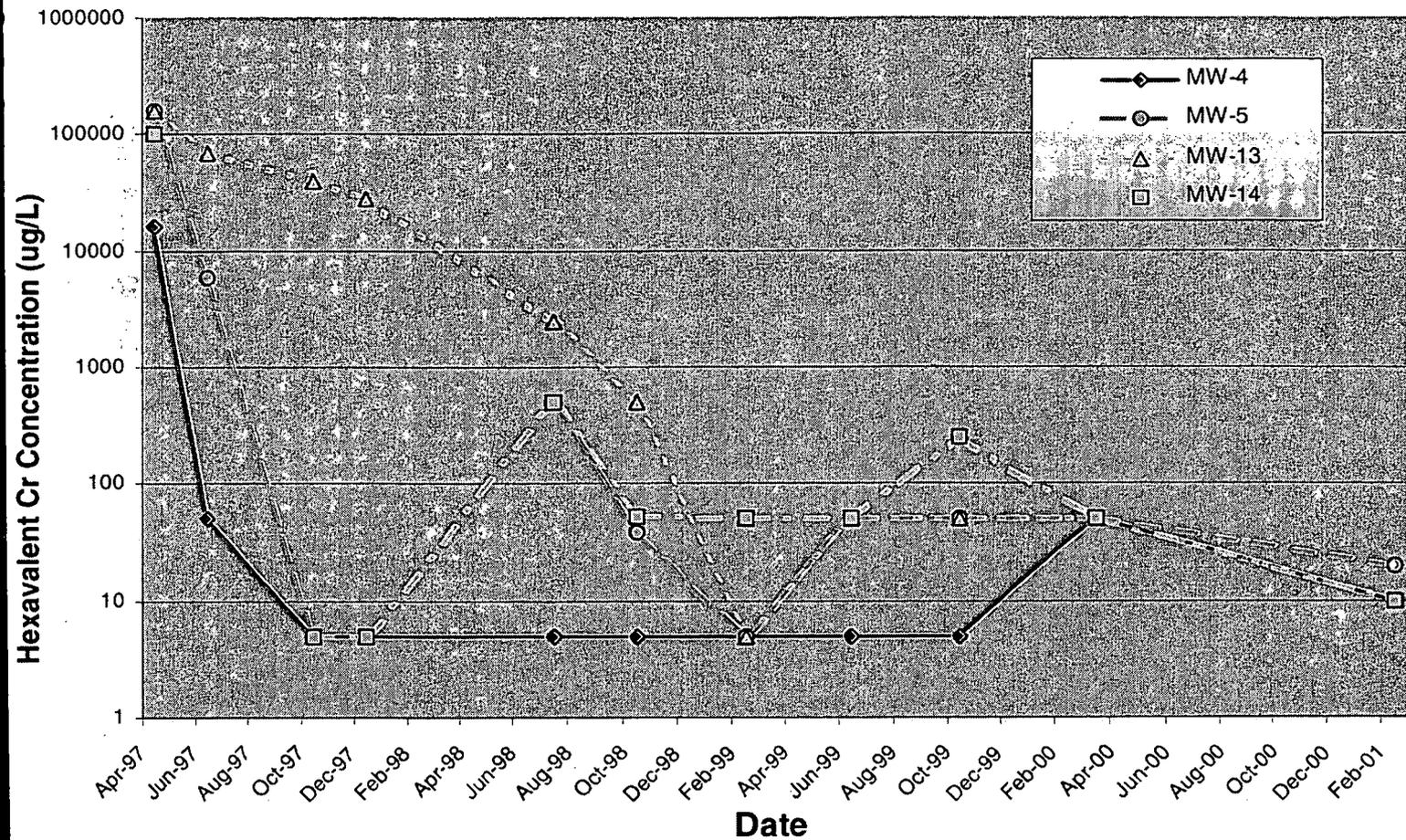


Figure 16: Confidential California Commercial Electroplating Facility – Data Showing Irreversibility of Precipitation Reaction after Treatment