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THE ACTINIDE SOURCE-TERM WASTE TEST PROGRAM (STTP)

Final Report

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VOLUME I

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Technical Requirements for the Actinide Source-Term Waste Test Program (STTP)

I. (a) Technical Requirements: Abstract and Introduction

Abstract

This document defines the technical requirements for a test program designed to measure time-dependent concentrations of actinide elements from contact-handled transuranic (CHTRU) waste immersed in brines similar to those found in the underground workings of the Waste Isolation Pilot Plant (WIPP). This test program will determine the influences of TRU waste constituents on the concentrations of dissolved and suspended actinides relevant to the performance of the WIPP. These influences (which include pH, Eh, completing agents, sorbent phases, and colloidal particles) can affect solubilities and colloidal mobilization of actinides. The test concept involves fully inundating several TRU waste types with simulated WIPP brines in sealed containers and monitoring the concentrations of actinide species in the leachate as a function of time. The results from this program will be used to test numeric models of actinide concentrations derived from laboratory studies. The model is required for WIPP performance assessment with respect to the Environmental Protection Agency's *40 CFR Part 191B.*

Introduction

This document defines the technical rationale and requirements for a test program designed to determine the concentrations of actinides in WIPP brines in contact with transuranic (TRU) wastes. This study is referred to as the Actinide Source-Term Waste Test Program (STTP). The long-term Waste Isolation Pilot Plant (WIPP) performance assessment program requires estimates of the concentrations of plutonium and other radionuclides in disposal rooms that may become partially or completely filled with brine. Once mobilized, these radionuclides may be released to the accessible environment under certain circumstances such as human intrusion into the repository. Actinide source-term data are thus necessary for determining compliance of the repository with Environmental Protection Agency (EPA) *40 CFR 191B* (Marietta et al., 1989).

The STTP will complement laboratory studies of radionuclide chemistry. The Actinide Source-Term laboratory program has previously determined solubilities and sorption coefficients of plutonium and its oxidation state analogs in synthetic brines under various conditions of pH and has examined actinide speciation and measured stability constants for complex ions (Brush, 1990). In addition, the program has measured distribution coefficients for actinides in brines in the presence of suspended bentonite. The current focus of the laboratory program includes chemical equilibrium modeling for dissolution and investigations of colloid stability and kinetics.

The results from these laboratory experiments will allow the development of a predictive numeric model of concentrations of mobile actinides in brine as a function of chemical conditions within the disposal rooms. The principal role of the STTP will be to test the utility of the predictive model by examining the degree to which actinides are mobilized in real TRU waste under repository realistic conditions.

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The goals of both the laboratory and real waste source-term test programs are to develop and evaluate a radionuclide source-term model that will provide a narrower uncertainty range of actinide concentration data to WIPP performance assessment than is currently available from expert judgments using existing data.

In brief, the test concept involves filling test containers with a variety of actual contact-handled (CH) TRU wastes and completely saturating the containers with a mixture of natural and synthetic brines with compositions chemically similar to those of intergranular brines found in the Salado Formation. Container size will depend on waste homogeneity; heterogeneous waste types such as combustibles will use "drum scale" vessels of approximately 250 L volume, while more homogeneous types such as sludges will use "liter scale" test containers of 2-5 L volume. The containers will permit regular sampling of brine and headspace gas. The wastes will be intentionally fortified or "spiked" with actinides to a level that will ensure that concentration measurements will reflect equilibrium conditions and will not be limited by the quantity of actinide in the waste sample. In addition, certain wastes will be spiked with waste constituents that are expected to increase solubility, such as complexing agents, to measure the sensitivity of actinide concentration to these matrix components. The test vessels will also be inoculated with halophilic and halotolerant microbes found in the WIPP underground and on the surface near the WIPP Site. This may identify effects of microbial activity on the mobilization of actinides. Prior to test initiation, the containers will be purged of oxygen to simulate the environment predicted for the WIPP disposal rooms after they have been filled and sealed.

During operation the test environment will be held at constant temperature, again to simulate the conditions of the post-closure WIPP disposal rooms. The test containers will be agitated to promote thorough mixing of the solids with the brine and to keep brine compositions homogeneous. Brine samples will be withdrawn at regular intervals throughout the experiment. The leachate samples will be analyzed to ascertain the chemical and physical form and concentration of actinides dissolved or dispersed in the brine. These experiments are expected to operate for approximately 2-3 years, although individual tests may run longer if trends in the measured actinide concentrations so warrant.

This document describes the rationale for the STTP and uses this rationale to develop and justify a set of test requirements; it specifically excludes discussion of detailed testing procedures. The requirements described in this document will be used to develop specific experimental requirements and procedures included in a separate Test Plan. This Test Plan will be written by Los Alamos National Laboratory (LANL), the facility chosen to perform these tests. It should be noted that information generated from the laboratory program, the modeling program or the STTP may require reconsidering one or more of the requirements stated in this document. Any changes in test requirements will be discussed with both LANL and the Department of Energy (DOE) WIPP Project Integration Office. If new or changed requirements result in no significant impacts in budget or schedule, they will be documented and implemented. LANL and Sandia National Laboratories (SNL) will discuss any changes causing significant budget or schedule impact with the WIPP Project Integration Office Change Control Board prior to implementation.

I. (b) Test Rationale

The WIPP performance assessment must evaluate compliance of the WIPP with *40 CFR 191B* from the end of the operational phase of the facility through the following 10,000 years. This regulation limits the amount of radioactivity that may be unintentionally released into the accessible environment during the post-closure phase. US EPA (1985) defines allowable releases over 10,000 years, normalized as a function of TRU inventory. The WIPP performance assessment is requited to consider the possibility of inadvertent human intrusion into the repository, and EPA *40 CFR 191B* permits the assumption that the intrusion rate does not exceed 30 boreholes/(km^2 • 10000 y) (WPD, 1991b). Future performance assessment estimates of intrusion rate may be time dependent and possibly less than this maximum rate. The probability of accidental release of radioactivity equal to the release limit must not exceed 0.10, and the probability of a release of up to 10 times the release limit must not exceed 0.001.

There are three possible mechanisms of radionuclide release: direct release of solids by drilling intrusion, release of volatile radionuclides (e.g., ^{14}C, ^{85}Kr, ^{222}Rn), and release through mobilization in local groundwater. Release of solids can occur through borehole erosion and transport of cuttings and drilling muds to the surface and includes 0 particulates suspended in brine that are neither dissolved nDr considered colloidal, These mechanisms will not be considered in the source-term program, though they dominate some parts of release in the human intrusion event. Volatile radionuclides are expected to be a minor component of release, as the only volatile isotope present in significant quantity in a TRU repository will be ^{222}Rn. Due to its short half-life the inventory of this isotope will be quite low, and due to its low solubility in brine its impact on the source-term will be negligible.

The Actinide Source-Term Program (modeling, laboratory studies, and real-waste tests) considers radionuclide release through mobilization in groundwater. Release of radionuclides by groundwater transport is possible due to the presence of brine in the Salado Formation, which surrounds the WIPP disposal rooms. Recent performance assessment calculations (WPD, 1991a) indicate this brine can be released into the accessible environment through human intrusion. If this occurs, contaminated Salado brine can enter the Culebra member of the Rustler Formation, which overlies the Salado and contains mobile groundwater. This contaminated Culebra water could be brought to the surface through wells used for watering livestock or for irrigation. Total release will depend on the concentration of radionuclides in Salado brines, the degree to which they can be dissolved or suspended in Culebra brines, the physical and chemical retardation they experience in the Culebra, and the activity of the cuttings brought directly to the surface.

Salado brine can enter the disposal rooms at a rate that depends on the permeability of the surrounding rock and the pressure inside the disposal rooms. Brine from reservoirs in the Castile can also fill the disposal rooms if intrusions through the WIPP penetrate into the Castile. In the most severe intrusion event, the double-borehole (E1E2) scenario, brine from the Castile is released into the rooms, travels through a portion of the repository, and is released to the Culebra via a second borehole.

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This scenario maximizes the interaction of brine with the waste, and in such an event the amount of radioactivity brought to the Culebra will strongly depend on the quantity of the principal radioactive elements in the WIPP inventory that can be dissolved or colloidally suspended in Salado brine.

The concentration of a particular radionuclide in brine within the disposal rooms will be limited either by the amount present in the disposal rooms or by its maximum possible concentration in brine. The radioisotopes of interest in a release scenario are those present in TRU waste and their daughters. Some of these decay products (e.g., ^{226}Ra) will be present in such small quantity that their release will be controlled by inventory alone; i.e., it can be assumed that all of the radioisotope dissolves. For *the* eight actinide isotopes that dominate the radioactivity of TRU waste, however, release will be controlled by the degree to which they can be dissolved or suspended. These isotopes are ^{239}Pu, ^{241}Am, ^{238}Pu, ^{240}Pu, ^{237}Np, ^{234}U, ^{233}U, and ^{230}Th* (Helton et al., 1992). At early times, the bulk of the activity Comes from Pu (^{238}Pu and ^{239}Pu) and ^{241}Am. However, other actinide isotopes come into play during the 10,000 year post-operational phase. The inventories of ^{234}U and ^{230}Th increase as ^{238}Pu decays (99.95% conversion to ^{234}U after 1000 years), and significant quantities of ^{237}Np result from alpha-decay of ^{241}Am (ca. 75% complete after 1000 years). Therefore, to ascertain compliance with *40 CFR 191B, WIPP* performance assessment requires estimates of the concentrations of Th, U, Np, Pu, and Am in Salado brine in contact with TRU waste under disposal room conditions.

It is not possible to predict a single value for the concentration of a given actinide in the disposal rooms. This is principally due to the variety of chemical conditions that can exist within the rooms and the fact that these conditions can vary with time and from room to room. However, such predictive power is not required because *40 CFR 191B* is a probabilistic rather than deterministic standard. Instead, a cumulative distribution function is defined for the range of possible concentrations of a particular actinide. Such a function assigns probabilities that the concentration of the actinide will be found below a certain value. This has previously been done by an expert panel elicitation using published values for actinide solubilities, which do not currently include data for brines. Using this process, the estimated concentration range of a cumulative distribution for an actinide depends on the quality of the data used. Currently, the range for Pu (as PuO_2^+) extends from 10^{-17} to 10^{-3} M or 14 orders of magnitude. The range for Am (as $AmCl_2^+$) extends from 10^{-14} to 1 M (Trauth et al., 1991). The upper concentration values and their probabilities are the parameters of greatest concern to Performance Assessment.

The test criteria in this document reflect the intent of the program to analyze the effects of various waste constituents on actinide concentrations in brines. Three independent processes are cumulatively responsible for the quantity of actinides that can be supported in the aqueous phase. These processes are dissolution/precipitation, sorption/desorption and colloid formation/destruction reactions.

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*The decay series that produce the non - TRU elements is: $^{238}\text{Pu} \rightarrow {}^{234}\text{U}, \alpha \rightarrow {}^{230}\text{Th}, \alpha$ and $^{241}\text{Am} \rightarrow {}^{237}\text{Np}, \alpha \rightarrow {}^{233}\text{Pa}, \alpha \rightarrow {}^{233}\text{U}, \beta$.

The test matrix is designed to identify influences or factors within the wastes that can participate in or influence these reactions. To adequately test a chemical model of the disposal room based on data obtained in the laboratory, it will be necessary to sample test conditions that represent all major influences on actinide mobilization. Given a matrix of reasonable scope and a finite test duration, it may not be possible to access all chemical environments that can be tested in the laboratory. However, this is not essential to testing a laboratory data-based model, which is the principal goal of the source-term test program.

Influences on Actinide Mobility

Disposal room characteristics that may influence actinide mobility include:

1. **pH.** Particularly high or low hydrogen ion activities may increase actinide solubilities by stabilizing cationic or anionic species in solution. pH may also affect actinide concentrations by altering the properties of sorbing or complexing agents present in the waste. For example, the complexing or chelating agents expected in the waste matrix are generally more effective at higher pH values. This is because ligands containing acidic functional groups (e.g., ethylenediarninetetraacetic acid [EDTA], citric acid) will be in their basic or anionic form under these conditions, enhancing their affinities for metal ions. It should be noted that the STTP will measure hydrogen ion concentration (pcH) rather than activity (pH) due to difficulties in measuring pH in brines.

2. **Eh (oxidation potential).** Changes in solution Eh (e.g., through radiolysis, anoxic corrosion, microbiological activity, etc.) may increase plutonium solubility relative to that of the very insoluble (IV) oxidation state by oxidizing or reducing the actinide to the more soluble (VI) or (III) states, respectively. The Eh-pH (or Pourbaix) diagram in Figure 1 shows the principal species of Pu produced by hydrolysis, and the conditions under which these species are stable. Active metals in the native state, such as Al or Fe, may reduce Pu to the more soluble (III) state. Alpha-radiolysis can produce highly oxidizing species in brines such as hypochlorite ion. Because the H_2 gas that is also produced is largely inert, the effect of alpha-radiolysis is to render brines more oxic. This can increase the system Eh and possibly oxidize early actinides to the more soluble (VI) state. This effect may be countered by oxic corrosion of steel. Figure 2 shows how various regions of Eh-pH space may be reached depending on the chemical processes dominant in the waste at a given location and time. Measurements of Eh in complex aqueous systems such as the brine leachates that will be studied in the STTP are difficult to interpret and depend on the electrochemical couple whose potential electromagnetic force (EMF) is being measured. This is due to variations in kinetic barriers among reduction oxidation (redox) equilibria, which are manifested as differences between "true" (thermodynamically reversible) and measured EMFs. The measure of Eh most relevant here is Pu speciation, but determining Pu oxidation states in brines is difficult.

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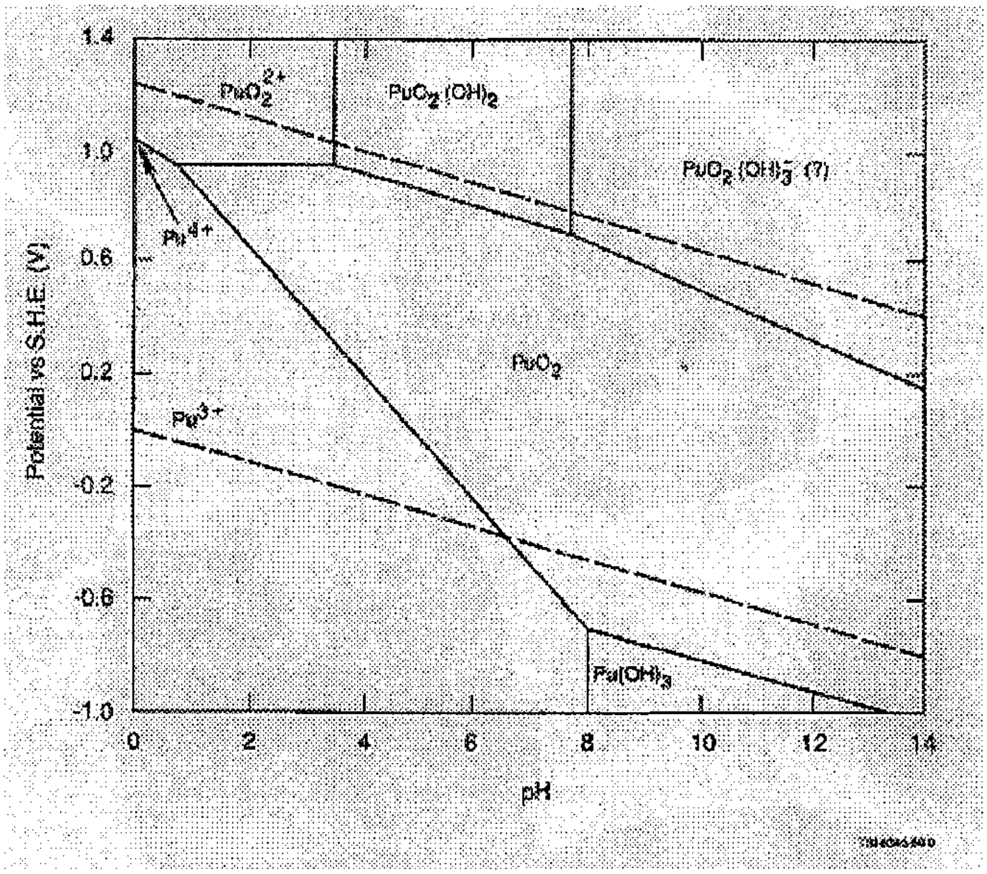

Figure 1.

Oxidation potential (Eh) vs. pH phase diagram for Pu in H_2O at 298 K (Baes and Mesmer, 1976, in turn from data of Silver, 1971). Dashed upper and lower lines represent equilibrium with 1 atm O_2 and H_2, respectively, and thus the stability limits of water under ambient conditions. Note that brine may affect Pu speciation, and that Pu(V), which is unstable with respect to disproportionation in water at high concentrations, may be present in significant quantity at low Pu concentrations.

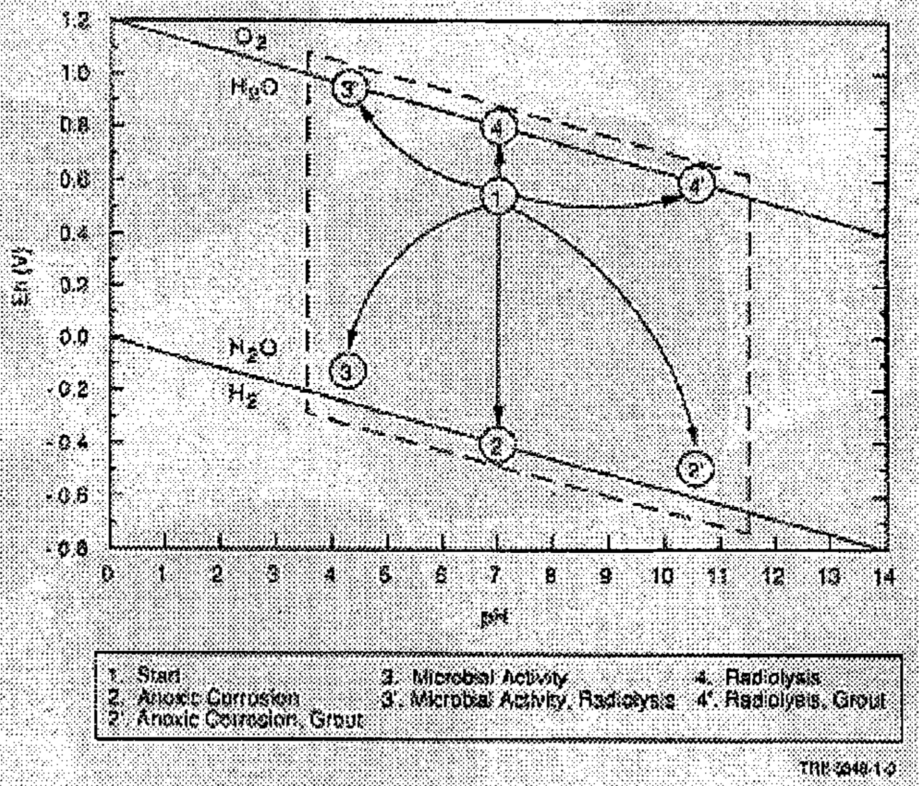

Figure 2.

Possible excursions and eventual conditions of disposal rooms in Eh/pH space. Figure courtesy of L.H. Brush.

3. **The presence of complexing agents.** Large quantities of complexing and chelating agents (such as EDTA) could increase the amount of actinides in the liquid phase. If significant microbial activity occurs in the waste-brine system, chelating agents may also be produced by the biodegradation of organic material, e.g., α-hydroxy carboxylic acids such as lactic and citric acid (Caldwell et al., 1988). A list of chelating and complexing agents that may significantly influence actinide concentrations in aqueous systems and are assumed to be present in TRU waste based upon process knowledge is given under "Conditions of Test Containers" in this section. Carbonate may actually be the most important ligand in the disposal rooms (aside from aquo or hydroxyl ligands resulting from hydrolysis) if it is present in high concentrations in intergranular brines, or if significant quantities of CO_2 are generated by microbial activity. A high CO_2 fugacity reduces pH and affects actinide speciation in solution as well as the composition of actinide-containing solid phases (e.g., forming carbonates from hydroxides). These effects have the potential of either increasing or decreasing solubility.

4. **The presence of sorbents.** Sorption of actinides occurs when dissolved, positively charged actinide ions become bound to negatively charged surface sites on solids such as clays. The sorbed actinide ions will equilibrate with solution phase ions in much the same way that solid phase actinide oxides or salts equilibrate with dissolved actinides. Sorption will tend to reduce solution phase actinide concentrations, assuming that no actinide-containing solids (other than the sorbents) are present. Sorption will tend to be less efficient under conditions favoring higher actinide concentrations. Sorp6ve capacity will also vary with pH and concentrations of other ions in the brines (such as Al are Fe) that can compete with actinide ions for surface sites.

5. **The formation or colloidal suspensions.** Mobile colloids may adsorb actinides by providing surface sites on which actinide species may be sorbed. These colloidal host particulates (termed carrier colloids or pseudocolloids) may be generated from native clays, backfills, sorbents packed in the waste containers, and from corrosion of iron. The term "colloid" is taken here to include polynuclear actinide species formed by condensation, in which colloidal actinide oxide hydrates (eigencolloids) may result from arrested precipitation of hydrous oxides, particularly $PuO_2 \bullet nH_2O$ (Ockenden and Welch, 1956).

   These factors form a five-dimensional parameter space that ideally defines a unique value of actinide concentration for a given set of assumptions about disposal room conditions. The range of possible actinide concentrations In the WIPP disposal rooms is thus determined by the range of conditions accessible within the parameter space. Ultimately, the concentration of each actinide should have a unique value at a given set of conditions once the disposal rooms reach chemical equilibrium. It is not possible to guarantee, however, that the waste-brine system will reach true equilibrium within the life of the STTP experiments or even over the 10,000 year post-disposal period.

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The test matrix attempts to account for certain perturbations to equilibrium such as high levels of radiolysis (which transiently increase Eh) and the chemical state of actinides in the waste (which can either increase or decrease apparent solubility) by providing experimental controls that either isolate the perturbation or cause the system to reach a steady state within the duration of the STTP. These controls are discussed in greater detail under "Test Matrix" in this section.

Relationship to Laboratory Program

The actinide source-term laboratory program provides data that will be used to develop a numeric model of actinide solubility and suspension in the Salado that accounts for the effects of various chemical influences present in the scaled disposal rooms. These influences include those that affect actinide speciation (pH, Eh, complexation), as well as sorption and colloid formation. With laboratory data it is possible, in principle, to arrive at a source-term model that allows calculation of the concentration of an actinide at any selected point in parameter space.

The actinide source-term model may consist of components for dissolution, sorption, complexation, and colloidal suspension. A numeric model for the solubilities of actinides in brine is being developed concurrently with the STTP. This model is based on the Pitzer activity model (see Pitzer, 1991) for concentrated saline systems and has been successful in predicting actinide solubilities in brines (Felmy et al., 1989; Roy et al., 1992). The equilibrium component of the Actinide Source-Term Model will describe solubilities of actinide-containing solid phases and the effects of complexing agents, both inorganic and organic, on these solubilities. Another component of the model will describe the formation and persistence of colloids. Several computer codes that use the Pitzer activity model are available, such as EQ3/6 (Wolery, 1979) and PHRQPITZ (Plummer et al., 1988). The data bases associated with these codes are not sufficient to model actinides in brines, but the necessary mathematics are included. The primary need in this area is data with which to parameterize the model, not model development. The mathematical form that a description of colloids will require is less clear and remains to be elucidated from laboratory data. It is unlikely that modules for calculating the influence of colloids on actinide concentrations will be added to existing codes.

Chemical equilibrium has not been assumed for the formation and persistence of colloids. Concentrations of colloidal forms of minerals, organics, and actinide (principally Pu) compounds will be measured in laboratory studies and the STTP. The stabilities of these colloids will also be measured for the expected ranges of ionic strength, pH, and other chemical variables in the pertinent waste-brine-rock systems. Chemical equilibrium has been assumed for adsorption of actinides onto mineral and organic colloids.

The principal objective of the STTP is to test the predictive utility of a numeric model using concentration data obtained from real TRU wastes subjected to conditions anticipated in the disposal rooms.

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The STTP is thus designed to complement the laboratory studies by supplying actinide concentration data along with information about chemical conditions present in the wastes and will test the numeric model using real wastes under conditions similar to those attained in the post-disposal phase.

An important caveat in this strategy is that although the STTP will sample actinide concentrations in subsets of parameter space that ought to resemble conditions of the disposal rooms, it is not possible to measure concentrations under truly authentic repository conditions. These conditions will evolve over hundreds of years, and it is not possible (or useful) to authoritatively predict a set of conditions at any given time in the post-disposal phase. This is why the source-term tests will be more useful for testing a source-term model than for directly predicting disposal room actinide concentrations.

It should be noted that other real waste test strategies exist that would deliver actinide concentration data to performance assessment directly. These include testing waste that is chemically representative of TRU waste in the DOE inventory and using waste types that would yield bounding values of actinide concentrations in the disposal rooms. This representative strategy fails because there is no way to identify any existing or synthetic waste that is statistically representative of the actinide source-term for future waste. The bounding strategy was initially considered for this test program, but due to the greater number of test conditions it must incorporate, this strategy requires a much larger test matrix and adds significant cost. It suffers, as does the current strategy, from inability to measure actinide concentrations under long-term disposal room conditions, but because the data from such a program would be directly used for performance assessment rather than used to evaluate a model, this flaw is much more serious. This does not rule out directly using data collected by the current test program for performance assessment, particularly if actinide concentrations remain at odds with model predictions or if they exceed the limits predicted by the model or the expert panel.

The laboratory studies of radionuclide chemistry and the source-term tests are viewed as complementary. It is useful to illustrate how they differ technically and programmatically by discussing tradeoffs between the two programs. The advantages of the laboratory program (vs. the STTP) are that test conditions are subject to greater control, allowing actinide mobilization mechanisms to be tested individually, and that actinide concentrations may be measured over a wide range of test conditions. These features allow one to construct a numeric source-term model from laboratory data. In addition, these data will be far less expensive than those collected by the STTP. However, the laboratory program is limited by its inability to test the numeric model with data from real wastes, which is scientifically desirable and significantly enhances the credibility of the model.

The principal advantage of the STTP is that it will measure actinide concentrations from real TRU wastes under repository-realistic conditions. This allows the program to collectively evaluate synergistic and/or antagonistic mechanisms of actinide mobilization, testing the numeric model developed by the laboratory program. A limitation of the STTP is that due to the short

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time-scale on which the tests are run (compared with the 10,000 years over which *40 CFR 191B* is applicable), it cannot test all conditions possible in the disposal rooms. In addition, some conditions that influence actinide concentrations are not readily subject to control prior to testing and instead must be measured, adding to the cost of the experiments.

Conditions of the Disposal Rooms

It is expected that the disposal room conditions will be anoxic in the long term due to consumption of oxygen by aerobic bacteria and possibly corrosion of steel, though some local microenvironments may be oxic due to radiolysis. Both aerobic and anaerobic bacteria will be present, though their ability to metabolize waste components is not presently known or assumed. The quantity of brine in the rooms will depend on inflow rates, room gas pressures, and whether human intrusion releases Castile brine into the rooms, and will be limited by the extremes of humid and inundated rooms. The rooms will also contain actinides, and most of the activity will be from ^{239}Pu (and, at early times, from ^{241}Am).

Possible conditions in Eh-pH space through which the disposal rooms may trend are shown in Figure 2. In general, anoxic corrosion and radiolysis compete to decrease or increase Eh, respectively. Microbial activity will generally render brine more acidic, and cement or grout will tend to increase pH. The range of attainable Eh-pH space is limited by the acidities (pK_as) of organic acids produced by the microbes, the basicity of the cement or grout in the waste or backfill (if any), CO_2 fugacity in the rooms, and the upper and lower stability limits of water (with some allowance for overpotentials, shown as dashed lines on Figure 1). A difficulty with both measuring EMFs of and constructing speciation diagrams for reactions involving the formation and cleavage of metal oxygen bonds (e.g., actinyl ions) is that such reactions are thermodynamically irreversible and that in most systems speciation as a function of Eh is controlled by kinetics. To illustrate, the speciation diagram in Figure 1 represents equilibrium states of Pu as a function of Eh and pH, and while it indicates that acidic and reducing conditions favor Pu(III), it does not imply that all Pu will be in the +3 state at, for example, an Eh of 0.0 V and a pH of 3. In certain circumstances microbes can effectively serve as redox. catalysts (Francis, 1990).

Halophilic and halotolerant bacteria have been identified in brines collected from the WIPP underground workings, and these microbial colonies can use cellulosic materials (which constitute a significant fraction of the total volume of TRU waste) as substrates for growth under both aerobic and anaerobic conditions. There are four major microbe-mediated processes that can take place in the disposal rooms after closure. First, fermentation can disproportionate polysaccharides (such as cellulose) into, among other species, alcohols, organic acids, and carbon dioxide. Denitrification can oxidize the organic products into α-hydroxycarboxylic acids (such as lactic and citric acid) while reducing nitrate ion to N_2 or NH_3. Sulfate reduction can further oxidize these acids to CO_2 while reducing sulfate to H_2S. Finally, methanogenesis can reduce CO_2 to methane (CH_4) in the presence of excess H_2 (which may be generated in the disposal rooms by anoxic corrosion of steel and radiolysis of brine or organic waste materials).

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Microbial activity can affect actinide concentrations by causing changes in system pH and Eh, and producing chelating agents. Halophilic and halotolerant anaerobic bacteria may serve as redox catalysts by reducing Pu(VI) to either Pu(IV) or Pu(III) directly, or through an intermediate couple such as Fe^{3+}/Fe^{2+}. Microbial reduction of U(VI) to U(IV) has been postulated to account for observed immobilization of uranium in sludges (Francis et al., 1991.). Denitrification in waste containing both nitrate (from process sludges) and cellulosics (from combustibles) may produce α-hydroxycarboxylate chelating agents in significant quantity. Sulfate reduction (using SO_4^{2-} in brine) may further oxidize these compounds to CO_2. Microbial degradation of cellulosics may also produce colloids capable of sorbing, and thus mobilizing, actinides.

Carbonate, hydroxide, and chloride are the ligands present in the disposal rooms in the greatest quantity, though the stability constants for their actinide complexes are estimated to be not nearly as great as those for complexes with organic ligands such as citrate or EDTA. Some of these ligands are in the waste inventory from decontamination procedures; others may be produced by the action of denitrifying bacteria on alcohols and organic acids. Sulfate-reducing bacteria may act as a sink for both natural and artificial chelating agents, oxidizing them to CO_2.

The principal sorbents in the WIPP disposal rooms will be rust (from corroded drums), bentonite (assuming this is used as a backfill component), vermiculite used in drum packing, and possibly anhydrite contained in the Salado marker beds. Although the presence of sorbents can only serve to reduce actinide concentrations (unless these sorbents form mobile colloids), their effectiveness may be highly variable, since sorptive capacity will depend on such factors as pH and actinide speciation. Calcium oxide may also be added to the backfill to act as a getter material for CO_2. It is not yet clear how the resulting increase in pH and calcium content of the rooms would affect actinide concentrations.

Colloidal suspension of actinides may occur as actinides in solution precipitate onto the surfaces of suspended particulates. Colloidally-sized particles are those that remain in suspension without appreciably settling and can be considered part of the liquid phase. Colloids are probably metastable in the disposal rooms, eventually either dissolving, precipitating, or becoming sorbed onto solid material. The definition of the size of a colloid particle is somewhat arbitrary, and we have defined the maximum size of a colloid to be 1 μm. Corroded steel, exfoliated clays, and products of cellulose degradation can all serve as hosts for radiocolloids, in the disposal rooms. They may also be produced by hydrolysis of soluble actinide salts. It is not yet clear under what conditions colloidal mobilization of actinides will be important, or if such conditions will be met in the repository.

Conditions of the Test Containers

To meet the objectives stated earlier in this section under "Relationship to Laboratory Program," the source-term tests would ideally start with these conditions:

1. The tests would use real TRU waste from existing inventory at a DOE site. Using "synthetic" waste prepared by adding actinides to nonradioactive items typical of the waste category (transuranic content [TRUCON] code) being tested introduces an unacceptable bias, as the range of materials disposed of under a given TRUCON designation is unknown. Sampling bias is also introduced if waste conforming to a certain TRUCON designation is culled from a mixture of waste types, To avoid these problems, only waste that has already been identified as fitting the TRUCON designations required by the test matrix may be used in the experiments.

2. The tests would use containers that are large on the scale of waste heterogeneity. For all waste types, the test vessels must be large compared to the scale of the waste constituents (the articles that comprise the waste) so that the tests will reasonably reflect conditions typical of the waste type being tested. This requires using containers of at least 210 L (55 gal) volume for highly heterogeneous waste types such as combustibles and metals. Tests involving these waste types are referred to as "drum-scale" tests in the matrix (Appendix A). For more finely divided, heterogeneous wastes (e.g., sludges, pyrochemical salts), containers on the order of 2-5 L volume ("liter-scale" vessels) will suffice.

3. The wastes would be selected in a way that avoids experimental bias. Specifically, integer numbers of waste drums must be used to load the drum-scale containers. It will be difficult to load only a fraction of the contents of a drum without introducing bias in waste selection. Obviously, the liter-scale vessels must be loaded with a small fraction of the contents of a waste drum, but because these wastes are heterogeneous on a much smaller scale, this problem is not nearly as significant. However, the tests would be biased if all liter scale experiments for a given waste type were filled with material from a single waste drum. Therefore, each liter-scale waste sample must be taken from a different drum.

4. The tests would use brines collected from the WIPP underground because they contain microbial populations that are local to the repository. In reality, it will probably not be possible to collect enough natural brine from the underground to operate the tests using only WIPP brine. See "Test Compromises" in this section.

5. The tests would include inventories of all elements of interest. The STTP is intended to determine concentrations of actinides (Pu, Am, Th, U, Np) that will be limited by the chemistry of the disposal room, rather than inventory.

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6. The test matrix would include steel because it is a significant component of the disposal room contents. It affects Eh, sorption, and colloid generation. Most tests will contain iron, though some tests will be run without any iron to evaluate the effects of anoxic corrosion and colloid sorption by steel or rust on solution-phase actinide concentrations. The surface area of the added steel must equal that of a 55 gallon drum in the drum-scale tests and must be proportional to the fraction of drum volume occupied by the waste sample in the liter-scale tests. The steel must be thick enough to prevent complete corrosion during the first three years of the tests. See section c, "Test Container Loading" for specific requirements.

7. The test matrix would include bentonite because it is a component of a proposed backfill material for the rooms. Certain waste types will be tested both alone and with added bentonite. This will test the effectiveness of the backfill material as a sorbent for actinides and will identify the potential for mobilization of actinides through adsorption onto exfoliated clay colloids.

8. The matrix would include some experiments run under high CO_2 pressure. The rooms may fill with CO_2 as cellulosics ferment, and the solubility of actinides under these conditions is highly relevant because CO_2 is a complexing ligand for actinides. The maximum total pressure attainable in the disposal rooms from anoxic corrosion and microbial degradation of high-organic wastes is approximately 150 bar because higher pressures will exceed in situ lithostatic pressure (though pressures of up to 200 bar may be attainable if the rooms can deform without fracturing the anhydrite beds). Tests with pressurized CO_2 will determine if the lower solution pH and/or formation of actinide carbonate complexes from CO, dissolution result in higher actinide solubilities. These tests will use CO_2 overpressures of approximately 60 bar. Beyond this pressure, the increase of CO_2 fugacity with pressure becomes much more gradual, and thus the decrease in pH with increased CO_2 pressure (up to 200 bar) is minor (Appendix B). The actual pressures to be attained in the disposal rooms will be determined by such factors as waste inventory, microbial processes, gas generation rates, permeability of the anhydrite beds, and the temperature of the rooms.

9. The test containers would be leak tight. After the repository is sealed, the disposal rooms will be airtight, and unless brine radiolysis prevents them, processes such as anoxic corrosion and anaerobic microbial activity will ensue in partially or completely brine-filled rooms once oxygen is depleted. A container with an excessive rate of oxygen ingress will not achieve these conditions and thus cannot realistically simulate post-closure disposal room conditions.

10. The temperature of the test environment would be controlled. The tests must be held at a reasonably constant temperature, the average of which should approximate the in situ repository temperature of the WIPP (ca. 30°C). Wide excursions in external temperatures may significantly perturb microbial activity.

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Aside, from maintaining the temperatures of the rooms in which the tests are conducted to 30°C, no attempt should be made to control the internal temperatures attained within the test vessels; again this may unduly influence microbial activity.

Test Compromises

Because only finite time and budget exist for conducting these tests, we must introduce certain compromises:

1. The test vessels must be agitated. Diffusion cannot be relied upon to bring actinide concentrations to a steady state. A quiescent system with multipoint sampling would increase analytical costs tremendously without improving data quality. The agitation system employed must ensure that all solid material has opportunity to interact with the brine and that actinide concentrations in the brine are approximately uniform throughout the test containers.

2. The waste must be "spiked" or augmented with actinides, as the actinide content of TRU waste currently in inventory consists almost exclusively of Pu and Am. Non-destructive analysis techniques such as passive-active neutron (PAN) spectroscopy can measure approximately how much Pu is in each drum, and Am content can be estimated from Pu/Am ratios (if known). 2.5 g Pu/100 L of brine will suffice to yield 10^{-4} M, which is estimated by an expert panel elicitation (Trauth et al., 1991) to be the upper limit of Pu concentration in the disposal rooms. A loading level of 5g Pu per 55 gal. drum meets this requirement. Loadings of the other actinides (Th, U, Np, Am) must be brought to this level by spiking with actinide salts. It is unrealistic, however, to spike with Am to this level in all tests because this would yield an activity of 20 times that of the average drum. (The median alpha activity of an equivalent drum is approximately 1 curie (WPD, 1991b), the equivalent of 14 g of weapons-grade Pu. 5 g Am-241 has an activity of 17.5 Ci, or the equivalent of ca. 250 g weapons-grade Pu.) This could easily cause a condition more oxic than is reasonable for the WIPP disposal rooms, and a lanthanide analogue of Am, such as Nd, will have to be used for spiking in nearly all tests.

   Tests must also be spiked with U, Th, and Np. These are very minor constituents of the current TRU waste inventory that will become significant during the 10,000 years following decommissioning. It should be noted that Th, U, Np, and Nd (or Am) serve as chemical analogs for the four water-stable oxidation states of Pu: ThO_2 (aq) for Pu(IV), NpO_2^+ for Pu(V), UO_2^{2+} for Pu(VI), and Nd^{3+} (or Am^{3+}) for Pu(III). Acquiring data for these elements will assist in preparing a model that will predict mobilities for Pu under different conditions of Eh than those actually encountered in a given sample.

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3. The material in the test vessels must be completely inundated with brine, except for a small headspace for gas collection. This is a limiting Condition for the disposal rooms, but if the test vessels are not completely filled, it will not be possible to ascertain that all of the waste and actinides are in contact with the brine.

4. Brines collected from the WIPP underground will be mixed with synthetic brine because the quantity of natural brine available is not sufficient for conducting the STTP. All tests will therefore contain a bacterial inoculum prepared from brines collected from the WIPP underground, rock salt obtained from both the underground and the surface of the WIPP Site, and material from surface lakes in the vicinity of the WIPP Site.

Text Matrix

The STTP is designed to measure radionuclide concentrations from the many sets of conditions that may be attained in the WIPP disposal rooms. This requires selecting waste types that will generate a broad spectrum of mobility-controlling variables in environments expected in the disposal rooms.

The test matrix is designed to quantify the sensitivity of actinide mobilities to these variables as they occur in existing waste, types. The range of chemical environments possible within a given waste type cannot be known with any certainty, and it is not reasonable to attempt to define a "representative sample" for a class of TRU waste. Rather, this program is intended to sample actinide concentrations principally from those waste types that are expected to yield combinations of influences typical of those that may be encountered in TRU waste stored in WIPP disposal rooms. These results can then be used to test the validity of laboratory data-derived numeric models to predict actinide mobility in TRU waste under disposal room conditions.

The test matrix uses waste types that collectively provide a set of unique conditions that sample each of the influences that affect steady-state concentrations of actinides. The waste types tested in the proposed matrix (Appendix A) are categorized by TRUCON code (Westinghouse, 1999) and are selected from these categories based on listed contents, process knowledge, and actinide content. Three replicates of each experiment are required so that probability intervals can be established for the actinide concentrations from each set of conditions tested.

1. combustibles, TRUCON 116/216 (D1-3)
   Of principal interest in these tests are the effects of cellulose degradation on actinide solubility. Aerobic oxidation and fermentation will serve to lower system Eli. Denitrification may produce complexing agents such as citrate and lactate. Complexing agents may already be present in the waste from decontamination activities. These will make up the bulk of complexing agents withdrawn from the leachate at early times.

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2. combustibles with bentonite backfill, TRUCON 116/216 (D4-6)
   The results from these experiments can be compared directly with those from D1-3, measuring the effectiveness of the backfill in removing actinides from solution and indicating whether the bentonite itself presents a significant colloid source.

3. "enriched" combustibles, TRUCON 116/216 (D7-9)
   Although fermentation and denitrification are predicted to yield complexing agents from cellulose, it is conceivable that this condition may not occur within the test period. These experiments test the effects on solubility of a system containing both "naturally occurring" ligands (such as lactate) and those introduced as part of the waste stream (such as EDTA). In addition, these tests will follow the evolution of ligand concentration over time to observe if microbial activity consumes or generates complexing agents.

4. combustibles with solidified aqueous inorganic process sludge, TRUCONs 116/216 and 111/211 (D10-12)
   In denitrification, cellulose or its fermentation products are oxidized by bacteria capable of using nitrate as an electron acceptor. The NO_3^- is in turn reduced to N_2 or NH_3. Denitrifying bacteria can oxidize organic acids to α-hydroxy acids, which are effective complexing agents. The presence of nitrate in process sludges may be significant in promoting this process in combustible waste.

5. metals, TRUCON 117/217 (D13-15)
   Metals capable of corroding under anoxic conditions will reduce system Eh below the stability limit of water, possibly stabilizing Pu(III) in solution. Both Fe (from mild steel) and Al will anoxically corrode in brines. Less active metals such as Cu and Ph may also corrode if H_2S (from sulfate reduction) is present.

6. solidified aqueous inorganic process sludge, TRUCON 111/211 (Ll-3)
   This sludge is principally obtained in the course of wastewater treatment, in which Pu and other actinides are coprecipitated with an iron floc, then filtered. These tests will thus determine the effectiveness of the floc as a sorbent for actinides. The floe may also be capable of generating colloids that can serve as hosts for suspended radionuclides.

7. solidified aqueous inorganic sludge, TRUCON 111/211 with CO_2 (L4-6)
   These tests will be conducted with a CO_2 overpressure of up to 60 bar. It is assumed that actinide solubilities can be affected both by decreased pH and by complexation by carbonate. The results from these tests will be directly comparable to those from tests L1-3.

8. solidified aqueous inorganic sludge, TRUCON 111/214, no iron (L7-9)
   Corroding steel in the disposal rooms provides a possible sink for actinides through sorption. However, it is possible that CO_2 in the rooms may passivate steel by forming a surface layer of siderite ($FeCO_3$), which would render much less iron oxide available for sorbing actinides. These experiments test the effect on actinide concentration of removing iron oxides from the system, eliminating sorption of actinides by these phases.

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9. solidified aqueous inorganic sludge, TRUCON 111/211, no iron, Am-241 spiked (L10-12)
   In addition to providing a source of sorbents, steel corrosion also lowers brine Eh in its vicinity. Without steel (or other active metals), the oxidizing effects of radiolysis dominate the Eh of the system. These experiments measure actinide concentration, and possibly speciation, under the most oxic conditions reasonably attainable in the rooms.

10. absorbed organic liquids, TRUCON 112/212 (L13-15)
    These experiments will determine if high concentrations of organic solvents and reagents in the brine significantly promote dissolution or suspension of actinides. If the waste contains exclusively solvent residues their effect will be minimal, but if chelating agents, extractants, or detergents are present their effect on actinide concentration could be quite significant.

11. absorbed aqueous laboratory waste, TRUCON 113 (L16-18)
    Chelating agents and extractants in this waste type may increase actinide solubility.

12. cemented inorganic particulates, TRUCON 114/214 (L19-21)
    These tests will mainly examine the effects of increased pH on actinide solubility. It is also possible that actinides may become incorporated into cementitious phases, rendering them less soluble. Cementing certainly affects the leach rate, that is, the rate at which actinide ions can come into equilibrium with the brine. Though this effect may not be significant at long time-scales, a highly retarded leaching rate would make data from these tests difficult to interpret, and the cemented material will have to be crushed before use.

13. cemented organic sludge, TRUCON 126/226 (L22-24)
    These tests combine the factors in (10) with the possible presence of complexing or chelating agents, which are generally more effective at the higher pH values caused by the cement.

14. pyrochemical salt waste, TRUCON 124/224 (L25-27)
    This waste type contains few actinide-concentration controlling influences and is thus effective for individually testing the effects of materials other than wastes that are present in the rooms, such as iron, backfill, and CO_2.

15. pyrochemical salt waste (TRUCON 124/224) with bentonite backfill (L28-30)
    These tests address the effectiveness of bentonite as an actinide sorbent in the presence of high concentrations of divalent ions (particularly Ca^{2+}) that compete with the actinides for sorption sites on the clay particles.

16. pyrochemical salt waste (TRUCON 124/224) with CO_2 (L31-33)
    As with tests L4-6, these experiments will test the effects of lower pH and carbonate complexation on actinide solubility. The results from these tests and L25-27 can be

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compared to determine the significance of CO_2 by itself as a solubility-controlling influence.

17. pyrochemical salt waste (TRUCON 124/224), no iron (L34-36)
These will test the effectiveness of steel corrodant as a sorbent for actinides.

18. pyrochemical salt waste (TRUCON 124/224), no iron, Am-241 spiked (L37-39)
As is the case in (9), the greater than typical alpha activity of this matrix (due to ^{241}Am) increases the rate of brine radiolysis, rendering the system more oxic, as the H_2 produced is relatively inert. The oxidizing products of radiolysis (such as O_2, H_2O_2, OCl^-) can in turn corrode steel, and the concentrations of these species in brine will be determined by the relative rates of brine radiolysis and oxic corrosion in the system. These tests will determine whether steel corrosion or radiolysis is the dominant influence on system Eh, and therefore on actinide speciation.

The test matrix in Appendix A includes all combinations of mobility-influencing variables sufficiently unique to require testing. Although certain waste types that do not appear in the matrix appear to be unique, the conditions they would yield in the test vessels would he similar to those wastes already tested. These include:

1. RH-TRU. No remotely handled (RH) TRU waste is currently being considered for testing in this program due to the increased difficulties involved in handling the test containers and leachate from these materials. It is unlikely that the enhanced β and γ activity in RH TRU waste will significantly impact brine chemistry because these types of radiation have a much lower linear energy transfer than α particles, limiting the impact of fission products on brine radiolysis. In addition, data on the concentrations of fission products are not currently considered to be important to demonstrating compliance with *40 CFR 191B* and may be estimated from laboratory data if the need arises.

2. Pu-238. Although a significant amount of alpha activity in the initial inventory is from ^{238}Pu (used as heat sources in radioisotope thermoelectric generator [RTG] systems), there is no intrinsic chemical difference between this isotope and ^{239}Pu. The indirect effects of higher alpha activity and consequently more intense radiolysis on system Eh and actinide mobilization will be explored in the ^{241}Am-enriched test vessels, and there is therefore no need to include ^{238}Pu-containing waste in the test matrix.

3. Modified waste forms such as grouted, incinerated, or vitrified waste are not currently in the inventory. Although these waste types may create conditions in the test containers that are not identical to those accessed in the rest of the matrix (such as biodegradable organics in an alkaline medium), these conditions will fall within the scope of the laboratory tests, and it is likely that these conditions will inhibit rather than provoke actinide dissolution. Also, these waste types do not exist in significant quantities in the current TRU Waste inventory.

Analytical Requirements

Leachate Sampling

The goal of leachate sampling is to recover brine from the test vessels such that leachate characterization ("Leachate Characterization," below) can determine the actinide content and composition of the brine as it existed in the vessel at the time of sampling. The leachate must therefore be sampled and stored in a way that prevents changes in the sample prior to analysis. For example, this means that the leachate cannot be exposed to air and that the walls of the sample container must be sufficiently inert to prevent sorption of actinides. Also, samples cannot be chemically treated to improve their stability (e.g., with respect to precipitation) because this will obviously alter the composition of the brine matrix. Therefore, the leachate must be analyzed as soon as possible after sampling and before sample deterioration becomes significant.

It is expected that actinide concentrations in the test vessels will reach a steady state within the duration of the STTP. It is anticipated that the tests will be operated for two to three years. The test design permits individual tests to be operated for longer periods at the discretion of the SNL principal investigator. This steady state differs from true chemical equilibrium in that the concentrations may be held steady by some condition that is itself transient, such as microbial activity or radiolysis. It is important, though, that leachate is sampled from each container with sufficient frequency and duration to demonstrate that a steady state has been reached at the end of the experiments. It is likely that sampling will be accelerated at early times (approximately the first three months) because the actinide concentrations in a given test container will initially be far from steady-state conditions, causing potentially large changes in concentration during this period.

Leachate Characterization

The objectives of leachate characterization are to measure actinide concentrations in the brine and to quantify the components of the brine that influence actinide mobility. To summarize, leachate characterization requires measuring actinide concentrations, pH, Eh, quantity and type of radiocolloids present in suspension, identifying and quantifying complexing agents, and determining concentrations of metal ions capable of competing with actinides for active sites on complexing and sorbing agents. A complete description of analytical requirements is given in section d, "Leachate Analysis."

The precision required for measuring actinide concentrations is determined by the sensitivity required by the numeric model. As this model is no more precise than the laboratory data that comprise it, which is typically ±10% of actinide concentration, this precision is sufficient. The detection limit is defined by performance assessment sensitivities. For a given concentration of

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an isotope, one can plot a range of possible releases, depending on assumptions made about the type of intrusion made and whether the actinides experience chemical retardation in the Culebra (Figure 3a). For the purpose of defining detection limits, we make the conservative assumption that no retardation takes place in the Culebra and that the detection limit corresponds to the minimum concentration yielding a normalized release of 10^{-2} in an E1E2 (double borehole) intrusion scenario (Figure 3b). For ^{241}Am and ^{239}Pu, this corresponds to a concentration of approximately 10^{-10} molar. For the other elements (Th, U, and Np), the minimum molarities run from 10^{-9} to 10^{-8}; however, because these elements are used as oxidation state analogs for Pu, their detection limits should also be 10^{-10} M.

The detection limits for the species contributing to actinide mobility (e.g., colloids, complexing agents) are not as rigorous because the ratios of actinide mass to total mass of carrier species will be small. Therefore, detection at the 1 ppm level is required for inorganic and organic anions that are capable of complexation. A detection limit of 10^{-7} M for Pu oxidation state speciation is set by the limits of the technique. Concentrations of suspended colloids are relevant only if they actually are carrying actinides; this is again more significant in the leachates with higher actinide concentrations. It is not possible to rigorously define the upper and lower limits of colloidal size that separate particles in this size range from suspended particulates and dissolved molecular or ionic species. The lower limit will essentially be defined by the experimental requirement of using a filter of sufficient pore size such that filtration takes place at a finite rate. It is expected that 20 nm wilt he smaller than all of the colloidal particles in the leachate, with the possible exception of hydrated PuO_2 colloids at very early times in the experiments. The available limits of precision and detection for suspended actinides are expected to depend on the nature of the host particle, but a detection limit of 10^{-7} moles of suspended actinide per liter of leachate will meet the needs of the program and should be achievable in most samples.

The concentrations of metal ions other than actinides are of interest as well because they can compete with actinides for active sites in chelating agents (which tends to depress solubility) or in sorbents (which tends to enhance solubility). The principal competing ions will be Fe and Al, and possibly Mg. Pb(II) is similar in chemical behavior to Ca and may be present in the leachate if corrosion of metallic lead (used in shielding) is significant. Competition from Fe(III) and Al(III) will occur if test conditions permit corrosion of these metals. The nonradioactive metals of analytical interest are thus Ca, Mg, Pb, Fe, and Al. Competing ion effects will principally affect actinide concentrations at higher metal concentrations, and detection limits of 100 ppb for these ions are sufficient.

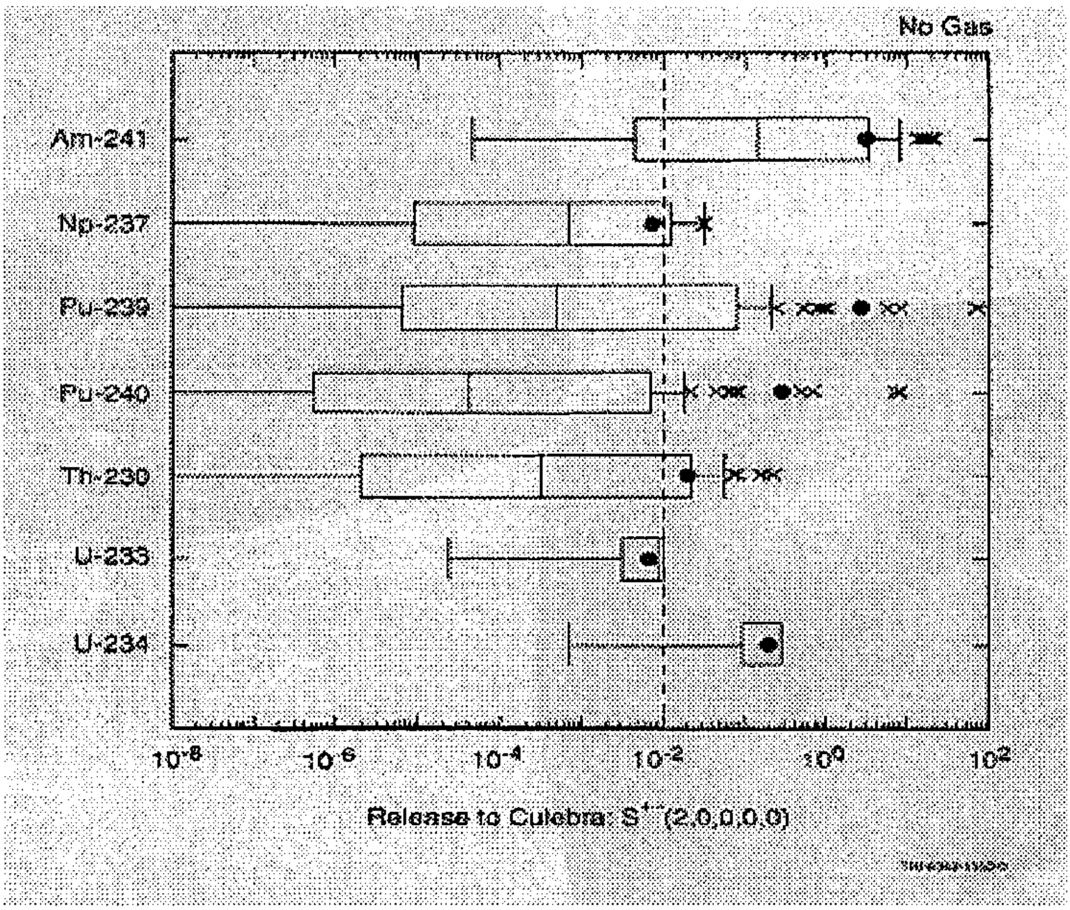

Figure 3a.

Ranges of normalized releases for various actinide isotopes at t = 1000 years in an E1E2 (double borehole) intrusion scenario (Helton et al., 1992). Actinide elements with isotopes exceeding a normalized release of 0.01 will he used in the SSTP.

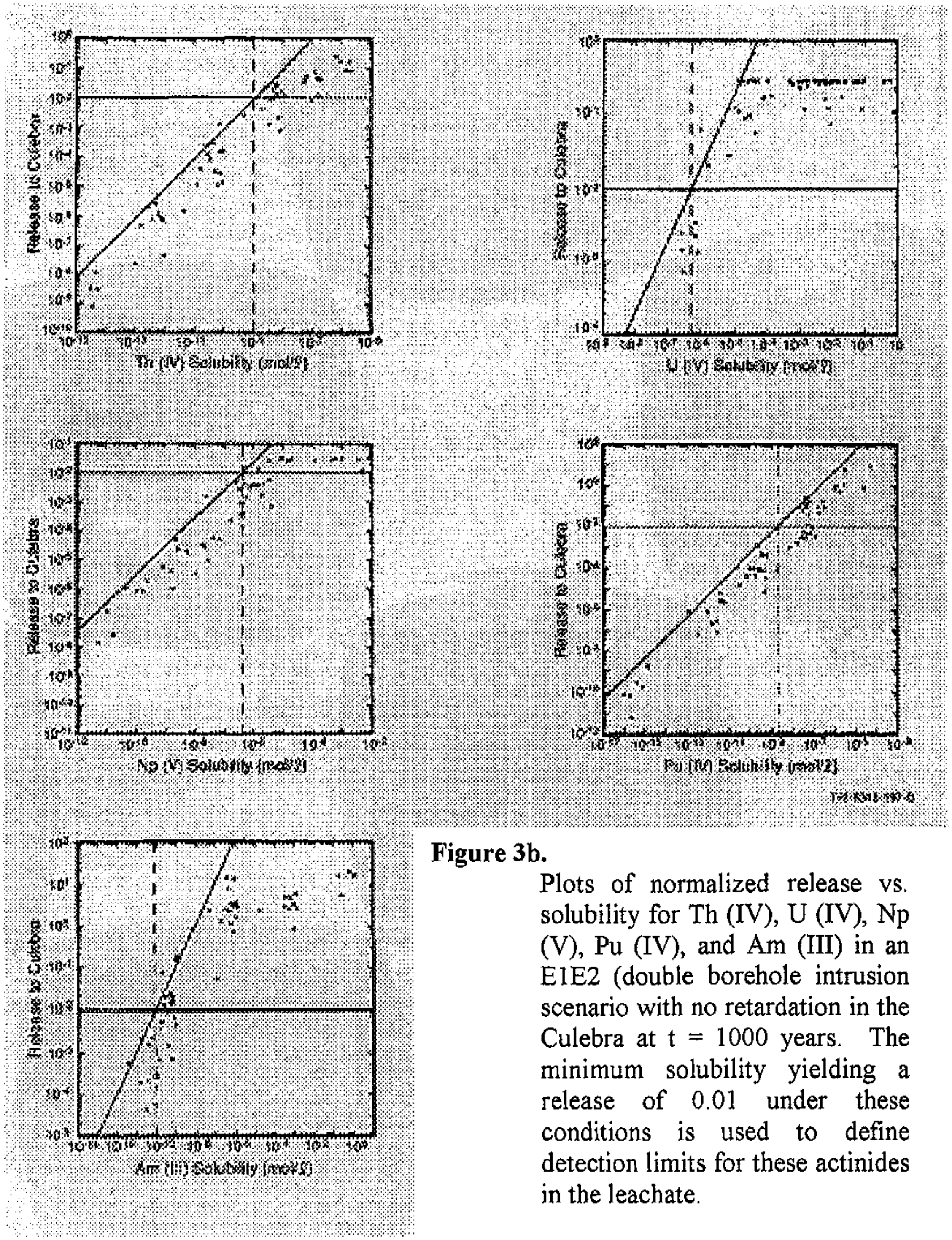

Figure 3b.

Plots of normalized release vs. solubility for Th (IV), U (IV), Np (V), Pu (IV), and Am (III) in an E1E2 (double borehole intrusion scenario with no retardation in the Culebra at t = 1000 years. The minimum solubility yielding a release of 0.01 under these conditions is used to define detection limits for these actinides in the leachate.

Gas Measurement

The purpose of measuring gas composition inside the test containers is to determine whether anoxic corrosion of steel is taking place and to monitor microbial activity. Gas data are essential to the latter because the principal modes of microbial metabolism (fermentation, denitrification, sulfate reduction, methanogenesis) will be identified only by their gaseous products. It must be noted that gas production rates are expected to be accelerated by agitation and inundation and that rate data from the source-term experiments are not appropriate for predicting gas-generation rates in the post-closure repository.

Because both steel corrosion and microbial processes are controlled by system Eh, gas composition is a qualitative Eh indicator. Gas should therefore be sampled simultaneously with the leachate, It may be desirable to sample gas more frequently than this because sampling frequency will ultimately be dictated by evolution of composition within the test vessels. Data are required for gases associated with corrosion behavior (H_2, CO_2), microbial activity (CO_2, CO, CH_4, N_2, H_2S), and leakage and radiolysis (O_2, H_2, N_2, CO, CO_2). Detection limit requirements are based on the sensitivities of corrosion and microbial processes to trace gases (e.g., CO_2, O_2, for corrosion, O_2, for microbes). It is estimated that a 1 ppm limit for all gases will suffice.

I. (c) Test Preparation Requirements

Waste Selection

Prior to waste characterization, it is desirable to learn as much as possible about the contents of the waste drums used in this experiment. Initially, it will be necessary to rely on the reported contents of the container, process knowledge, and TRU waste content. The reported ^{239}Pu (or weapons-grade Pu) content of each 55-gal. waste container selected for further characterization must be at least 5 g. Five grams of Pu in 210 L of brine would yield a 10^{-4} M solution if it were to completely dissolve.* The other required actinides (Th, U, Np, and Am) are desirable constituents, but are not present in all waste types and must be added during test container loading as needed (see section b, "Conditions of the Disposal Rooms"). ^{239}Pu should be the predominant plutonium isotope in the waste, though the precise value of the ^{239}Pu/^{240}Pu isotope ratio is not very significant. This test program does not require any tests with ^{238}Pu, which would create additional difficulties in handling the test containers and leachate samples without yielding any technical benefit. The effects of higher alpha activity and consequently more intense radiolysis on system Eh and actinide mobilization will be explored in ^{241}Am-enriched test vessels (see section b, "Test Matrix").

To ensure that at least 5 g Pu will be included in each test container and to prevent possible experimental bias, the complete contents of a waste container will be used in the drum-scale tests. At the discretion of the SNL principal investigator or his/her designee, specific items may be culled from the waste and discarded. Samples for the liter-scale tests will be obtained from waste containers individually; that is, a single waste container can supply material for only one liter-scale test. Samples may be withdrawn from densely packed, semi-homogeneous waste forms (e.g., cemented sludges) by coring.

For the subtests using "enriched" waste (section b, "Test Matrix"), waste containers should be selected appropriately according to content lists and knowledge of process history, if any.

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* Some preliminary results have shown transient Pu concentrations of up to 10^{-3} mol/L in Brine A. However, supplying sufficient Pu to yield a 10^{-3} mol/L solution upon complete dissolution would require 50 g Pu per drum equivalent of waste, which is not representative of the alpha activity of the drums in the current DOE inventory. If brine analyses indicate that complete dissolution has been attained in one or more test containers, they may be spiked with additional Pu per section c, "Mixing and Sampling Requirements."

Pre-Test Waste Characterization

Prior to opening the waste drums, a radionuclide assay is to be performed using passive-active neutron (PAN) spectroscopy-based nondestructive analysis (NDA), or a technique yielding equivalent or better precision. This will ascertain whether sufficient quantities of Pu (principally ^{239}Pu) are present for conducting the tests. Total Pu and Am may be estimated from the quantity of ^{239}Pu measured and ^{239}Pu/total Pu and ^{241}Am/^{239}Pu ratios, if known. Waste that has been previously assayed using PAN or a more precise technique need not be re-assayed, provided that the measurements were performed at a level of quality assurance that is compatible with the WIPP Quality Assurance Program Plan (QAPP). NDA must be performed individually on all waste samples to be used for the liter-scale tests to ensure that each sample contains a sufficient quantity of Pu.

The contents of the drums will then be examined using real-time radiography (RTR) to ensure that the selected drums meet both the descriptions of their content code and the WIPP Waste Acceptance Criteria (WAC). Drums that do not fit their TRUCON or do not meet the WIPP WAC will not be used for testing. The drums will then be opened, their non-nuclear contents identified visually, and in the case of heterogeneous waste types such as combustibles and metals, individual items will be weighed and cataloged. Waste characterization will require removing all levels of containment so that individual items may be visually characterized. Specific data quality objectives for visual characterization will be defined in the Test Plan.

Non-permeable (grouted or cemented) wastes must be broken or ground to allow intimate contact between the actinides in the solids and the liquid phase, Cemented wastes should be broken into pieces of a size that is reasonably expected to be fully leachable in brine during the first year of testing. This size criterion will be determined through an experiment performed prior to test initiation that measures the leach rate of cesium ion from Portland cement and Envirostone into WIPP brine.

Adequate visual and physical characterization of the heterogeneous waste types will require removing all levels of containment so that individual items can be examined and identified. Any sealed containers present will need to be exfoliated to permit access of the brine to container contents. Adequate visual and physical characterization of the heterogeneous waste types will require removing all levels of containment so that individual items can be examined and identified. Any sealed containers present will need to be exfoliated to permit access of the brine to container contents.

Test Container Loading

Drum-scale test containers will contain the contents of a standard 55 gal. waste drum and allow at least 40 L residual volume to accommodate the brine mixture. Bentonite will be added to the appropriate test containers during container loading. The desired brine-backfill proportion will be determined by experiments that will measure brine-solid ratio and liquid filterability as a function of the brine-backfill proportion.

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Brine will be added until the remaining headspace occupies less than 10% of the container volume. The level of brine in the test containers must be monitored during the filling procedure to prevent overflow, Provisions must be made to control floating objects white the containers are being filled with brine by, for example, placing a screen in the container top.

The ambient-pressure liter-scale experiments must be loaded so that at least 1 L of free liquid volume remains after brine addition and mixing. The high-pressure experiments will contain at least 0.5 L free liquid volume after mixing.

The total loading of actinides in each test container must be at least 2.5 g per 100 L of test container volume. It is anticipated that ^{232}Th, ^{238}U, ^{237}Np, and ^{241}Am (or Nd, using 1.5 g per 100 L) will be used to spike the containers that have less than 5 g per drum equivalent of these elements. Either the chloride or sulfate salts are suitable for use as spiking agents. Thorium should be added as the tetravalent ion (e.g., $ThCl_4$), neptunium as NpO_2^+ (e.g., NpO_2Cl), uranium as UO_2^{2+} (e.g.,UO_2Cl_2), and Nd as Nd^{3+} (e.g., $NdCl_3$). The weights of each actinide salt should be known to within at least 0.5%.

Certain liter-scale tests on sludges and pyrochemical salt waste (Appendix A) will use the same 2.5 g/100 L criterion for ^{241}Am in addition to the other four actinides. Test containers falling short of this level may be spiked with an americium salt such as $Am_2(SO_4)_3$. The total amount of Am required for spiking will depend on the chosen size of the liter-scale containers, but should not significantly exceed 0.75 g (5 L x 6 vessels x 2.5g/100 L).

The brine to be used throughout the test program is a mixture of synthetic Brine A with an inoculum consisting from brine collected from the WIPP underground, salt from the WIPP tailings pile, and mud from surrounding saline lakes (Appendix B). The temperature of the test vessels must be monitored externally while the brine mixture is being added to the test containers because temperature excursions caused by exothermic reactions may harm microbes in the WIPP brine if sufficiently severe, e.g., to temperatures beyond 50°C. Such excursions (which are unlikely except in waste that contains uncured cement) may be mitigated by slowing the brine addition rate or by placing the vessel in a water bath. After the containers have reached thermal equilibrium, they will be topped off with the appropriate brine mixture, then sealed. The volume of brine in the test container must be known at least to within 1% of the total added brine volume and should be measured at 30°C. The headspace within the test vessels should allow sufficient space over the brine for gases to accumulate without overpressurizing the container, but it should not allow the waste to float in such a way that it cannot be efficiently agitated.

Waste forms requiring enrichment with complexing and chelating agents will be spiked with both natural (occurring from cellulose degradation) and synthetic (added to waste stream) ligands. Complexing agents in the waste inventory that may influence actinide solubilities in brine include acetamide, acetate, ascorbate, citrate, bis(2-ethyihexyl) phosphoric acid (DHP), EDTA, 2-hydroxybutyrate, 8-hydroxyquinoline, lactate, oxalate, 1,10 phenanthroline, thenoyltritluoroacetonate (TTA), and thiocyanate.

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Several of these ligands will be used to spike the "enriched" combustibles tests (D7-9) based on their stability constants with actinides and their estimated abundance in the DOE inventory. It is currently thought that these ligands will include acetate, ascorbate, citrate, EDTA, oxalate, and thiocyanate. The identities and quantities of ligands will be finalized prior to test initiation, based on laboratory screening studies.*

The STTP requires that most test vessels (drum and liter-scale) contain iron or mild steel to simulate the effects of container corrosion in the post-closure WIPP disposal rooms, Several liter-scale tests will be run without iron to determine if the iron is significant in generating Fe-based colloids, removing Pu-based colloids, or controlling solution Eh. For the drum-scale tests, the surface area of the added steel must be equivalent to that of a standard 55-gal. waste drum, which is approximately 4m^2 (considering both internal and external surface). The liter-scale tests require corrodant with area equal to (4m^2) (waste volume/210 L). The corrodant must be thick enough so that corrosion will be incomplete after five years of testing. A sample calculation that may be useful for selecting a corrodant mesh is given in Appendix G.

It will be necessary to remove oxygen from the test containers after they are loaded with waste and brine. Procedures and criteria for oxygen removal will be developed and documented by SNL and LANL prior to test initiation and will be approved by the SNL principal investigator or his/her designee.

Design Requirements

The container designs will not be specified in this document, although the requirements and considerations for adequate container design are addressed here. Engineering designs will be finalized in conjunction with LANL.

Container Requirements

The high chloride concentration characteristic of WIPP brines and Brine A is corrosive to steels. Even stainless steels such as SS316 experience a high rate of stress corrosion when exposed to these brines at elevated temperatures (Braithwaite and Molecke, 1980; Molecke et al., 1993). Insofar as the test containers may contain brine for many years, ferrous alloys are not recommended for use in STTP container construction. Inert liners or coatings that can be scratched or abraded by waste items during agitation will not adequately protect the surface of a steel container. It is therefore recommended that the drum-scale containers be fabricated from an inert metal such as a Ti alloy. Liter-scale containers may be fabricated from standard nonferrous, corrosion-resistant materials such as Inconel, Hastelloy, Ti, Ni, or Zr.

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*G. Choppin (Florida State University) estimates that these ligands (in addition to hydroxide and carbonate) have the highest potential for increasing actinide solubilities in brine in contact with TRU waste (Brush, 1990). This list is based on assumptions of quantities of ligands in the inventory and their solubilities in brine. If insoluble ligands are present in significant amounts, and if they emulsify during agitation, they will have to be extracted from the leachate samples using organic solvents.

For the waste types used in the drum-scale tests, increased test container size will tend to "average out" waste inhomogeneity, leading to better agreement between replicates and thus less uncertainty in the actinide concentrations for a given waste type. The selection of a container size, which will be determined by LANL, will depend on factors such as container availability, overpack requirements, and compatibility with radionuclide-assay equipment. The drum-scale test containers are required to use the contents of an integer number of waste drums ("Waste Selection" earlier in this section). This requirement can be met by using a test container that will accommodate the contents of a 55-gal. drum, backfill material (as required), and approximately 40 L of brine present as free liquid. It is estimated that a test container capacity of 65 L will be sufficient. While container volumes much larger than this are suitable technically, the larger brine volume thereby required increases any problems associated with brine disposal during test decommissioning.

Containers on the order of 2-5 L volume can be used for the liter-scale tests. Smaller containers will not accommodate sufficient free brine volume to permit the sampling schedule described in the "Mixing and Sampling Requirements" section just below.

Mixing and Sampling Requirements

To allow all of the solid phase material the opportunity to react with the brine and render the results from leachate sampling more meaningful, it is essential that both the liquid and solid contents of the test containers are thoroughly mixed. Several design concepts involving external agitation of the test containers may provide reliable mixing. These include shaking or oscillating the drums using a device similar to a large paint shaker or turning drums that incorporate curved ribs fixed to the inside walls on a rotary mill or tumbler.

Leachate samples will be withdrawn from ports on the ends or sides of the containers. Each test vessel should have two sampling ports located on opposite sides of the container or dip tubes of different lengths connected to the lid. This will allow leachate samples of at least 50 mL to be withdrawn so that air cannot contact the sample or intrude into the test vessel, and dissolved gases cannot escape from the leachate. The efficacy of mixing will be tested by sampling from both ports and comparing the compositions of the two samples. The frequency of dual sampling will be determined for each container based on previous results, though in general, dual sampling will probably not be required every time leachate is withdrawn.

Prior to test initiation, the efficacy of agitation in the drum-scale containers will be tested in a prototype that will contain nonradioactive combustible waste and a bentonite backfill material.

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A neodymium (III) salt tracer will be added by soaking a cloth with a solution of the tracer and adding the cloth to the mock waste. At least one sample will be taken after each agitation cycle from each of two sampling ports located at opposite ends of the prototype vessel. One port must be located along the inside of the drum wall; the other located along the longitudinal axis of the drum. The criterion for acceptable agitation is defined here as less than 10% difference in tracer concentration in samples taken from different ports. The prototype will he tested to determine the number of agitation cycles required to meet this requirement.

Container agitation must be stopped between 18 and 32 hours prior to sampling, Ambient-pressure experiments will be sampled semimonthly during the first three months of the experiment and bimonthly thereafter. High-pressure experiments will be sampled every four months, due to the lower volume of free brine and the greater difficulty of sample collection in these tests. Any gas pressure exceeding 3 psig will be vented prior to sample collection from the ambient pressure tests. Liquid must be collected from the high-pressure vessels without significant loss of gas pressure from the container and filtered under pressure. In all tests, sampling equipment must be preconditioned so that no significant quantities of radionuclides are lost through sorption.

Test containers must be able to accept additional liquid or suspended actinide spikant during operation if leachate analyses indicate that the concentrations of one or more actinides in the brine have become limited by actinide inventory.

Temperature Monitoring and Control

Temperature of the test environment should be held at 30°C with a maximum deviation of ± 5°C. This range is specified so that the chemistry and biology of the waste-brine system will be WIPP repository relevant and will not be unduly perturbed by temperature excursions external to the test vessel. A thermocouple should be installed on each test container to monitor the temperature within the vessel, which may change as a result of microbial activity. Temperature data will be recorded, and it is anticipated that temperature measurement to within 2°C will be sufficient.

Gas Sampling and Relief

Gas may build up in the test containers as the result of anoxic corrosion of steels, microbial activity, or brine radiolysis. The test containers will allow for periodic sampling of gas for compositional analysis (section d, "Gas Sampling and Analysis"). All containers will have provisions for venting any gases before the pressure exceeds the normal limits of the container. Excess gas pressure (>3 psig) must also be released prior to sampling, and gas samples may be taken concurrently with leachate sampling. Both sampling and venting must take place without introducing air into the vessels. Gas may be vented or sampled into individual traps or into a manifold. Both drum- and liter-scale vessels will require fixtures for venting and sampling, with the exception of the high-pressure liter-scale vessels, which do not require gas sampling ports.

Leak-Tightness

The maximum rate at which radioactive brine may be leaked from the test containers during the experimental phase is an important operational concern. For the purposes of calculating the highest acceptable brine-leak rate, it may be tentatively assumed that the maximum specific activity of the leachate will be 200 µCi/mL.*

It is essential to the success of the STTP that the chemical conditions within the test container resemble those in the disposal rooms during the post-disposal phase. This requires that atmospheric oxygen be excluded from the containers to the extent possible because even trace quantities of oxygen can interfere with anaerobic microbial metabolism and anoxic steel corrosion and oxidize Pu from the trivalent to the tetravalent oxidation state. However, it is also recognized that it is impossible in a finite amount of time to ascertain that the O_2 ingress rate in a container is "zero." Also, very small quantities of oxygen leaked into the containers will probably have little effect on the system as long as these quantifies are less than those generated by radiolysis, or are insufficient to inhibit anoxic corrosion or anaerobic activity. Unfortunately, the maximum O_2 concentrations tolerated by these processes are unknown, and it will be very difficult to derive these data through experiment. However, it is apparent that an O_2 ingress rate that does not exceed the rate of production of oxygen (or other oxidizing species) through radiolysis will not bias the experimental conditions. From data on radiolysis of Brine A solutions containing ^{239}Pu (Reed et al., 1993), it is calculated that radiolysis from a solution of 10^{-7} mol/L ^{239}Pu in brine in a 250 L container will generate oxidizing species equivalent to 1.3 ppm O_2 per year.

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* This assumption is based on a maximum Pu and Am concentrations of $2x10^{-4}$ M in the brine, and alpha-curie contents of 0.07 Ci/g and 3.5 Ci/g for weapons-grade Pu and ^{241}Am, respectively (Zerwekh, 1979).

While data required to make meaningful estimates of radiolytic production from actinide-containing solids are not available, it is observed that gas production from undissolved alpha sources is much less efficient than from dissolved sources. It is concluded that an O_2 ingress rate yielding no more than 2 ppm oxygen per year in an empty container will aid in rendering the data from the STTP experiments defensible and is therefore a goal of the project. It is required that no drum- or liter-scale container has a calculated or measured O_2, ingress rate exceeding 20 ppm O_2 per year.

It should be noted that due to their smaller size, the allowable leak rate (in mL/s) of the liter-scale containers will be approximately 100 times less than that of the drum-scale containers. All containers must be leak-checked prior to use. If helium is used to leak-check the containers, a correlation between O_2 ingress rate and He leak rate must be established either by calculation or by experiment using prototype containers.

High-Pressure Experiments

The CO_2 overpressure to be used in these experiments is 60 bar. It is assumed that commercially available Hastelloy autoclaves will be suitable for these experiments with minor modification. Leachate must be withdrawn and filtered under pressure, but filter(s) may be made a part of the sampling apparatus. The pressure drop across the filters should not he great enough to cause them to rupture. Pressure must be held constant during sampling using an external source of CO_2. Only one leachate sampling port is required on these containers. Leachate will be stored at ambient pressure. Particle sizes will not be analyzed; instead, the leachate will be digested to bring all precipitated and suspended material into solution prior to elemental analysis. These containers will not be resupplied with fresh brine during the tests; therefore, it is anticipated that fewer than ten brine samples will be taken from these containers. Gas samples will not be taken from the high-pressure experiments.

I. (d) Test Operation

The source-term tests will be operated in accordance with the quality requirements of DOE Order 5700.6C, with the applicable supplemental requirements of NQA-1, or with future, revisions of these standards. The WIPP QAPP pertains to the source-term tests because data from these tests will ultimately support WIPP Performance Assessment.

Leachate Sampling

A liquid leachate sample of approximately 50 mL volume will be periodically drawn from each test container. The leachate sample will be drawn through a 1 μm filter. All dissolved species and suspended colloidal particles in the liquid sample (defined here as having an effective, diameter of less than 1 μm) will pass through this filter. Although filtration should be performed as soon as possible after sampling, no experimental constraint requires that the filter(s) be a part of the sampling apparatus. Particulate materials collected on the 1 μm filters will not be analyzed. The filtered samples must be collected in containers treated to minimize sorption of the actinide ions onto the container walls. It is essential that the samples he withdrawn so that contact with air is prevented and that they be stored in airtight vessels to prevent both oxidation of metal ions in the leachate and loss of dissolved gases in the brine prior to analysis. In addition, exposure of the sample to light should be minimized. Liter-scale containers may require periodic reinjection of WIPP brine/Brine A mixture to prevent depleting the test vessel of brine.

The stability of the leachate samples over time is unknown. Results from aging studies on standards used in analytical method development and on the leachate samples taken from the initial experiments will define the maximum allowable interval between sampling and leachate analysis.

Relevant sampling data to be recorded include date and time of sampling, volume drawn, and other observations, including difficulties encountered during the procedure. It is assumed that the test facility will withdraw leachate samples quarterly, although an accelerated sampling schedule will be followed during the first few months of the experiments. It is assumed that 16 samples will be withdrawn from each test container, on average, over the lifetime of the experiments.

Leachate Analysis

The criteria for the techniques and requirements of the analyses used to characterize the leachate samples are defined in this section. The following analyses and procedures will be performed on all samples, generally in the order given here:

1. **pH measurement.** This is complicated by the high ionic strength of the brine, which renders unequivocal hydrogen ion activity measurements difficult. It is desired that pH actually be determined as pcH ($-\log_{10}[H^+]$, as opposed to $-\log_{10}\alpha H^+$) and that measurements will be accurate to within 0.2 pcH units. The technique required uses a combination glass electrode calibrated using spectrophotometric methods (Byrne, 1987; Felmy et al., 1989). SNL will provide a procedure for the execution of the pcH measurement.

2. **Oxidation potential (Eh).** It is recognized that this measurement will not definitively determine the distribution of oxidation states within the samples, due to kinetic barriers to reduction of actinide oxy-cations (Lindberg and Runnels, 1984). However, anomalies in Eh among leachate samples from the same waste types will indicate whether a full determination of the oxidation states of Pu should be performed for these samples. Eh measurements may be estimated using a saturated calomel (SCE) reference electrode with a platinum working electrode or from relative concentrations of species in redox couples such as Fe^{+3}/Fe^{+2}.*

3. **Filtration:** half of the leachate sample will be sequentially filtered to remove all suspended material. One possible series of pore sizes would be $1\,\mu m \rightarrow 450\,nm \rightarrow 220\,nm \rightarrow 100\,nm \rightarrow 50\,nm \rightarrow 20\,nm$. Some pre-test experimentation may be necessary to determine the ideal pore size for the smallest membrane filter. Both the volumes of the original sample and the filtrate should be known to within ±2%. In subsequent analyses, coarsely filtered leachate refers to brine that has passed a 1 μm filter, and finely filtered leachate denotes brine that has passed through a 20 nm filter.

4. **Rough concentration measurement.** Liquid alpha-scintillation or energy-dispersive x-ray fluorescence (ED XRF) can be used to approximately measure relative actinide concentrations in the filtered and unfiltered leachate portions. This will determine the workup procedure to be followed prior to using ICP-MS (step 7) and to aid in selecting standards for same. The purpose of measuring concentrations in both portions is to establish whether significant activity in the brine is actually in suspension. If activities are similar in the coarsely and finely filtered leachates, actinides are probably not borne by colloids in the sample and particle size analysis (step 6) is unnecessary. It should be noted that high precision actinide determination at low concentrations in the unfiltered leachate using LSC will be difficult if actinide-carrying colloids are present.

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* A description of oxidation potential measurement in saline waters is given in Breck, 1974.

If it is apparent that actinide concentrations are significantly higher in the unfiltered leachate, the colloids will be dissolved and the actinide concentrations remeasured to give values for total liquid phase and colloidally bound actinides (step 7). Alternatively, the filters used in step 4 may be analyzed for actinides and possibly their colloid host matrices, using XRF or a related technique.

5. **Particle size analysis.** The unfiltered leachate may contain suspended colloidal particles ranging in size from 1 μm or larger (resulting from exfoliated clays) to 1-2 nm (polynuclear plutonium species). It will be necessary to measure dispersion of particle size in the leachate, that is, to determine the fraction of suspended particles within a given size range. Light scattering measurements or sequential filtration should be adequate for dispersion measurements in the size regime expected for exfoliated clay particles. Scanning electron microscopy (SEM) or transmission electron microscopy (TEM), in combination with a microanalysis method such as energy-dispersive x-ray, will be required to characterize the smaller colloids.

6. **ICP-ES and/or ICP-MS** (Inductively coupled plasma emission spectroscopy, mass spectrometry). ICP-MS will be used to measure the concentrations of the actinide elements Th, U, Np, Pu, Am, and Nd. Detection limits for all actinides should be at least 10^{-10} M with 100% precision or better at this concentration and 10% precision at 10^{-9} M and higher.[*]

7. Flame or furnace atomic absorption spectrophotometry (AAS), to determine Fe, Pb, Al, Mg, and Ca. These elements may be determined using ICP-MS (except for Fe and Ca, which suffer from poor detection limits due to isobaric matrix interferents) if convenience dictates. If no AAS is available, ICP-ES or ISE may be used for determining Fe and Ca. Detection at 1 ppm is desired.

8. Ion chromatography, to measure concentrations of free fluoride, nitrate, phosphate, sulfate, and carbonate anions in the portion of the sample passed through the smallest membrane filter.

9. Total inorganic carbon (TIC) analysis. This will determine both free and complexed carbonate ion concentrations in the filtered leachate.

10. Total organic carbon (TOC) analysis on both the filtered and unfiltered leachate. This will indicate whether significant quantities of organic material are suspended in the unfiltered leachate, either as colloids or as emulsified liquids. If this is the case, and if actinide concentrations are substantially greater in the unfiltered leachate, extraction may be indicated to reveal whether the actinides are associated with the suspended organics.

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[*] This requirement is derived from the minimum Pu and Am concentrations yielding a normalized release fraction of 10^{-2} for that element, assuming a double borehole (E1E2) intrusion with no retardation in the Culebra. This requirement is extended to Th, U, and Np as well because they serve as oxidation state analogs of Pu.

11. **Analysis of dissolved organics:** the organic components that need to be characterized are those ligands that are part of the original waste matrix, those used as spikants, and those produced by microbial degradation of cellulose. These ligands include acetamide, acetate, ascorbate, citrate, bis(2-ethylhexyl) phosphoric acid (DHP), EDTA, 2-hydroxybutyrate, 8-hydroxyquinoline, lactate, oxalate, 1, 10 phenanthroline, thenoyltrifluoroacetonate (TTA), tartrate, and thiocyanate. This list may be expanded in the Test Plan to include other ligands produced by degradation of cellulose. Analysis should reflect the total quantity of these ligands in solution, both complexed and uncomplexed, although it is not necessary to differentiate between these. Ion chromatography and high-performance liquid chromatography (HPLC) may be appropriate techniques, depending on whether a given analyte is analyzed as a charged or neutral species. Required precision levels and detection limits will be determined in the course of analytical method development, although ±20% and 1 ppm are considered target values. Only the filtered leachate (leachate that has passed the smallest membrane filter used for workup) will be analyzed.

Unusual results from the preceding analyses may require an extended workup of the leachate, at the discretion of the principal investigator or the lead analytical chemist. These investigations include:

12. **Speciation studies.** An unusual solution potential (Eh) measurement or abnormally high Pu concentrations may warrant a detailed breakdown of the distribution of dissolved Pu among its four expected oxidation states (III, IV, V, and VI). Depending on the Pu concentration in the solution, either spectrophotometry (Stumpe et al., 1984) or extraction/coprecipitation (Nitsche et al., 1988; Kobashi et al., 1988) may prove to be most effective, although it is most likely that only samples sufficiently concentrated in Pu to allow spectrophotometric determination ($> 10^{-7}$ M) will be considered for this analysis. High Pu concentrations may also indicate complexation or chelation by either organic or inorganic figands. If these processes cannot be adequately identified in analyses 8 through 11 (above), it will be desirable to attempt to measure the proportions of free and complexed Pu in solution. Photoacoustic spectroscopy may be useful, but prior analytical methods development will be required.

13. **Characterization of microorganisms in leachate.** Unusually high rates of gas production suggestive of microbial activity (e.g., generation of CO_2, CH_4, H_2S, etc.) will indicate culturing a sample of coarsely filtered leachate and measuring the concentration of colony-forming units (CFUs) in the brine. This analysis wilt reveal if signs of microbial activity are associated with significant multiplication of halophilic and halotolerant bacteria introduced into the test containers via the brine collected from the WIPP underground (section b, "Conditions of the Test Container"). If possible, both the concentration of CFUs and their taxonomic classification should be determined. A qualified microbiologist trained in the handling of alpha-emitting materials should perform the bacterial culturing and counting procedures. Descriptions of these procedures will be provided by SNL.

Gas Sampling and Analysis

The STTP experiments will sample and analyze the gas to identify major light gas constituents and their relative proportions over time. Information on gas composition is critical to the experiments because it will aid in identifying anoxic corrosion and brine radiolysis and may indicate the type and extent of microbial processes taking place. Gas data will thus be a principal indicator of effective Eh within the test vessels. Test containers will require a pressure-relief mechanism, a particulate filter that will prevent release of radioactive material, and either a carbon composite filter (or some other type of gas scrubber) for sorbing VOCs, or a system for venting these gases in a controlled fashion.

All tests require sampling of the headspace or effluent gas to determine composition. Gases of interest include H_2, O_2, CH_4, CO, CO_2, H_2S, and N_2, because these gases signal such events as anoxic corrosion, microbial activity, radiolysis, and container leakage. One possible sampling method requires drawing gas through the particulate filter into an evacuated stainless steel container and measuring gas composition using gas chromatography (GC) with mass spectrometry (MS) or other techniques. Gas composition can also be measured in "real-time" by drawing gas from a vent trap directly into a GC-MS apparatus, though it may be difficult to sample while agitating the test vessels, and agitation may be interrupted to permit sampling. In any case, gas will be sampled at a point in the system upstream of the carbon composite filter. It is anticipated that gas will initially be sampled every three weeks, then monthly after the first 12 weeks of the experiment.

Other Operational Considerations

Data from the brine leachate analyses must be available for rapid review by both the SNL Actinide Source-Term Program staff and the lead analyst at LANL to permit possible changes in test sampling schedules, to help evaluate potential problems, and to provide timely, periodic input to support model evaluation and WIPP Performance Assessment.

The analytical procedures described above have not been fully developed for use in high ionic strength solutions (such as the brine leachate from these tests) and will require preliminary investigation to determine their applicability to leachate characterization. The complexity of the leachate matrix introduces a significant degree of unpredictability into its chemistry, and certain procedures listed in this section may require modification by the laboratory conducting the analyses or a future redefinition of analytical criteria. Full development of analytical methods must therefore precede the initiation of both the drum- and liter-scale tests.

Following analysis, any unused leachate sample will be archived at 30°C for possible additional work. Residual leachate samples will be retained for a minimum of one year at the analytical laboratory location or until released by the SNL principal investigator and SNL WIPP QA. It is assumed that the residual leachate will be disposed of by the analyzing laboratory after release.

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The STTP tests are anticipated to continue for approximately 2-3 years, though individual tests may be extended at the discretion of the SNL principal investigator or his/her designee. After leachate analyses indicate that the actinide concentrations in individual experiments have reached a steady state, tests may be decommissioned or subjected to settling experiments, again at the principal investigator's discretion. These settling experiments will monitor colloidal concentrations in unagitated containers as a function of time. After brine has been removed from the containers as part of decommissioning, solid samples may be recovered for post-test analysis to determine how actinides are distributed within the solid phases present. If possible, the solids responsible for controlling actinide solubility will be identified.

Specific requirements for decommissioning and decontamination will be defined by LANL.

STTP Technical Requirements: References, Appendices, and Figures

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Appendix A:
STTP Test Matrix

Appendix A: STTP Test Matrix

Expt. no.	TRUCON code	description	backfill
Drum-scale tests:			
D1, D2, D3	1161216	combustibles	none
D4, D5, D6	1161216	combustibles	bentonite
D7, D8, D9	1161216	combustibles, enriched	none
D10, D11, D12	116/216+111/211	combustibles and sludge	none
D13, D14, D15	1171217	metals	none

Total: 15 drum-scale tests

Liter-scale tests:

Expt. no.	TRUCON code	description	backfill
L1, L2, L3	111/211	dewatered aqueous inorganic sludge	none
L4, L5, L6	111/211	dewatered inorganic sludge w/CO_2*	none
L7, L8, L9	111/211	inorganic sludge, no iron	none
L10, L11, L12	111/211	sludge, no iron, ^{241}Am spiked	none
L13, L14, L15	112/212	absorbed organic liquids	none
L16, L17, L18	113/213	absorbed aqueous lab waste	none
L19, L20, L21	114/214	cemented inorganic sludge	none
L22, L23, L24	126/216	cemented organic sludge	none
L25, L26, L27	124214	pyrochemical salt waste	none
L28, L29, L30	124/214	pyrochemical salt waste w/CO_2*	none
L31, L32, L33	124/214	pyrochemical salt waste	bentonite
L34, L35, L36	124/214	pyrochemical salt, no iron	none
L37, L38, L39	124/214	pyrochemical salt, no iron, ^{241}Am spiked	none

Total: 39 liter-scale tests

- CO_2 = 60 bar CO_2 overpressure.

Appendix B:

Procedure for Preparing Inoculated Brine

Appendix B: Procedure for Preparing Inoculated Brine

Section b, "Test Compromises" indicates the need for diluting brine obtained from the WIPP underground (e.g., from G-seep) with synthetic brine, as there will otherwise be insufficient brine for conducting the source-term tests. However, synthetic brine does not contain microbes native to the WIPP underground. A procedure has been developed by A. J. Francis et al. (Brookhaven National Laboratory) and M. A. Molecke (SNL) to produce a brine from natural and artificial sources that contains microbial populations that resemble those found in the WIPP underground and at the surface in the vicinity of the WIPP site.

The inoculated brine is prepared by adding 5 parts by volume of the brine inoculant mix described in the following memorandum and 2.5 parts by volume of brine collected from G-seep in the WIPP underground with 92.5 parts by volume of synthetic Brine A. The following reagents yield 200 L Brine, A when mixed:

58.42 kg $MgCl_2 \bullet 6H_2O$ *or* 39.73 kg $MgCl_2 \cdot 2H_2O$
20.02 kg NaCl
11.44 k-g KCl
1.24 kg Na_2SO_4
390 g $Na_2B_4O_7 \bullet 10H_2O$
332 g $CaCl_2$
192 g $NaHCO_3$
104 g NaBr
25.0 g LiCl
5.45 g RbCl
3.0 g $SrCl_2 \bullet 6H_2O$
2.6 g KI
2.5 g $FeCl_3 \bullet 6H_2O$
0.25 g CsCl
2.5 mL 12 N HCl
H_2O deionized, to 200 L

Reagents are added to water in a plastic barrel while stirring, using an electric mixer. $MgCl_2$ should be added to the water and dissolved prior to adding the other reagents. After all reagents are dissolved, water is added to yield a total volume of 200 L. No solids should precipitate from the mixture. This recipe may be scaled as appropriate.

The complete procedure is described in the following memo.

BROOKHAVEN NATIONAL LABORATORY
MEMORANDUM

DATE: August 16, 1993

TO: Marty Molecke, Sandia National Laboratories

FROM: J.B. Gillow and A.J. Francis

SUBJECT: Details of the Preparation of a Mixed Inoculum for the Bin Tests [Revised]

The following describes the components, preparation, addition, and storage of a mixed inoculum to be used for large-scale bin tests. A mixed inoculum has been effectively used in laboratory studies at Brookhaven National Laboratory (BNL) to: (i) examine the activity of specific groups of microorganisms such as cellulose degraders, denitrifiers and fermenters and (ii) examine gas generation due to biodegradation of cellulose under inundated and humid hypersaline conditions.

The purpose of using a mixed inoculum is to provide diverse groups of microorganisms for the test system without specifically pre-enriching for a group of microbes with a limited metabolic function. The dominant groups will be selected by the most abundant substrates in the test system.

The mixed inoculum used at BNL has essentially been G-Seep brine from the repository amended with aliquots from various sources: a brine solution prepared by dissolving halite from the WIPP underground workings in distilled water and brine and sediment slurry from surficial hypersaline lakes adjacent to the WIPP site. The mixture consisted of 50% G-Seep brine, 30% (200g/L) muck pile salt, and 20% brine and sediment slurry from 5 surficial lakes. Bacteria have been detected in brine from the surficial lakes (10^6-10^7 cells/ml), G-Seep brine (10^4- 10^6 cells/ml), and in the muck pile salt.

Inoculum Preparation:

The inoculum is composed of: i) G-Seep brine from the WIPP repository, ii) muck pile salt from the WIPP underground workings, and iii) brine and sediment slurry from the lakes adjacent to the WIPP site. The G-Seep and muck pile salt can be stored at room temperature prior to preparation. The sediment and lake brine should be stored at 4°C soon after collection. Microbial activity in the sediment and lake brine should be minimized as much as possible prior to preparation of the inoculum in order to prevent the proliferation and enrichment of specific microorganisms due to the metabolism of nutrients (if any) present in the samples. This is not a problem with G-Seep as it contains very low levels of dissolved organic carbon (DOC), and it has been shown to maintain a steady population of 10^4 viable cells/ml when stored at room temperature.

COMPOSITION OF MIXED INOCULUM

Source			Volume (ml)
G-Seep brine from the WIPP underground workings			2500
Muck pile salt from the WIPP underground workings dissolve 200 g/L S2180, W30 in distilled water and stir for 2 hours in a sterile glass Erlenmeyer flask.			1500
Sediment slurry and brine from the WIPP surficial environment are mixed together in the above solution.			
	Sediment slurry (ml)	*Brine (ml)*	
Laguna Quatro	100	100	
Laguna Cinco	100	100	
Laguna Tres South	100	100	
Lindsey Lake	100	100	
Surprise Springs	100	100	
Total	500	500	1000
TOTAL			5000

Particulates present in the sediment can be removed by passing through sterile cotton.

The above components are combined in a 6.0 L sterile Erlenmeyer flask under anoxic conditions in a N_2 atmosphere and stirred. Aliquots of the mixed inoculum are removed and analyzed for:

i) The total number of bacteria by direct microscopic counts using the DAPI (4',6-diamidino-2-phenylindolc dihydrochloride) method, and viable cells by microscopic examination with a redox indicator 5-cyano-2, 3-ditolyl tetrazolium chloride (CTC).

ii) Inoculum activity by assaying for denitrification (acetylene blockage technique).

iii) Total and dissolved organic carbon.

iv) The distribution of microorganisms (aerobes, anaerobes, denitrifiers, sulfate reducers and methanogens) by the most probable number (MPN) technique.

v) Chemical characteristics such as pH, organic acids, NH_4^+, NO_3^-, PO_4^{3-}, and $SO_4^=$.

Information on the characteristics of the inoculum for large-scale tests is essential in order to establish a baseline from which changes in the microbial populations can be monitored by sampling the brine in the test bins during the course of the experiment. Changes in the microbial community will have a direct impact on the rates and types of gaseous and liquid metabolitic products generated.

Addition of Inoculum Mixture to a Test-Bin:

The mixed inoculum can then be added in the appropriate quantity directly to a 100L, test bin to provide approximately a 3-5% v/v inoculum. The inoculum should be added to a pre-inundated bin in order to disperse the inoculum throughout the bin. It is advisable to add the inoculum at the start of the experiment in order to prevent unnecessary perturbations of the test system later.

Storage of the Inoculum Mixture:

The inoculum, mixture should be stored at 4°C in order to prevent the growth of microorganisms in the mixture. Activity may occur if the mixture is allowed to stay at room temperature for more than 24 hours due to the presence of DOC in the inoculum.

Test Plan for the Actinide Source-Term Waste Test Program (STTP)

II. (a) Test Plan: Abbreviations and Revision History

Abbreviations

ALARA	As Low As Reasonably Achievable
CAO	Carlsbad Area Office
CID	Charge-injection detector
CST-*X*	Analytical chemistry group within LANL's Chemical Science and Technology Division
CMR	Chemistry and Metallurgy Research
DHP	bis(2-ethylhexyl) phosphoric acid
DOE	Department of Energy
DQO	Data Quality Objective
EDTA	ethylenediamine tetraacetic acid
EDXRFS	energy-dispersive x-ray fluorescence spectroscopy
Eh	oxidation-reduction potential
EPA	Environmental Protection Agency
GC	gas chromatograph
ICP-AES	inductively coupled argon plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometer
LANL	Los Alamos National Laboratory
LCS	laboratory control standard
LSC	liquid scintillation counting
MDL	method detection limit
NESHAPS	National Emission Standard for Hazardous Air Pollutants
NIST	National Institute for Standards and Technology
PAN	passive-active neutron
pH(pcH)	hydrogen ion concentration
RPD	relative percent difference
RSD	relative standard deviation
RTR	real-time radiography
SAR	safety analysis report
SEM	scanning electron microscopy
SNL	Sandia National Laboratories
SRM	standard reference material
STTP	Actinide Source-Term Waste Test Program
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
TRUCON	transuranic content (code)
TTA	thenoyltrifluoroacetonate
USQD	unreviewed safety question determination
WCRRF	Waste Characterization, Reduction, and Repackaging Facility
WIPP	Waste Isolation Pilot Plant
WDXRFS	wavelength-dispersive x-ray fluorescence spectrometry

Revision History

This historical section of the final report is the first effort at identifying the necessary chapters to be included in the test plan. The level of detail included is driven by the available knowledge of the capability of the Los Alamos National Laboratory to provide the necessary equipment, hardware, instrumentation, and expertise in fulfilling the requirements of the Actinide Source-Term Waste Test Program (STTP) technical requirements document written by Sandia National Laboratories (SNL). Revision will be made as progress during the operation of the STTP reveals the need for change to the technical requirements of increased technical capabilities or unachievable technical specifications.

The following pages are the first revision of this test plan. It reflects changes in the technical requirements agreed upon between LANL, SNL, and CAO. It also reflects changes in organizational designation, affiliation, and responsibilities within LANL. Technical changes to the Test Plan originated in Memos of Understanding between LANL and SNL on 11/94 and 2/95. The Memos of Understanding are stored in *SWCF-A:WBS 1.1.2.2. AST/STTP.*

Introduction

Objectives and Goals

This test plan presents the approach, methods, and procedures that Los Alamos National Laboratory (LANL) will use to meet the technical requirements specified for the STTP. These technical requirements are given in SAND91-2111, *"Technical Requirements for the Contact-Handled Transuranic Waste Source-Term Test Program."* This test plan is a collaborative effort by LANL and SNL to meet the requirements in a timely manner. SNL is responsible for providing the technical requirements and LANL is responsible for providing the test plan.

Rational and Depiction of STTP

Congress authorized the Waste Isolation Pilot Project (WIPP) in 1979 (Public Law 96-164, 1979) as a research and development facility. The WIPP is designed as a full-scale pilot plant to demonstrate the safe management, storage, and disposal of defense transuranic (TRU) wastes. Environmental Protection Agency (EPA) regulations governing the disposal of TRU wastes are set forth in part in *40 CFR 191, Subparts B and C*. The containment requirements of *40 CFR 191.13 (a)* state that disposal systems for TRU radioactive wastes shall be designed to provide a reasonable expectation, based upon performance assessments, that the cumulative releases of radionuclides to the accessible environment for 10,000 years after disposal from all significant processes and events that may affect the disposal shall have a likelihood of less than one chance in 10 of exceeding radioactive release limits and one chance in 1000 of exceeding the release limits by a

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factor of 10. The release limits for containment requirements are given in *40 CFR 191, Subpart B, Appendix A, Table 1*. "Performance Assessment" is defined in *40 CFR 191.12 (q)* as "an analyses that: (1) identifies the process and events that might affect the disposal system; (2) examines the effects of these processes and events on the performance of the disposal system; and (3) estimates the cumulative releases of radionuclides, considering the associated uncertainties, caused by all significant processes and events. These estimates shall be incorporated into an overall probability distribution of cumulative release to the extent practicable."

Performance assessment calculations (WPD 1991a) have shown that the only credible potential mechanism for actinide transport to the accessible environment is by flow of brine and drilling mud in boreholes drilled through the disposal area. Drilling occurs in human intrusion scenarios. In these scenarios, Salado and Castile brines and drilling muds enter the waste disposal area, contact waste, and become carriers of mobilized actinide species. The brines and muds are transported up boreholes under the driving force of pressurized fluids in the disposal area. Some of the actinide carriers reach the surface; others move laterally toward the boundary, principally through the Culebra Member of the Rustler Formation.

Predicted concentrations of dissolved and suspended actinides in the brines that can act as transport media are a priority need for evaluating WIPP compliance with requirements in *40 CFR 191, Subparts B and C*. Brines originating in the Salado Formation, the Castile Formation, and the Culebra Member of the Rustler Formation, and their mixtures are the pertinent brines. The predominant types of mobile actinide-bearing species in these brines are expected to be dissolved species in several possible oxidation states and suspended colloidal particles. The concentrations of these actinide species are important parameters for mass transfer and release models. Specifically, the rates of actinide transport from the disposal area, up boreholes, and in the Culebra Member depend on these actinide concentrations.

An actinide source-term model is needed to predict actinide concentrations. Following results from recent performance assessments (WPD 1991a, 1991b) plutonium, uranium, americium, thorium, and neptunium are the current priority elements, plutonium and uranium having the highest priority.

The actinide source-term model will be a product of the SNL source-term program. This SNL program includes model development, laboratory studies to support the model development, and tests with actual TRU waste. Laboratory studies of actinide solubility, complexation, sorption, and colloid formation will be designed to develop the required chemical understanding and database. Conceptual models for dissolved and colloidal species will be

Continued on next page

developed from the laboratory test data and chemical understanding, and a quantitative model will be developed from the conceptual models. The STTP will provide data on concentrations of actinides, actinide-containing colloids, complexing agents, and other chemical reactants in simulated WIPP brine in contact with candidate backfill materials and actual TRU types. SNL will interpret the model. The technical requirements for the STTP are given by SNL in the technical requirements document, SAND91-2111, published as a companion document to this test plan.

A primary objective of the STTP is to test the following hypotheses:

- For each dissolved actinide, the highest concentration within the uncertainty range (as expressed by error bars) of the maximum solubility as predicted by the Dissolved Species Submodel for applicable STTP test containers will not be exceeded by the highest measured dissolved concentration within the uncertainty range of composition analyses for that STTP test container when at steady state conditions. For the Dissolved Species Submodel, the STTP will not be used to lower the maximum, thermodynamically predicted solubility limit for dissolved actinides under the conditions evaluated by the model because of the potential in the STTP for sorption on immobile substrates and the impossibility of isolating and identifying the solubility-limiting, actinide-bearing minerals from the waste matrix.
- For colloidal species containing actinides, the largest concentration within the uncertainty range (error bar) as predicted by the Colloidal Species Submodel for applicable STTP test containers will not be exceeded by the colloidal concentration measured for that STTP test container when at steady state conditions.

A secondary objective of the STTP is to corroborate information and hypotheses on the oxidation state distribution of the actinides under anticipated repository like conditions. To accomplish this objective, those containers with sufficiently high actinide concentrations will be analyzed to establish the oxidation state distribution under the conditions of the tests. Based on preliminary analytical methods development, it is anticipated that a concentration of approximately 1 x 10^{-6} moles/liter will be required to determine by spectrophotometry the oxidation state distribution of applicable actinides in brine samples taken from STTP containers. Although lower concentration limits may be achievable by using other solvent extration, and co-precipitation techniques, spectrophotometric techniques are preferred to minimize the potential of the oxidation state distribution being corrupted by the analytical procedures. The details of this work are covered in "Actinide Redox Reactions Important in WIPP Site" Rev. 0 by Rai et.al.

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The STTP is being performed by LANL with technical guidance provided by SNL. To determine the effect of influencing variables on the dissolved concentrations of actinides, actual TRU waste types typical of DOE waste inventories have been characterized and loaded into specially designed test containers that are filled with brine. The TRU waste types were selected according to the test matrix provided by the technical requirements document and based on the waste types in the DOE inventories. The test containers are sized to provide sufficient waste to permit study of the parameters that may influence the concentration of actinides in the brine. Heterogeneous waste types such as combustibles, glovebox gloves, protective clothing, and tissues have been used in the drum-scale tests; homogeneous wastes such as solidified inorganic and organic sludges, cemented wastes, and pyrochemical salt wastes have been used in the liter-scale tests.

The test containers have been loaded with waste, brine, and additives then sealed and housed in two specially designed, prefabricated enclosures having temperature conditions simulating the WIPP disposal room temperature of 30°C. The brine leachate in the test containers will be sampled 6-8 times per year for a period of 2-5 years. The headspace of the test containers will be sampled at a similar frequency for analyses of headspace gases generated by radiolytic, microbial, and corrosion activities in the wastes immersed in brines.

Analyses that may be performed on the brine leachate samples include:

- hydrogen ion concentration (p*c*H),
- oxidation-reduction potential (*E*h),
- alpha activity,
- particle-size distribution,
- colloid characterization,
- total inorganic carbon (TIC),
- total organic carbon (TOC),
- actinide concentrations,
- elemental analytes,
- toxic elements identified in the Resource Conservation and Recovery Act (RCRA),
- complexing and chelating agents,
- inorganic and organic gases
- plutonium speciation,
- total inorganic anions, and
- characterization of microorganisms in the leachate.

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Other analyses (as distinguished from physical analyses such as temperature and volume measurements) or experiments may be requested as the STTP progresses and results are evaluated. All analyses performed on the brine leachate and headspace gas samples requires state-of-the-art instrumentation and technologies and an analytical facility with the capability of handling, analyzing, and disposing of highly radioactive plutonium-containing solutions.

II. (b) Influencing Variables

Impact on Test and Analysis

Only wastes with certain transuranic content (TRUCON) codes have been selected for the STTP. The choice of waste types was based on characteristics of the waste that are expected to significantly affect the concentration of actinides in concentrated brine solutions. The SNL technical requirements document has identified the major parameters that may be in WIPP-destined wastes and may influence the concentration of actinides in brine. These parameters are outlined below.

pH (p*c*H)

The p*c*H (see section i, "Development of Analytical Methods for Brine Leachate") in wastes immersed in WIPP brines can influence the relative concentrations of actinides as anionic or cationic species. Under acidic conditions (low p*c*H), actinides are more likely to be in uncomplexed cationic form. Ligands and chelation compounds that may be present in wastes generally have higher stability constants in basic solutions than in acid solutions. Carbonates tend to solubilize uranium [$U^{(VI)}$] and precipitate neptunium [$Np^{(V)}$] and plutonium [$Pu^{(III)}$] in slightly basic solutions but can solubilize all actinides in concentrated basic solutions (pH >9). For the STTP, the p*c*H of the solution will affect the sign and magnitude of the electrical potential at the surface of the carrier colloids. The nature of the surface charge of the carrier colloids is an important factor controlling separation of radionuclides.

*E*h

The *E*h of brine will influence the solubility of actinides because actinides in higher oxidation states are generally more soluble than in lower oxidation states. Also, brine having greater oxidizing potential may increase the solubility of other metallic components.

Chelating and Complexing Agents

The presence of complexing agents in WIPP brines can increase the total amount of dissolved actinide concentrations. The solubility of actinides by reaction with complexing agents strongly depends on the p*c*H of the brine solution and the availability of excess uncomplexed ligands. Carbonate may become the most important ligand in the disposal room (aside from aqua or hydroxyl ligands produced by hydrolysis) if it is present in high concentrations in brine solutions. The presence and concentration of stronger complexing agents such as ethylenediaminetetraacetate (EDTA), thenoyltrifluoroacetonate (TTA), citrate, and tartrate may also influence the solubility of uranium and plutonium in the brine solutions in the STTP test containers. The presence of transition metal ions such as magnesium, iron, and chromium in the brine will influence the availability of uncomplexed

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chelating compounds and tends to decrease the solubility of the actinides. The STTP brine solutions will be exposed to relatively high concentrations of iron and may have very few uncomplexed chelation compounds available for complexation of actinide species. Iron is expected to be the greatest sink for chelating agents because it forms complexes having very high stability constants.

Sorption

Actinides are sorbed when dissolved actinide ions become bound to sites on solids such as clay minerals and iron oxyhydroxide and tend to reduce the concentration of actinides in solution. Sorption will be less efficient in brines containing greater concentrations of complexing agents and more basic pHs. Actinide sorption is expected to be particularly strong on clay minerals (for example, bentonite) used for backfill and hydrated iron oxides produced from corrosion of iron-bearing materials. Much of the hydrated iron oxide may be filtered out by larger pore size filters.

Colloidal Suspension

For the STTP, SNL has defined "colloid" as particles having characteristic size between 0.001 μm and 1 μm, suspended in a liquid and maintained in suspension for very long times by Brownian motion. Two main types of colloids are recognized: carrier colloids and actinide intrinsic colloids. Carrier colloids have the potential to take on actinides by adsorption or ion exchange and carry them in brine. Carrier colloids may occur naturally in brines, and they may be formed by reactions of waste containers, waste, and compounds by polymerization of actinide monomers in solution. The most widely reported actinide intrinsic colloid is the plutonium (IV) polymer ($PuO_2{\bullet}nH_2O$). The size range, distribution, concentration (particles per unit volume), and actinide elemental concentration will be determined for samples in which a statistically significant difference in actinide concentration is found before and after filtration.

The five influencing variables discussed above form the basis for establishing the necessary analytical measurements to be performed on brine from the different test wastes. Chemical analysis will provide data on the effect each influencing variable will have on the mobility or immobility of actinides in natural WIPP brines under WIPP disposal room conditions. The test matrix specified in the technical requirements document has been designed to provide data on the response to varying additives such as iron, backfill material, CO_2, and ligands.

II. (c) Selection of Wastes

Drum-Scale Tests

Before the waste was characterized, it was essential to learn as much as possible about the contents of the waste drums used in this experiment. Initial drum selection was based on contents reported on the container, process knowledge, and TRU content. Selected waste drums were then further characterized to confirm the contents.

The reported ^{239}Pu (or weapons-grade plutonium) content of each 55-gal. waste container had to be at least 5g. Five grams of plutonium in 210L of brine would yield a 10^{-4}M solution if the plutonium were to dissolve completely. Plutonium concentrations as high as 10^{-3}M have been observed in Brine A in the absence of reducing agents. However, incorporating the amount of plutonium needed to emulate this condition (50g per drum) would introduce bias, as few drums in the waste inventory have such a high plutonium content or equivalent alpha activity.

In addition to plutonium, the daughter actinides thorium, uranium, and neptunium are desirable constituents. However, they are not present in all waste types and must be added during loading to yield 5g each per drum-scale test container. Americium-241 may be present in the containers selected for testing, but spiking with this isotope increases the alpha activity unnecessarily and could influence chemistry toward a more oxic *E*h. (The effects of higher alpha activity and consequently more intense radiolysis on system *E*h and actinide mobilization will be explored in ^{241}Am-enriched test vessels (sections d "Actinides," e "Pyrochemical Salt Wastes with Added CO_2," and e "Pyrochemical Salt Wastes with $Ca(OH_2)$ & Chelators"). The ^{239}Pu/^{240}Pu ratio is not very important because the relative half-lives of the two isotopes do not significantly change the alpha activity in the waste. This test program does not require any test with ^{238}Pu, which would not only create additional difficulties in handling the test containers and leachate samples but would also fail to yield any technical benefit. The higher ^{241}Am concentrations in pyrochemical salts will be an indicator for ^{238}Pu effects on the brine.

The complete contents of a waste container will be used in the drum-scale tests; that is, each drum-scale test vessel will contain the contents of a single waste drum.

Samples for the liter-scale tests were to be obtained from waste containers individually; that is, a single waste container can supply material for only one liter-scale test. Samples may be withdrawn from densely packed, semihomogeneous waste such as Envirostone or Portland cement by coring. Each sample must contain at lest 0.025g of plutonium per liter (equivalent to 5g of plutonium per 55 gal.-drum), though it is desirable to select from drums having higher plutonium concentrations if plutonium concentrations within the drum are not uniform (for example, in cemented sludges).

Pre-test Waste Characterization

The technical requirements document states that a radionuclide assay by passive-active neutron (PAN) spectroscopy or the equivalent should be performed on each waste drum by a nondestructive assay technique before the drum is opened. A radionuclide assay ensures that the waste drum contains the minimum quantity of total plutonium (>5g per 55-gal. [208-L] drum). Also, the waste drums selected for experimentation are to be examined by real-time radiography (RTR) to ensure that the selected drums meet the description of their TRUCON code. After RTR, the contents of the waste drums selected for the 15 drum-scale test containers will be visually characterized. The contents of homogeneous (cemented) waste drums will be core-sampled for placement into liter-scale test containers.

Non-Destructive Radionuclide Assay

Nondestructive radionuclide assay will be conducted on the 15 waste drums selected for the drum-scale tests. The drums will not be opened unless the contents have been certified to contain >5g plutonium by a more accurate measurement technique (for example, mass spectrometry). The purpose of the radionuclide assay is to:

- ascertain that sufficient quantities of ^{239}Pu are present
- determine that ^{241}Am is not present in unacceptably high concentrations
- ascertain whether ^{238}Pu is present in concentrations too high to be handled safely, and
- identify any criticality concern within an array of drums

For a 55-gal. Waste drum to be acceptable for the STTP, it must contain at least 5g of ^{239}Pu. Drums failing to meet this criterion will not be used for testing. The ^{241}Am, ^{238}Pu, and total fissile material measurements are important for radiological health, contamination control, and criticality safety.

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The data quality objective (DQO) for the determination of ^{239}Pu in a waste drum is that the radionuclide assay method verify that the total ^{239}Pu content in a 55-gal. drum is at least 5g or >5g + 200%. At the 20g content level, the DQO is 10g + 100%, - 50%. In summary, the DQOs for radionuclide assay are:

- 5g + 200% - 0%
- 10g + 200% - 50%, and
- 20g + 100% - 75%.

The type of measurement to be made may be any method such as PAN spectroscopy or comparable gamma-ray tomography available to LANL, provided the method can meet the DQOs. A radionuclide assay will not be required if documentation certifies that the plutonium concentration of a drum has been determined by a more accurate method.

After the radionuclide assay has been completed or the certification documentation has been assessed, the concentration or total content of ^{241}Am and ^{238}Pu allowable within a drum will be assessed by the STTP project leader in collaboration with safety personnel from the Chemistry and Metallurgy Research (CMR) Building and the analytical chemistry groups.

Radionuclide assays on homogeneous or semihomogeneous waste drums for the liter-scale tests will be conducted on the cores extracted from the drums after a gamma-ray survey has been made on each drum to screen them for minimum and maximum actinide content. The concentration of ^{239}Pu in homogeneous waste core samples taken from 55-gal. drums must be >25mg per liter of test waste.

Radionuclide assay of the entire contents of homogeneous waste will not be necessary if a gamma-ray survey of each drum indicates that sufficient actinide activity is available to yield a total ^{239}Pu concentration of 25 mg per liter of waste. The DQOs for radionuclide assay of core samples taken from the semihomogeneous waste drums are:

- 25 mg/L + 100% - 0%,
- 50 mg/L + 100% - 50%, and
- 100 mg/L ± 50%

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Core samples for the liter-scale tests will be obtained from waste containers individually; that is, a single waste drum can supply material for only one liter-scale test. During radionuclide assay, the ^{239}Pu will be measured by instrumentation that has been calibrated for such measurements. Radionuclide assay equipment will be calibrated before an array of drums is analyzed. To address criticality concerns, measurements will be made to keep the fissile material content under the criticality limit for an array of drums within the Waste Characterization, Reduction, and Repackaging Facility (WCRRF). The WCRRF safety analysis report (SAR) gives a WCRRF administrative limit of 150g of fissile material.

Real-Time Radiography (RTR)

To ensure that the TRUCON code of waste drums matches the radiographic results, RTR will be performed on the waste drums to be used to load the drum-scale test containers. Because the waste drums are not to be transferred to WIPP or any other location outside of LANL, their contents need not necessarily meet the WIPP Waste Acceptance Criteria. RTR will not be used to examine the contents of the waste drums containing homogeneous (cemented or sludge) wastes unless a gamma-ray survey of the drums indicates that the waste is not homogeneous. Also, the weight of the homogeneous waste drums indicates whether the waste is homogeneous or if it contains combustibles.

Waste Characterization

Drum-Scale Tests

After RTR measurements, each of the waste drums to be used to load the drum-scale test containers will be opened so the waste can be visually characterized. Each waste drum will be opened at the WCRRF and individual items will be inspected for content and composition. For example, rubber gloves might be contained within a plastic container. All levels of containment will be breached to expose the contents of bags, cans, or containers inside the drum. Plastics, rubber, and other carbonaceous materials will be identified by a near-infrared technique. Major metals will generally be identified by an energy-dispersive x-ray fluorescence method. A video camera will record the visual characterization of each of the drums. Drums will be identified according to the TRUCON code and the STTP test matrix. Specific DQOs for the visual characterization of each of the drums are listed below:

- Each drum will be weighed before it is opened.
- Each bag within the drum will be weighed.

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- Each bag will be opened and its contents identified to a technician, who will record the information in a content log. The contents will be confirmed by video camera.
- The component of greatest mass will be identified for each bag. The technician will visually estimate the percentage of the total mass, or if possible, weigh the major component. The weight of the remaining components will be estimated relative to the major component, or if possible, weighted directly.
- The estimated weights may not differ from the total weight by more than 20%.
- To the extent possible, each item within a bag will be identified for composition.
- After identification, weight measurements, and video operations are complete, the entire contents of a drum will be amply slashed and placed in a single test container.
- Any sealed container within the waste will be amply punctured to allow brine to enter.

The technicians visually characterizing the waste will be trained to perform those tasks according to similar work performed in the Size Reduction Facility at Rocky Flats Plant and the bin-scale waste-characterization work at Argonne National Laboratory-West. Experienced waste handlers will be available to aid the technicians in identifying diverse waste components.

Liter-Scale Tests

Visual and physical characterization of the core samples drilled from the homogeneous waste drums will consist of the following:

- The core sample will be weighed.
- The volume of the core sample will be estimated relative to the volume of the core drill, which will be known.
- The density of the cored sample will be estimated from the estimated volume and the measured weight.
- Visual and physical characteristics will be noted.
- The volume of the core(s) to be placed in the liter-scale test containers will be, at most 75% of the volume of those containers. Exceptions to the waste volume-to-brine ratio may be necessary to achieve a sufficiently liquid sample for selected experiments.
- More than one core may be taken to meet the required core sample volume. The core of cemented material (Envirostone, Portland, or other solidification agents) may be as much as 2 to 4 in. in diameter and of various depths.
- The top of the 55-gal. drum will be visually inspected to ascertain whether the cemented or homogeneous content appears to be fairly uniform.

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- The contents from core sampling will be placed in a comminution device, if necessary, to reduce the pieces to millimeter and centimeter size. Less than 10% of the comminuted waste may be centimeter-sized particles.
- Comminution of a certain fraction to micrometer-sized particles will be acceptable. The optimal size of comminuted particles has been established by experimentation.

The coring drill used for obtaining the cores will be constructed to yield a core volume of 1L or more with several core-sampling operations. Cores from one 55-gal. drum will be used to load only one liter-scale test container.

II. (d) Design and Loading of Test Containers

Test Container Design

The test containers for the drum-scale tests must hold the entire contents of actual waste from a 55-gal. waste drum. The liter-scale test containers must hold an aliquot drilled from a 55-gal. drum of, what has been termed, homogeneous waste. The wastes in both sizes of test containers will be immersed in brine for at least 2 years with the possibility of extending the time to 10 years. The test containers must have a sampling system that can sample headspace gas and brine leachate without spreading contamination. Each test container must be designed to be agitated in a manner that completely mixes the waste within the brine. The drum-scale test containers will have a pressure-relief device that relieves the pressure at about 5 psig. LANL will test prototypes of the drum-scale and liter-scale containers for all necessary parameters including leak-tightness.

Drum-Scale Test Containers

Materials

The drum-scale test containers designed for the STTP will be fabricated from titanium metal that is resistant to long-term corrosion by saturated brine at 30°C. Materials considered for internal components are titanium and Kynar- or Halar-coated type 316 stainless steel, but titanium was the material selected for both liter-scale and drum-scale test containers.

Pressure Indicator and Pressure Relief Valve

Each drum-scale test container will have a pressure indicator to provide a means to monitor the rate of pressure buildup and the total pressure at any time. A pressure-relief device will relieve the pressure at about 5 psig.

Heating

The brine in each drum-scale test container will be heated to 30 ± 5°C by air temperature heating in the enclosure.

Temperature Monitoring

The temperature of the brine inside each test container will be monitored and recorded to provide a semicontinuous record of the brine temperature. The temperature sensors may be disconnected during the agitation step of the test and reconnected afterward.

Container Size

Each drum-scale test container must contain the entire waste contents of a 55-gal. drum, additives, backfill if required, and sufficient brine to yield an aqueous solution that will totally immerse the waste and remain liquid. A

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container size of 65 gal. is sufficient to ensure immersion and liquidity for the 2-year test period or longer.

Gas Sampling

The drum-scale test containers will be designed to allow accumulation of gas near the top end of the drum when the drum is lying on its side. The drum will be placed at a slight angle to allow the gases generated by the various processes to accumulate in the gas accumulation chamber near the top of the container. A headspace volume of less than 10% of the volume of the test container is acceptable. A rough mesh filter will surround the gas volume to prevent it from becoming clogged with waste material during agitation. Samples of headspace gas will be taken with a specially designed gas syringe or sample loop for injection into a gas chromatograph (GC).

Leachate Sampling

The brine leachate in the drum-scale test container will be sampled with a sampling syringe capable of taking a 50-mL sample through one of two brine leachate ports on the lid of the drum. The two sample ports will include leak-tight septa and will be designed to permit sampling from two different locations within the test container, one near the top and another near the bottom third of the container. Samples taken from the sample port extending to the bottom third of the test container will be taken until the sample tube is flushed out. The sampled solutions may be re-injected into the test container after sampling. To prevent the two sample ports from clogging, screens will cover the ends of the tubes extending to different elevations in the containers. The test containers will be designed to allow injection of brine or other solution additives should the need arise. The sampling syringe will be tested to ensure that actinides are not adsorbed onto the surface of the syringe. Tests conducted to determine the adsorption of radioactive species will include addition of actinides at different tracer concentrations into Brine A solutions and measurement of the percentage adsorbed onto the syringe walls.

Agitation Device

Each drum-scale test container will have an agitation device that will allow complete rotation of the container to totally mix the contents immersed in brine. The containers will be agitated once per week for the entire 2-year or longer test period to ensure that all solid material is mixed with brine and that the actinide concentrations are homogeneous in the brine. The sample port that extends to the bottom third of the drum-scale test container will serve as a paddle during rotation to ensure total immersion of all objects in the brine. The drums will nominally be rotated at a rate of approximately 8-14 revolutions per minute for a period of ~ 5 minutes. This time period may be either increased or decreased as the project continues.

Leak-Tightness

The drum-scale test containers were initially designed to meet the theoretical leak-rate criterion for brine containing activity levels of 200 μCi/mL. A prototype to meet this criterion was built and tested. SNL established criteria for oxygen ingress and set a theoretical limit of 5 ppm of O_2 ingress per year (5 μL/L/yr or 0.0137 μL/L/day). The containers cannot be evacuated to high vacuum, so leak testing must be conducted by purging or controlled-vacuum leak testing with helium. To meet the O_2 in-leakage target limitation, the titanium drum-scale test containers are fabricated with two O-rings (viton). A groove between the O-rings can be evacuated or purged to eliminate O_2 in-leakage by diffusion through the O-ring material. The three major connecting penetrations into the lid will be sealed with TORRseal to eliminate leaks through the fittings used for sampling brine and headspace gases. Further, the existing pressure gauge will be replaced with a higher quality pressure gauge or a pressure transducer. The septum used for taking samples will be valved off after a sample is taken. The containers will be tested by helium leak testing.

Liter-Scale Test Containers (Low Pressure)

Materials

The liter-scale test containers will be fabricated of titanium. A prototype container will be tested to meet performance standards before the other low-pressure containers are fabricated.

Pressure Indicator and Pressure-Relief Valve

Each liter-scale test container will have a pressure indicator to provide a means to monitor the rate of pressure buildup and the total pressure at any time. The pressure in the liter-scale test containers can be relieved to about 5 psig through a manual valve; the pressure relief valve will operate at 30 psig.

Heating

Initial heating of the brine to 30 ± 5°C in the liter-scale test containers will be accomplished by air heating within the temperature-controlled enclosure.

Temperature Monitoring

The temperature of the liter-scale test containers will be monitored in a manner similar to that for the drum-scale test containers.

Container Size

The size of the liter-scale test containers will be driven by the capacity necessary to contain ~1L of a homogeneous (cemented or otherwise solidified) waste that has been drilled to yield millimeter- to centimeter-sized particles and remains fully liquid after addition of brine and additives. The volume of the liter-scale test container is ~3L.

Gas Sampling

The liter-scale test containers will be designed to allow gas generated by microbial, radiolytic, or corrosive reactions to accumulate at the top of the container when it is in an upright position. Screens will be added to the internal headspace volume to prevent the gas volume from becoming clogged with waste material during agitation. Headspace gas samples will be extracted with a specially designed syringe through a leak-tight septum or a sample loop for injection into a gas chromatograph (GC).

Leachate Sampling

Brine leachate from the liter-scale test containers will be sampled with a syringe through a leak-tight septum. The specially designed syringes will be capable of extracting 50-mL sample from a single sample port near the top of the container. The sample nozzle inside the container will be protected by a screen to prevent the sample port from being clogged by comminuted waste. Fresh brine will be injected with a syringe to replace the sampled brine leachate.

Agitation Device

The liter-scale test containers will be placed in several linear arrays that will allow agitation by 360° rotation. A set of 8 to 12 containers will be rotated by a motor. Temperature leads and pressure-relief connections may be disconnected during agitation, which will be once per week for 10 to 20 minutes (nominally 15 minutes). The agitation must be sufficient to ensure that all solid material is completely immersed in brine and that actinide concentrations are homogeneously distributed.

Leak-Tightness

Each test container prototype will be leak-tested with helium or an equivalent means and certified by the vendor before shipment to LANL. LANL personnel will also test the container for leak-tightness using an inert-gas (preferably helium) leak-check technique. LANL will test the prototype by adding a brine solution and examining the containers for leaks. The sampling system will be tested with a filled test container. The goal is for a test container to be free of detectable brine leaks. The containers must be leak-tight to simulate the oxygen-depleted environment in the WIPP disposal rooms that will promote anaerobic and anoxic reactions in the test containers.

The liter-scale test containers were initially designed to meet the leak-rate criterion to maintain contamination control for brine having activity levels of 200 μCi/mL. A prototype to meet this criterion has been built and tested. SNL established criteria for oxygen ingress at a theoretical limit of 5 ppm of O_2 per year (5 μL/L/yr or 0.0137 μL/L/day).

The prototype liter-scale test container without the pressure gauge has been helium leak-tested at LANL to a helium leak rate of less than 1×10^{-9} cm^3/s.

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The containers can withstand vacuum and can be helium leak tested. To meet the target criterion of 5 ppm of O_2 ingress per year, the containers will be fabricated with two O-rings (viton). A groove milled in the lid between the two O-rings will be evacuated or purged with an inert gas to eliminate in-leakage of O_2 by diffusion through the O-ring material. The two connecting penetrations with fittings screwed into the lid for sampling of brine and headspace gases will be TORRsealed to eliminate leaks. The septum used for extracting samples of brine or headspace gases can be valved off after samples are taken. The existing pressure gauge may be replaced with a higher quality pressure gauge or a pressure transducer, if appropriate.

Pressurized CO_2 Test Containers

The STTP test matrix includes six liter-scale tests to be conducted at 60 bars with CO_2 gas. The pressurized CO_2 tests will determine if the lower p*c*H will affect actinide concentrations or if an increase in the carbonate concentration at lower (more acid) p*c*H will increase actinide carbonate concentration at lower (more acid) p*c*H will increase actinide carbonate complexing (solubility). These six containers will undergo a more extensive review--including a review by the LANL Pressure Vessel Committee--than will the low-pressure containers. The containers will be constructed of titanium that can safely contain the waste at 60 bars and is inert to brine at that pressure and 30°C. The 60-bar test containers will be pressurized with CO_2 gas as well as headspace gases generated during the test. The containers will have a single sampling port and perhaps a pressure-adjustment port to maintain the pressure at 60 bars. The containers will have a pressure gauge with a range of 0 to 2000 psig. A sample of about 25 mL of brine will be taken at 60 bars and forced through a series of filters having nominally 5 and 1 μm pore size at 60 bars. The filters will be tested to determine the maximum differential pressure allowable. No attempt will be made to re-inject fresh brine into these test containers. The ratio of comminuted waste to brine will be decreased, and samples will be taken three times per year. The filtration of the brine leachate sample at pressure is important, and every effort must be made to complete the filtration even if one or two of the filters must be eliminated.

Loading of Test Containers

The waste having the proper TRUCON codes will be characterized and prepared for loading into each test container as described in section c. Once each container is loaded with waste, additives will be added as specified in the test matrix of the technical requirements document. The test matrices for the drum-scale and liter-scale tests are shown in Appendix A. The opening of the waste drums, waste characterization and preparation, and subsequent loading with all required additives will be done at the LANL WCRRF. The technical requirements document specifies addition of actinides, neodymium, brine, bentonite, iron, and chelation/complexing agents to specific tests. These additional operations are described below.

Bentonite

The technical requirements document specifies that the test matrix include bentonite because it was considered a potential backfill material for the WIPP disposal rooms. Three drum-scale experiments containing TRUCON code 116 (typical combustibles) and six liter-scale experiments containing TRUCON codes 111 (dewatered, aqueous, inorganic process sludge) and 124 (pyrochemical salt wastes) are to receive a mixture of 70 wt% crushed WIPP salt and 30 wt% bentonite. To determine the proper amount of brine to add, various mixtures of brine and salt-bentonite will be periodically shaken for 2 weeks and allowed to settle for 1 day. The ratio of free liquid to settled solids will be estimated to determine if enough free liquid is present to allow unimpeded sampling of leachate. SNL personnel will conduct an experiment following the guidelines specified in the technical requirements document to determine the brine-to-backfill ratio. The addition of bentonite to the containers will test the effectiveness of bentonite as a sorbent for actinides and will identify the potential for mobilization of actinides through adsorption onto exfoliated clay colloids. For the drum-scale tests requiring backfill, the test containers will be half-filled with waste and loaded with the appropriate brine-backfill mixture to fill the drum. The crushed WIPP salt will be furnished by SNL. The bentonite will be provided by SNL.

Actinides

The major objective of the STTP is to measure the solubility- and colloid formation-determined concentrations of thorium, uranium, neptunium, plutonium, and americium in brine leachate. Therefore, the total quantities of actinides in the test containers must be sufficient to ensure that the concentrations are not limited by the actinide quantity. The actinides will be added as soluble salts from an individual capsule.

Plutonium

The STTP technical requirements document specifies a plutonium loading of 5g per 55 gal. or 25mg/L. Waste drums having appropriate TRUCON codes will have >5g of plutonium per 55 gal. drum. Core samples taken from homogeneous (cemented or solidified) wastes will contain a minimum of 25 mg of plutonium per liter of waste. Plutonium-239 will be the predominant isotope in the waste. Drums failing the 5g per 55-gal. volume criterion will not be used for the tests. Preliminary review of the waste profile sheets for the waste drums earmarked for the STTP shows that the drum-scale test containers will contain an average of ~20g of plutonium.

Thorium-232, Uranium-238, and Neptunium-237

The drum-scale test containers will be loaded with an equivalent of 5g of each isotope per 55 gal. of waste drum volume. The liter-scale test containers will be loaded with an equivalent of 25mg of each isotope per liter of waste volume. The three actinide isotopes will be added as soluble salts, preferably, chlorides. The spike isotopes will be added as Th(IV), U(VI), and either Np(IV) or Np(V). The weight of each actinide salt will be measured to an accuracy of 0.5%.

Americium-241

Approximately six liter-scale test containers (TRUCON 111 and 124) will receive 25mg of ^{241}Am per liter as a soluble americium salt if that concentration is not already present. The other three actinides (^{232}Th, ^{238}U, ^{237}Np) will also be added to these containers. The remaining liter-scale and drum-scale test containers will receive an equivalent quantity of neodymium as Nd(III) added as a surrogate ^{241}Am. The quantity and form of the neodymium are described in section i, "Development of Analytical Methods for Brine Leachate."

Iron

A principal sorbent in the WIPP disposal rooms is expected to be rust from corroded drums. Because the key design of the test containers uses materials inert to brine, iron must be added in the form of low-carbon steel wire mesh to most tests to simulate the effects of corroding steel drums and boxes in the WIPP disposal rooms. The total surface area of the iron added to each container will be such that the ratio of surface area to container volume will be approximately the same as that of a 55-gal drum having a bare steel interior. The estimated surface area of a drum is 4m^2. The wire will be thick enough to prevent complete rusting through over the lifetime of the tests based on rates of anoxic corrosion in brine.

Iron in the brine leachate will affect *E*h, sorption, colloid generation, and usurpation of chelating agents. All drum-scale tests and approximately 33 of the liter-scale tests will have added iron; 6 liter-scale tests will be run without iron to determine if the iron is significant in generating iron-based colloids, replacing plutonium-based colloids, or controlling solution *E*h. SNL will determine the quantity of iron to be added as given in the technical requirements document.

Chelating/ Complexing Agents

Carbonate, hydroxide, and chloride are the anions present in the WIPP disposal rooms in the greatest quantity. However, the stability constants of the actinide anionic complexes with carbonate, hydroxide, or chloride may be considerably lower than for organic complexants such as citrates, tartrates, oxalates, or EDTA. Some of these ligands are present because of their use in decontamination procedures and others are produced by denitrification by alcohols and organic acids, which act as reductants. The ligands listed in the technical requirements document that are present in the waste inventory and may influence actinide solubilities include:

- acetamide,
- acetate,
- ascorbate,
- tartrate,
- citrate,
- lactate,
- oxalate,
- bis(2-ethylhexyl) phosphoric acid (DHP),
- EDTA,
- 2-hydroxquinoline,
- 1,10-phenathroline,
- TTA,
- thiocyanate, and
- DHDECMP

The chelators that have been added to the test containers were to be added in two batches. A batch of major chelators added at the ~200mg/L concentration in the three drum-scale test containers and 75 to 100 ppm in the three liter-scale test containers.

1) Ascorbic acid,
2) oxalic acid, sodium salt • $2H_2O$
3) Acetic acid, sodium salt
4) Citric acid, sodium salt • $2H_2O$
5) Acetamide
6) Sodium thiocyanate

A batch of minor chelators may be added at a later date, if appropriate, with a concentration of 30 mg/L including the following compounds.

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These minor chelators (30mg/ml) are:

1) Lactic acid, Na salt
2) 1,10 phenathroline
3) α-hydroxyisobutyrate
4) 8-hydroxquinoline
5) DHDECMP (Dihexyl-N-N-diethylcarbamoyl methyl phosphonate)
6) EDTA.

Brine

The brine solution used to fill the test containers will be a mixture of synthetic Brine A or Castile Brine with brine collected from the WIPP underground or brines developed from salts taken from the WIPP underground. There is not a sufficient volume of brine available from the WIPP underground to conduct the tests solely with natural brine. For this reason, all tests will use a brine consisting of a mixture of 90% Brine A or Castile Brine and ~10% inoculum prepared from natural sources. Table 1 illustrates the composition of these Brines:

Table 1. Composition of Salado (Brine A) and Castile Brines

Compound	*Brine A (g/l)*	*Castile Brine (g/l)*
$MgCl_2 \cdot 6H_2O$	292.10	3.86
NaCl	100.10	261.64
KCl	57.20	7.23
Na_2SO_4	6.20	23.70
$Na_2B_4O_7 \cdot 10H_2O$	1.95	6.00
$CaCl_2$	1.66	1.33
$NaHCO_3$	0.96	0.00
NaBr	0.52	1.13
LiCl	0.125	0.00
RbCl	0.027	0.00
$SrCl_2 \cdot 6H_2O$	0.015	0.00
KI	0.013	0.00
$FeCl_2 \cdot 6H_2O$	0.0125	0.00
CsCl	0.00125	0.00

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The proportion of Brine A to the bacterial inoculum will be supplied by SNL. The temperature of the test vessels will be monitored externally while the brine is added to the loaded test containers to preclude temperature excursions to greater than 50°C, which may harm the microbes. Alternatively, addition of the natural brine containing the microbes may follow the synthetic brine. The brine volume added to the containers will be known to at least 1% of the total brine volume as measured by the mass of brine added. The headspace volume after the test container is filled with brine should be less than 10% of the volume of the test container. The sealed container will be purged with an inert gas before the tests are begun.

II. (e) Test Matrix

The STTP is designed to measure radionuclide concentrations in brine under sets of chemical conditions that can reasonably be expected within the WIPP disposal rooms. Therefore, incorporation of waste types that will generate a broad spectrum of conditions are required. The test matrix is designed to quantify the sensitivity of actinide concentrations to these conditions. The range of chemical environments possible within a given waste type cannot be known with certainty, and it is unreasonable to attempt to define a "representative sample" for a class of TRU waste. Rather, this program is intended to sample actinide concentrations principally from those waste types that are expected to yield combinations of influences typical of those that may be encountered in WIPP disposal rooms. These results will be used to test the hypotheses outlined in section a, Introduction, "Rationale and Description of STTP." The test matrix specifies waste types that create a set of conditions that sample each of the variables that are expected to influence actinide concentrations. The waste types tested in the proposed matrix are described in the following subsections. These waste types are categorized by TRUCON code (DOE/WIPP 1989) and are selected from these categories based on listed contents, process knowledge, and actinide content. Three replicates of each experiment are required so that probability intervals can be established for the actinide concentrations from each set of conditions tested. Note that the STTP is a highly technical experiment requiring research and development. Therefore, the waste types selected could change depending on the needs of the experimenters. Further, the test matrix specifics may also need to change as the project progresses.

Drum-Scale Tests

Combustibles, TRUCON 116/216 (D1-3)	Of significance in these drum-scale tests are the effects of cellulose degradation on actinide concentration. Aerobic oxidation and fermentation will lower system *E*h. Denitrification may produce complexing agents such as citrate and lactate. Complexing agents from decontamination activities may already be present in the waste and will make up the bulk of complexing agents withdrawn in the leachate at early times.
Combustibles with Bentonite Backfill (D4-6)	The results from these experiments can be compared directly with those from tests, D1-3. These results will indicate the effectiveness of brine equilibrated bentonite, a reference backfill, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids.

Combustibles with Added Chelation Agents (D7-9)

Although fermentation and denitrification of cellulose are predicted to yield complexing agents, this condition conceivably may not occur during the time frame of the STTP. These experiments test how actinide solubility is affected by a system containing both "naturally occurring" ligands (such as lactate) and ligands introduced as part of the waste stream (such as EDTA). As it is not reasonable to assay drums for chelating agents as part of waste selection, these drums must be prepared by spiking the ordinary combustible waste with the major chelators described in section d, "Actinides."

These tests will follow ligand concentration over time to observe if microbial activity can act as a sink or source of complexing agents.

Combustibles with Added Nitrate and Phosphate, TRUCON 116/216 and 111/211 (D10-12)

In denitrification, cellulose or its fermentation products are oxidized by bacteria capable of using nitrate as an electron acceptor. The NO_3 is in turn reduced to N_2 or NH_3. Denitrifying bacteria can oxidize organic acids to α-hydroxy acids, which are effective complexing agents. The presence of nitrate in process sludges may be significant in promoting this process in combustible waste.

In these experiments, nutrients in the form of sodium nitrate and sodium phosphate are added to the test containers to study their effect on microbial activity. $NaNO_3$ and NaH_2PO_4 was added at the 0.01M level for the 210 liter volume, 180 and 300 grams, respectively.

Metals, TRUCON 117/217 (D13-15)

Metals capable of corroding under anoxic conditions can reduce system *E*h below the stability limit of water, possibly stabilizing Pu(III) in solution. Both iron (from mild steel) and aluminum will anoxically corrode in brines. Less active metals such as copper and lead may also corrode if H_2S (from sulfate reduction) is present. A protective polyethylene liner was added to these drums to prevent damage to the test container walls during rotation.

Liter-scale Tests

Solidified Aqueous Inorganic Process Sludge, TRUCON 111/211, (L1-3)

This sludge is described as Los Alamos 111A, concreted aqueous waste, which is a corrosive and radioactive liquid waste that has been neutralized to a slightly basic slurry with $Ca(OH)_2$, ferric sulfate, and a flocculation aid. This slurry was solidified in 55-gallon drums with various portions of Portland Cement, vermiculite, and sodium silicate.

Solidified Aqueous Inorganic Process Sludge, TRUCON 111/211 with CO_2 at 60 Bar (L4-6)

The composition of these sludges is similar to L1-3. These tests will be conducted with a headspace pressure of about 60 bar with CO_2. The pressurized test containers will be sampled for brine at pressure and filtered at pressure. It is reasonable to assume that the actinide solubilities, especially U, could be affected by decreased pH and carbonate complexation. The results from these tests could be directly compared with L1-3.

Solidified Aqueous Inorganic Process Sludge, w/o Fe, TRUCON 111/211 Portland Cement (L7-9)

Corroding steel in the disposal rooms provides a possible sink for actinides through sorption. However, CO_2 in the rooms might passivate steel by forming a surface layer of siderite ($FeCO_3$), which would render much less iron oxide available for actinide sorption. These experiments test the effect on actinide concentration of removal of iron oxides from the system, eliminating sorption of actinides by these phases.

Solidified Aqueous Inorganic Process Sludge w/o Fe, TRUCON 111/211 Portland Cement; ^{241}Am added (L10-12)

In addition to providing a source of sorbants, corrosion of steel also lowers brine *E*h in its vicinity. Without steel (or other active metals), the oxidizing effects of radiolysis may dominate the *E*h of the system. These experiments measure actinide concentration, and possibly speciation, under the most oxic conditions reasonably attainable in the rooms.

Absorbed Organic Liquids, Envirostone, TRUCON 112/212 (L13-15)

These experiments will determine if high concentrations of organic solvents and reagents in the brine significantly promote dissolution or suspension of actinides. If the waste contains exclusively solvent residues, their effect will be minimal. However, if chelating agents, extractants, or detergents are present, their effect on actinide concentration could be significant.

Absorbed Aqueous Laboratory Waste in Envirostone, TRUCON 113/213 (L16-18)	These are laboratory wastes that have been neutralized or made slightly basic and solidified with Envirostone. The high salt content and possible high organic content including chelating agents may increase actinide solubility.
Cemented Inorganic Particulates (Sludge) in Envirostone, TRUCON 114/214 (L19-21)	This waste form is process residue from evaporator bottoms and other discardable solutions, process leach solids, ash, filter cakes, salts, metal oxides, fines, etc. These tests will determine the effect of increased pH and particulates from process waste streams.
Cemented Organic Sludge Solidified with Envirostone, TRUCON 126/226 (L22-24)	These wastes are process residues from evaporator bottoms and other discardable solutions, process leached solids, ash, filter cakes, salts, metal oxides, fines, etc. This waste has been immobilized in Envirostone with a possible presence of chelators.
Pyrochemical Salt Wastes, TRUCON 124/224 (L25-27)	The pyrochemical waste forms used for the STTP tests were the wastes developed from the Direct-Oxide Reduction (DOR) process or the Oxygen Sparging process and included pieces of MgO crucibles that had been ground up. The waste from the DOR process could contain $CaCl_2$, CaF_2, Ca metal, CaO, and magnesia (MgO) from the MgO crucible. The pyrochemical salt wastes from DOR and O_2 sparging processes generally contain relatively higher levels of Pu and Am which could result in increased levels of brine radiolysis and perhaps more oxic conditions from oxidizing products of radiolysis. If unreacted Ca remains in the waste or if higher concentrations of CaO or $Ca(OH)_2$ are in the waste, the brine become more basic upon dissolution of the Ca or Ca compounds. L25, 26, and 27 were pyrochemical salts from the DOR process.
Pyrochemical Salt Wastes with Added CO_2, TRUCON 124/224 (L28-30)	This test has pyrochemical salt wastes from the DOR process as discussed in "Pyrochemical Salt Wastes" just above, but with added CO_2 pressure at about 60 bars (~870 psig). Any basicity from the Ca compounds should be neutralized by the CO_2 headspace. The bicarbonate and carbonates formed from the CO_2 may increase the solubility of actinides, especially uranium.

Pyrochemical Salt Wastes with Brine-Equilibrated Bentonite, TRUCON 124/224 (L31-33)

These tests contain wastes from the oxygen-sparging process with added brine-equilibrated bentonite. The O_2 sparging process resulted in wastes as discussed in the "Pyrochemical Salt Wastes with Added CO_2" section above but also contained oxidized salts (Ca, Na, K) generated by the electro-refining process. The results from these tests could indicate the effectiveness of brine-equilibrated bentonite, a potential backfill material, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids. These tests could also determine the effectiveness of bentonite as an actinide sorbent in the presence of high concentrations of divalent ions (particularly Ca^{2+}), which compete with the actinides for sorption sites on the clay particles.

Pyrochemical Salt Wastes with $Ca(OH_2)$ & Chelators, TRUCON 124/224 (L34-36)

This set of tests consists of L34 with pyrochemical salt wastes from the O_2 sparging process and L35 and 36 with wastes from the DOR process. All three tests have added $Ca(OH)_2$ to increase the basicity of the brine and to determine the effect of the basic solution on generated CO_2 and increased carbonate production. Major chelators have been added to the three test containers as discussed earlier in this section under "Combustibles with Added Chelation Agents" for the drum-scale test containers. These tests should indicate the solubilizing effect of major chelators on actinides in a basic solution.

Pyrochemical Salt Wastes with added ^{241}Am, TRUCON 124/224 (L37-39)

This set of tests consists of L37 with pyrochemical salt wastes from the DOR process and L38 and 39 with wastes from the O_2 sparging process. All three tests have added ^{241}Am, which may render the system more oxic and provide an indication of Pu-238 effects on brine chemistry. The oxidizing products of radiolysis such as O_2, H_2O_2, or OCl^- if they are stable in the high brine solutions may enhance corrosion of iron that could in turn actually provide a reducing effect on the system. These tests may provide an indication of the redox chemistry with increased radiolysis.

The test matrices for drum- and liter-scale test containers include all combinations of solubility-influencing variables judged sufficiently different to require testing. The two test matrices were developed by collaborative effort between SNL and LANL.

II. (f) Sampling and Analysis of Brine Leachate and Headspace Gases

Sampling of Brine Leachate

Brine leachate samples of 50-mL volume will be taken from one of two sample ports on the top (lid) of the drum-scale test containers for analyses of all the parameters specified in the STTP technical requirements document. Samples will be taken from a single sample port on the top of the liter-scale test containers for analyses of all the parameters specified in the STTP technical requirements document. Fresh brine with inoculum will be re-injected into the liter-scale containers but not to the drum-scale test containers. The pressurized, liter-scale test containers will be sampled by a different procedure developed specifically to sample at 60 bars pressure. Pressure will be maintained as close to 60 bars as possible, and an ~25mL sample will be taken and filtered at pressure with a minimal pressure differential across the filters. Samples will be taken three times per year. In the pressurized test containers, fresh brine will not be added to replace the sampled brine.

The goal of the brine leachate sampling is to obtain and analyze a representative sample without changing its composition during sampling, sample transfer or preparation, and interim sample storage. Leachate will be placed in polyethylene bottles that have been purged with an inert gas. Analysis will be conducted as rapidly as possible to avoid deterioration of the sample. Dual samples will be taken during the initial three samplings to evaluate whether samples taken from different regions within the drum-scale test containers are well mixed as demonstrated by similar actinide concentrations and brine chemistry.

A sampling schedule for each test container will include a plan to modify the schedule if unforeseen delays are experienced. About 16 samples will be taken from each container over the 2-year period with about 3 initial dual samples or about 10 samples per year.

The settling time of each test container will be at least 18 to 32 hours after agitation. Exact specifications of time are inappropriate because the settling time may be adjusted throughout the tests based on prior results and the needs of the experimenters. Experiments in which colloid concentrations are measured as a function of settling time in quiescent containers may be performed after solubility studies in these containers have been completed.

The sampling operation will be conducted according to a procedure that includes the most meticulous approach to enhance contamination control of the STTP Wing 9 enclosure. The sampling operation has been tested repetitively on nonradioactive samples as part of the training of samplers to preclude confusion and delays during sampling of radioactive brine and to shorten time an analyst must spend in the enclosure, thereby promoting the principle of "as low as reasonably achievable," ALARA.

Sampling and Analysis of Headspace Gases

The test containers have been designed to allow for a minimum of headspace gas volume to accumulate at the tope of a container lying on its side and at a slight uphill angle. Initially, the headspace gas will be a mixture of an inert gas used to purge the headspace volume and the accumulated gases that percolate to the headspace by outgassing of soluble gases in the brine and entrapped gases in the waste. Eventually, the headspace gases will be vented or sampled so that the gases accumulating in the headspace will be those generated by microbial, corrosion, and radiolytic processes. SNL has allowed a headspace volume of up to 10% of the test container volume.

The composition of the gas in the headspace will be measured to determine whether microbial decomposition of cellulose and anoxic corrosion of steel is taking place. Because both corrosion and microbial processes are controlled by system *E*h, gas composition is a qualitative *E*h indicator. Gas will be sampled simultaneously whenever possible so a particular set of brine leachate samples so analytical measurements made on the brine leachate can be correlated with the gas composition. The composition of gases in the headspace may be influenced by the four processes shown in Table 2.

A requirement of sampling the headspace volume is to minimize ingress of air so that the relative concentrations of the radiolytic, corrosion, and microbe-generated gases can be measured. The STTP test containers have been designed to minimize ingress of air into the headspace volume.

Table 2. Composition of Gases Produced by Various Processes

Process	*Gas Composition*
Corrosion	H_2, CO_2
Microbial decomposition	CO_2, CO, CH_4, N_2, H_2S, and N_2O
Radiolysis	O_2, H_2, CO, CO_2
Leakage	O_2, N_2, Ar, CO_2 (Air)

Design and Procedure

The drum-scale test containers will be filled with brine so that the headspace is less than 10% of the test container volume to allow generated gases to accumulate at the top (lid) of the container while the container is positioned on its side. The 360° rotation of the container will ensure that the waste contents are adequately mixed with the brine. The brine leachate sampling tube extending to the lower section of the test container will serve as a mixing paddle during agitation and promote the release of gas bubbles. Tilting the test container so the gas chamber is the highest part of the container will allow the gas to percolate to the accumulation chamber.

Continue on next page

Samples will be obtained from the gas chamber by a specially designed syringe with a long needle that will penetrate a leak-tight septum or with a multiloop sampling device that can be evacuated and purged. The internal nozzle of the gas accumulation chamber will be screened to prevent clogging by waste items. Once a sample of gas (about 2 to 10 mL) is extracted, the gas sample will be allowed to come to ambient temperature, then transferred in a sample carrier via the CST Sample Management Task Area (Sample Management) to the gas analysis laboratory. A portion of the sample will be injected into a GC having a thermal conductivity detector, discharge ionization detector, or other appropriate detector system or combination of detector systems.

Control of Contamination

The sample of headspace gas will be taken with a long-needle syringe through a leak-tight septum or with a sample loop. A contamination-control apron will be placed under the sample port during the sampling. The syringe or sampling look will be placed in an enclosed sample carrier during transfer to the laboratory. The needle will be decontaminated before the sample is injected into the laboratory GC. The insertion septum in the GC will be valved-off and replaced periodically to ensure leak-tightness and control of contamination.

Composition of Headspace Gases

The gases accumulated in the headspace will be analyzed qualitatively for all major components. However, the gases listed in Table 3 are specified in the STTP technical requirements document and will be analyzed semi-quantitatively according to Level II DQOs.

Table 3. Gases Determined Semi-quantitatively

Gas	*Requirement*
H_2	STTP
O_2	STTP
CH_4	STTP
CO	STTP
CO_2	STTP
H_2S	STTP
N_2	STTP
N_2O	LANL
VOCs	Waste characterization (State of New Mexico Requirement)
Other	LANL (as determined by LANL)

Schedule of Sampling and Analyses for Gas and Brine

The gases to be analyzed in the headspace of liter-scale and drum-scale test containers are expected to be dominated by N_2 and O_2 because of the continual evolution of soluble gas dissolved in the brine. After several purging cycles with He, the gases generated by corrosion, microbial, and radiolytic processes should become the major gases in the headspace. Several gases are anticipated to be generated by the different processes including H_2, CO_2, CO, and CH_4. N_2O could be significant as microbial activity increases. The different gases to be determined on a relative and semi-quantitatively basis are given in Table 3. The schedule for gas sampling is included in Table 4. Other gases may be analyzed as determined by their identity as the experiments progress. More samples may be scheduled to identify the source of rapid gas producers.

The brine samples to be taken from the liter-scale and drum-scale test containers will be scheduled as each of these experiments are completed at the WCRRF and come to temperature equilibrium in the liter-scale and drum-scale environmental enclosures in the CMR Building. The sampling schedule for brine from the liter-scale and drum-scale test containers is given in Table 4. The sampling schedule for the six pressurized test containers is also included in Table 4.

Table 4. Sampling Schedule for Brine and Headspace Gas

Scheduled Frequency	*Drum-Scale Tests*	*Unpressurized Liter-Scale Tests*	*Pressurized Liter-Scale Tests*
# of containers	15*	33	6
Brine			
First Year			
Months 1-3	15 x 2 x 3 = 90**	33 x 3 = 99	
Months 4-12	15 x 4 = 60	33 x 4 = 132	6 x 3 = 18
Total	150	231	18
Subsequent Years	15 x 6 = 90	33 x 6 = 198	6 x 3 = 18
Gas			
Each Year	15 x 12 = 180	33 x 12 = 396	No Gas Sampling

* 2 brine blank drums sampled occasionally.
** 15 x 2 x 3 means all 15 drums sampled both long- and short-tube samples each month for 3 months.

Quality Assurance/ Quality Control and Data Quality Objectives

The headspace gas samples will be analyzed by direct injection into a GC with a specially designed syringe or sample loop. The GCs will be calibrated with a standard gas containing all the analytes of interest; the standard gas will be analyzed with each batch of samples. The target DQOs for the headspace gas analyses is ± 100% at the 1-ppm level and ± 10% at the 10- to 20-ppm level. Automating the sampling and analyses of each headspace volume would be beneficial, but the rate of gas accumulation is unknown at this time, and the schedule will be modified if insufficient gas is generated. The current plan calls for gas sampling and analyses to be performed manually.

II. (g) Data Packaging

Data Quality Objectives

The DQOs for the STTP are established by a collaborative, iterative, and interactive process between the needs of the data user/decision-maker (SNL) and the data generator (LANL). This effort defines the level of certainty required before the data can be used to augment or allow an inference to be made about the capability of predictive models for dissolution and suspension of actinides in WIPP brines in contact with TRU waste. The DQOs are a means by which criteria may be developed for the STTP for assessment of data quality; they provide a quantitative, measurable objective toward which analyses can be performed. Quality assessment of the data generated to meet the DQOs will provide an objective measure of the success of the analytical processes used to complete each STTP technical analysis. DQOs have been assigned to all STTP processes leading up to and including the test period so that the variables associated with the final data package can be evaluated and assigned a quality factor. DQOs will be assigned to the up-front preparatory activities in the form of instructional criteria, waste characterization guidance, or conditional boundaries, and in the form of detection levels, precision, accuracy, and completeness during the analytical activities conducted to generate the data.

The STTP is a highly technical experiment that requires unique and specialized applications of engineering, waste preparation, test-period activities, and analyses including data reporting. The analyses of brines laden with a diversity of waste constituents and particle sizes and the examination of variables and active processes that influence those analyses require an extensive methods-development period to perform the research and development required to initiate chemical analyses on this complex matrix. Also, the use of actual waste incorporates several unknown variables with each of the experimental tests conducted as part of the STTP test. The detection levels for several analytes challenge the most advanced state-of-the-art instrumentation. Finally, all the STTP analyses will be performed on samples potentially containing high levels of plutonium and americium and will be conducted in gloveboxes or other containment enclosures. Because of the complex and challenging analytical matrices, a collaborative effort between LANL and SNL of what data are needed and the capability of the analytical laboratory to meet those needs and any newly-established needs under the constraints of the experiment will be an on-going process. To meet the requirements of the STTP management plan and the SNL technical requirements document, the following guidelines for establishing DQOs has been established for Level I, II, and III DQOs.

Level I Data Quality Objective Criteria

Level I DQOs are established for performance of qualitative analyses to augment contamination-control requirements, ALARA practices, laboratory safety, or to establish process-knowledge parameters that do not require full quality control elements. Level I DQOs will establish limited quality control parameters and limits; they will be instructional or will provide guidance for

Continued on next page

generation of information that may subsequently be needed for interpretation of data. In general, Level I DQOs will have a target accuracy of ± 30%.

Level II Data Quality Objective Criteria

Level II DQOs are established for performance of analyses or activities that provide technical information on samples that will aid in determining the extent of further analysis on a sample. Level II analyses will serve as a screening tool to establish analytical conditions for other analyses. These analyses will be used to provide the data that analysts will need to determine sample dilutions or concentrations of standards to be used for Level III analyses. Level II analyses will result in relative concentrations of analytes that are based on semiquantitative analytical techniques. Laboratory control standards (LCSs) will be used with an estimate of the precision and accuracy of the analyses. Level II analyses will require the use of primary or well-characterized secondary standards for calibrating equipment and analytical procedures. In general, Level II DQOs have a target accuracy of ± 15-25%.

Level III Data Quality Objective Criteria

Level III chemical analyses are performed with the most meticulous quantitative techniques. These quantitative analyses will include such quality control parameters as LCSs, measurement of method detection limits (MDLs), precision, accuracy, and completeness. The analytical results will be verified by check standards and will be independently reviewed by at least two technical analysts before being incorporated into a data package. Most of the analytical data required by the STTP technical requirements document will be performed according to Level III DQO criteria. The calibration of equipment and analytical procedures will be accomplished with primary standards of well-characterized secondary standards traceable to National Institute for Standards and Technology (NIST) as available.

Table 5 shows the STTP analytical methods along with their established DQO Levels. Table 6 shows estimated target quality control parameters for each measurement as specified in the technical requirements document or established by LANL-SNL collaborative communications. Table 7 shows the DQOs for STTP preparatory activities. In general, Level III DQOs will have a target accuracy of ±10% or less.

Table 5. DQO Levels for STTP Activities

Technical Requirements	*Method/Instrument*	*DQO Level*
Headspace gas analyses	Gas chromatography	II
Brine leachate filtration	Amicon centrifuge	II
Alpha activity measurements	Liquid scintillation counting	II
Total elemental analyses	WDXRFS	II
p*c*H	p*c*H meter, UV/VIS spec.	II, III
*E*H	*E*H electrode	II, III
Actinide concentrations	ICP-MS	III
Elemental analytes	ICP-AES	III
RCRA elements	GFAA, ICP-MS, ICP-AES	II, III
Inorganic/organic anions	IC, ISE	II, III
Total inorganic carbon	Carbon analyzer	II, III
Total organic carbon	Carbon analyzer	II, III
Particle size distribution	Particle size analyzer, SEM	II, III
Colloid characterization	XPS, SEM, EDXRFS	II, III
Filter characterization	WDXRFS, RFS, EDXRFS	II, III
Dissolved organics	HPLC, LC-MS, CE, GC	II, III
Am-241 surrogate, Eu	ICP-MS	III
Waste characterization	Visual, mass	I, II
Brine addition	Brine pump	I, II
TRUCON verification	RTR	I
Pu estimation in waste	SGS, GRT	I, II
Am-241 estimation in waste	SGS, GRT	I
Pu-238 estimation in waste	SGS, GRT	I
Temperature control (enclosure)	Temperature ind/cont	II
Temperature control (test container)	Temperature ind/cont	II
Bentonite/salt addition	Mass	I
Addition of Fe	Mass/surface	I
Test container pressure relief	PSIG relief valve	I
Volatile organic compounds	GC-MS	I, II

Table 6. DQOs for STTP Activities

STTP Activity	*Target Limit of Quantitation*[a]	*Target Limit of Detection*[a]	*Target Precision*
GC for headspace gas	5-10 ppm	1 ppm	± 10%
Brine leachate filtration	<20 nm		
LSC for alpha analysis			± 5%
WDXRFS for elements	5-150 ppm		± 15%
pcH			± 0.2 pcH
*E*h			ND[b]
ICP-MS for actinides (a)		10^{-10} M	± 100%
(b)		10^{-9} M	± 10%
ICP-AES for analytes		100 ppb	± 10%
GFAA for RCRA		100 ppb	± 20%
Anions by IC, ISE		1 ppm	± 10%
TIC	5-10 ppm	1 ppm	± 15%
TOC		1 ppm	± 10%
Particle size analysis			ND[b]
Colloid characterization			ND[b]
Dissolved organic chelators	5-10 ppm	1 ppm	± 20%
Eu by ICP-MS/ICP-AES		100 ppb	± 10%
VOCs by GC-MS		1 ppm	± 20%

[a] Notes on units of measure and terminology. Throughout this test plan, the unit of ppm has generically been used to indicate a level of sensitivity. The term ppm may be used differently for each measurement method as follows:

- gas analysis: ppm = microliters per liter or micrograms per liter, as indicated.
- brine leachate: ppm = micrograms per milliliter or micrograms per gram, as indicated.

A target detection limit may be an indicator for the sensitivity of a method. However, this depends on the background of a blank. For example, TIC/TOC analyses may have an instrument detection limit of 1 ppm over a Brine A background of 100 ppm. The limit of detection in this case will be determined by the relative standard deviation of the signal and the noise level for that analytical method. Because the STTP is a research and development analytical project, the limit of quantitation, limit of detection, precision, and accuracy are target DQOs at this time until methods development activities are complete.

[b] Not Determined.

Table 7. DQOs for STTP Preparatory Activities

Activity	*DQO*
RTR for TRUCON verification	Results must be certifiable
PAN; SGS; GRT for ^{238}Pu and ^{241}Am in waste drums	**For Drum-Scale Test Containers**: @ 5-g level + 200%, - 0% @ 10-g level + 200%, - 50% @ 20-g level + 200%, - 75% **For Liter-Scale Test Containers** @ 25 mg/L + 100%, - 0% @ 50 mg/L + 100%, - 50% @ 100 mg/L + 50%, - 50%
PAN; SGS; GRT for ^{238}Pu and ^{241}Am in waste drums	For Drum-Scale Tests - evaluation For Liter-Scale Tests - evaluation
Actinide loading of test containers	For mass of each actinide: ± 0.5% by weight
Waste characterization	For weight of wastes: ±10% by weight
Brine addition	For volume: ±1% by volume
Bentonite/crushed salt addition	For mass: ±5% by weight
Addition of Iron	For weight: ±5% by weight
Addition of chelators	For amount added: ±20% at 100-200 ppm level
Temperature control of test containers/enclosure	For temperature of Containers: ±2°C For temperature of Enclosure: ±5°C

Data Package Compilation for Brine Leachate and Gas Analysis

Each analytical batch of headspace gas samples and/or brine leachate samples taken during a sampling week will be analyzed along with a set of calibration standard(s).

STTP data management will be according to the *"STTP Data Reduction, Validation, and Reporting Procedure,"* CST-STP-QAP5-017/latest revision.

The data package containing the results of headspace gas and/or brine leachate analyses consists of the following information:

- cover page
- table of contents
- Project Leader's checklist (one per data package)
- summary information for the data package
- information by sample
    - note (for QAM checklist)
    - QAM checklist by test container
    - ITCR (summary) summary checklist by test container
    - Brine analysis data
        - Sample request form
        - Sampling information sheet - brine
        - STTP Sample Filtration/Distribution Checklist
        - STTP Analyst/ITCR Checklist explanation by analysis
        - Task results by analysis
        - Analyst Checklist
        - ITCR checklist by analysis
        - Variance forms for analysis (as needed)
        - Any raw or supporting data (as needed)
    - Gas analysis data
        - STTP Analyst/ITCR Checklist explanations for gas analysis
        - Sample Request form
        - Checklist for gas sampling
        - Gas results
        - Sampling information sheet - gas
        - Analyst Checklist
        - ITCR Checklist by analysis
        - Variance forms for analysis (as needed)

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Each sample in the data package contains the following information:

- test container (liter or drum) identification, e.g., L01, D15
- analytical tracking number (LIMS number, e.g., 2000xxxxx) labeling the sampling syringe
- date and time the sample was taken
- volume of sample taken
- pressure in the test container
- name of the sample taker
- any problems encountered during sampling
- chain-of-custody form (if required)
- name of analysis
- sample result/data
- name of analyst
- holding time for each analysis
- analysis date
- information as to calibrations used
- type of data reduction analytical limits of method

The checklists for each sample are described above under the data package contents.

II. (h) Sample Management

Sample Management obtains a unique sample identification number from the LIMS system to initiate sample tracking and begin the data accumulation process before the sample is drawn. These numbers are attached as barcode labels to the specialized sampling syringes used to sample and transport each sample.

Brine samples taken in the basement of Wing 9 are transferred directly from the Test Enclosures where sampling is performed to the Filtration Area in Wing 5. Only brine samples transferred to analysts outside the CMR Building require a chain-of-custody form. If this is necessary, samples will be transferred according to the *"CST/CMR Chain-of-Custody and Sample Transfer Plan,"* CST-ADM5-008/latest revision. Brine samples have a yellow radioactive material tag identifying each sample as radioactive.

Brine leachate samples taken from STTP test containers will be maintained at 30°C in a temperature-controlled sample carrier and transported to a specially designed temperature-controlled glovebox for filtration and sample preparation before distribution to the analysts in the CMR Building. Every effort will be made to minimize contact of the brine leachate sample with air for those analytical measurements that may be air-sensitive.

Gas samples are brought by the sample takers directly to the gas chromatography laboratory for analysis. The gas samplers and analysts are the same, but the gas samples require neither temperature maintenance nor filtration. These samples are not radioactive.

Holding times for each analysis were determined by the analyst who wrote the procedure for the particular analysis.

Sample Preparation

Temperature Controlled Hood or Glovebox

A specially designed, temperature-controlled glovebox will be the principal receiving point for brine leachate samples from Sample Management. The glovebox will be equipped with heaters and will maintain controlled ventilation and exhaust to ensure a temperature of 30 ± 5°C.

Drum-Scale Test Containers

Brine Leachate Sampling, Filtration, and Sample Preparation

SNL prefers sampling at near-ambient pressure for drum-scale brine samples. This preference will require releasing any pressure buildup greater than 3 psig (as indicated on the pressure gauge) to near ambient before sampling. A 50-mL sample will be extracted from one of two sample ports on the container with a specially designed sample syringe and transferred to the laboratory for filtration in the specially designed sample carrier maintained at 30°C.

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Fresh Brine A will not be injected into the drum-scale test containers to replace the volume of sample taken. The headspace volume will be increased every time a sample is taken but must not exceed 10% of the test container volume. Other parameters to be considered in sampling the containers are discussed under "Sampling of Brine Leachate" of section f.

Liter-Scale Test Containers

SNL has stated a preference for sampling liter-scale test containers at near-ambient pressure because sampling at pressure if the pressure increase is due to CO_2 may change the p*c*H. This preference will require releasing any pressure buildup of >3 psig to near ambient before sampling. A 50-mL sample will be extracted from the single sample port with a special syringe and transferred to Sample Management in the specially designed sample carrier maintained at 30°C. Fresh Brine A will be injected into the liter-scale test containers to replace the volume of sample taken. The headspace volume will increase if fresh brine is not re-injected every time a sample is taken. Other parameters to be considered when sampling the containers are discussed in "Sampling of Brine Leachate" of section f.

Filtration and Sample Preparation

Except for samples earmarked for microbial studies or radiochemical experiments, brine leachate samples (~50mL) will be filtered in the temperature-controlled glovebox through a series of sequential filters (8,5,1μm) to produce a sample that can be filtered through a <20nm filter. If appropriate, specified filters will be analyzed for the material trapped on the filter. The sample will be filtered as soon as possible, and the filtrate will be collected in plastic or silanized glass containers having a positive seal to prevent ingress of air into the container. The filtrate passing through the 1 μm filter will be identified as "coarse-filtered" leachate. An aliquant of coarse-filtered leachate (probably 30-40 mL) will be filtered to <20nm pore with a target of 10nm. Once filtered, sample aliquants will be prepared for each specified analysis (for example, dissolution, dilution, acidification, neutralization) as needed. The filtered material will be saved for potential analysis if required but will not be archived. Brine leachate samples from pressurized test containers will be filtered as described in section d, "Pressurized CO_2 Test Containers."

Distribution of Samples

Once the brine sample preparation is complete according to individual analytical procedure, each sample aliquot (unfiltered, coarse filtered, or fine filtered) is transported to the appropriate analytical laboratory. Holding times for each analysis were established according to the results of the methods development for each analytical method and documented in individual analytical procedures.

Quality Assurance

The quality control elements described in the following sections are the basic elements used to ensure reportable data. A more comprehensive discussion of definitions and definitive calculation is presented in the *"STTP Quality Assurance Project Plan,"* MST5-STP-QAP1-016, latest revision.

Introduction

The objective of quality assurance and quality control for the STTP is to ensure that all activities--selecting the waste, characterizing the waste, loading the test containers, configuring space and equipment in the CMR Building, and controlling test parameters--are an integral part of the data-collection process resulting from analyses of brine leachate and headspace gas samples. DQOs have been targeted for each activity that affects the validity and usefulness of the data package for each set of samples. Level I and Level II DQOs have been assigned to certain preparatory activities designed to yield qualitative data or instructional or descriptive information that is not amenable to statistical analysis but may influence the completeness of the final data package. The DQO for preparatory activities and data derived from those activities is to ensure that the information will be of known and acceptable quality when these data are integrated with later analytical data. The quality assurance objective for analytical data from samples of brine leachate and headspace gases is to ensure that data are of high quality and are amenable to statistical analysis.

The quality assurance/quality control elements that will be included in generation of analytical data and data packages include descriptions and assessments of the precision, accuracy, and completeness at the DQO level assigned to the analysis. Each analytical method having a Level II or III DQO will determine an MDL, a lower limit of detection, an instrument detection limit (IDL), or a detection limit appropriate for that method by standard methods or by the equations given, following. The specific equations to assess precision, accuracy, completeness, and MDLs or IDLs for the STTP are taken from SW-846, "EPA Test Methods for Evaluating Solid Waste," Rev. 1, the textbook, *Quality Assurance of Chemical Measurements*, by John Keenan Taylor, formerly of the National Bureau of Standards, and other sources for analytical statistics.

Precision

Precision for duplicate measurement of STTP samples or an LCS is expressed as relative percent difference (RPD):

$$RPD = \frac{C_1 - C_2}{(C_1 + C_2)/2} \text{x}100$$

where, RPD = relative percent difference
C_1 = analytical results from the first sample
C_2 = analytical results from the second sample, and
C_1 = larger of the two samples.

Precision for three or more replicate measurements of an STTP sample or samples is expressed as the relative standard deviation (RSD) and given as a percentage:

$$RSD = \frac{\sigma}{\bar{y}} \text{x}100$$

where, RSD = relative standard deviation,
σ = standard deviation, and
= mean of the replicate analyses.

The standard deviation σ is defined as:

$$\sigma = \left(\sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n-1} \right)^{1/2}$$

where, y_i = measured value of the ith measurement and
n = number of replicates.

Accuracy

Accuracy for STTP sample analyses is expressed as the percent recovery (%R) of a standard reference material (SRM) (or LCS) or matrix spike:

$$\%R = \frac{C_m}{C_{srm}} \text{x}100,$$

where, C_m = measured concentration level against calibration standard and
C_{srm} = true or certified concentration of the analyte(s) in the sample.

Continue on next page

When a matrix spike is added to a sample or the method of standard additions is used,

$$\%R = \frac{S - U}{C_{ac}} \mathrm{x}100$$

where, S = measured concentration in spiked aliquot,
U = measured concentration in unspiked aliquot, and
C_{ac}= actual concentration of spike added.

Completeness

Completeness for STTP samples and sample analyses can be expressed in two ways. Completeness of sample and analysis describes the number of samples taken relative to the number of samples analyses completed. Likewise, completeness for each analytical method can be determined by the number of samples received relative to the number of samples analyses completed. Completeness %C is given by:

$$\%C = \frac{V}{n} \mathrm{x}100$$

where, V = number of valid analytical results obtained, and
n = number of samples collected and/or received.

Both processes for analyzing completeness will be used to indicate the success of the sampling and analyses efforts.

Method Detection Limit (MDL)

The MDL for applicable measurements for the STTP may be calculated by:

$$MDL = t(n-1, 1-\alpha\ = .99)\mathrm{x}\sigma$$

where, $t\,(n - 1,\ 1 - \alpha = .99)$ = t-distribution values at the 99% (1-.01) level of significance for a one-tailed test and n - 1 degrees of freedom and,
σ = standard deviation of replicate measurements.

Safety

The design of the following hardware has taken into account operational and personnel safety. Safety begins with the design of equipment and hardware.

Design of Test Containers

The test containers for the drum-scale tests are constructed of titanium metal. Each container has a maximum headspace volume of <10% of the container's volume. Each test container will have a pressure relief valve to release headspace gases when the pressure exceeds 5 psig. An independent pressure gauge will permit monitoring of existing pressure and rate of pressure buildup in each container.

The headspace volume will be sampled regularly, to provide information on the concentrations of headspace gases and reduce their pressure. The headspace gases will not be radioactive. Titanium metal specimens have been tested by exposure to Brine A at 30°C and 45°C for several weeks. No corrosion of titanium was found after 6 weeks in Brine A at 40°C. Each drum-sale test container will have a primary spill-containment vessel.

Liter-scale test containers will have the same pressure-relief device and corrosion resistant materials as the drum-scale containers.

Pressurized Test Containers

The technical requirements document calls for six liter-scale tests to be conducted at pressures up to 60 bars (~870 psig) of CO_2. These containers are commercially available titanium containers having a maximum allowable working pressure of 2000psi at 121°C (250°F) and a test pressure of 3000psi at 22°C (72°F). These pressurized test containers are treated as a separate work breakdown structure element because of the more stringent design criteria and safety reviews required. The design review will involve the concurrence of at least two safety groups within LANL.

Waste Characterization, Reduction, and Repackaging Facility (WCRRF)

All STTP activities at WCRRF will meet the technical specifications of the STTP technical requirements document and will be conducted according to the SAR and standard operating procedures established for the WCRRF operations. The tasks will be delineated by the STTP principal investigators and conducted by WCRRF personnel who are trained to conduct these activities in a safe manner. Any deviations from the requirements of the WCRRF SAR or standard operating procedures will be handled administratively or through unreviewed safety question documentation that will be reviewed on a case-by-case basis.

Transporation of Waste Drums to and from LANL Facilities

Transportation of waste drums between LANL facilities will be conducted according to established operating procedures. These transfers may require road closures depending on the quantity of radioactive material and the type of container being transported.

Transportation from WCRRF to the CMR Building

The transportation of loaded STTP test containers, including actinide-loaded waste and brine, will require special operational procedures beyond those pertaining to the normal transport of waste drums.

Wing 9 Design Activities

The design, fabrication, and implementation of two enclosures in the basement of Wing 9 of the CMR Building is a major preparatory engineering activity that must be completed before test containers can be transferred there. The design of the two enclosure, which has been reviewed by safety representatives from the CMR Building, includes a review of the life safety codes required for an enclosure constructed to house the test containers for at least 2 years at 30°C. Radiological and industrial safety have been integrated into the enclosure design.

Analytical Instrumentation (Gloveboxes)

The design of all instrumentation having associated glovebox enclosures will be reviewed before the procurement process begins. Radiological, industrial, and environmental safety experts review each task area principal investigator's proposal for new equipment, instrumentation, or gloveboxes. An environmental safety and health (ES&H) questionnaire was completed for modifications of gloveboxes, equipment, analytical instrumentation, or emplacement of new equipment within the analytical laboratory.

Chemical Analyses

The analytical analyses of potentially high radioactively contaminated brine leachate samples will require the most meticulous laboratory safety practices. All STTP brine leachate samples will be analyzed according to established operational procedures for ensuring radiological safety for the analysts. All STTP chemical analyses will be performed by trained analysts according to the *"MST-5 Training and Qualification Plan,"* MST5-GEN-QAP2-003, latest revision.

Continue on next page

Analysts must complete safety training, and a record of the training will be maintained by the STTP training coordinator or a designated document control specialist for the STTP. All analytical work will be conducted according to the ALARA statement for the STTP. Laboratory safety will be ensured by existing laboratory safety protocols and applicable chemical hygiene plans. Workers will have ready access to material safety data sheets from the VAX computer according to instructions provided. The analyses will be conducted in such a manner that contamination will be controlled according to an STTP contamination control statement. Analytical laboratory personnel who work with high-voltage electrical instrumentation and systems must have completed a LANL electrical awareness training class. All analytical laboratory modules with the CMR have approved life safety code equipment and provisions. All laboratories will have adequate fire protection and prevention equipment, and analysts will be familiar with fire protection measures and fire prevention methods. All analytical activities will be conducted according to applicable waste minimization procedures and the LANL waste minimization policy. All analyses will be conducted so as to minimize sample exposure to the environment. Sample aliquots will be as small as possible and contained during analysis inasmuch as possible.

All STTP personnel are trained in emergency response and evacuation according to CMR training exercises. As part of the training program, analysts working on STTP samples will be trained in spill control measures.

II. (i) Data Reporting

The results of analyses of an individual sample or a sample set will be compiled into a data package consisting of the information listed in "Data Package Compilation for Brine Leachate and Gas Analysis" of section g. Two levels of review and two levels of approval are required for each individual data package or set of data packages. All quality control analyses performed in support of the analytical results will be included in the data package. A checklist of required items to be checked by each reviewer and approver will be completed and signed by the reviewer or approver. The data package will be transmitted to the SNL point-of-contact and to the project monitor at DOE CAO. LANL will retain the original copy as part of the data retention and storage process. Complete data packages will be transmitted to SNL and CAO as soon as they are completed.

Analysis of Leachate Samples

Technical Procedures

Each analytical task area performing an analyses on STTP brine leachate samples will conduct such analyses according to a documented procedure that has been written, reviewed, and approved according to the *"MST-5 Document Control Procedure,"* MST5-GEN-QAP4-002/0. Modifications to the analytical procedures will be made according to the document change format given in the *"MST-5 Document Control Procedure."* The analytical procedures will be written to accommodate the variety of complex problems that are expected to accompany samples containing unknown constituents in an already-complex matrix. All procedures will be developed during the method analysis period planned for the STTP and must target the DQOs listed in Tables 4 and 5. The STTP analytical activities and tasks that will require documented procedures include:

- sampling of the brine leachate,
- chain-of-custody, as applicable,
- sample transport, filtration, and aliquotting,
- alpha analysis with liquid scintillation counting (LSC),
- gross elemental analysis by wavelength-dispersive x-ray fluorescence spectrometry (WDXRFS),
- measurement of p*c*H in brine leachate,
- measurement of *E*h in brine leachate,
- actinide analysis by inductively coupled plasma-mass spectrometry ((ICP-MS),
- elemental analysis by inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES),
- RCRA toxic analysis by graphite furnace atomic absorption spectro photometry,

Continued on next page

- particle-size distribution by Doppler shift and SEM,
- particle counting by laser scattering,
- colloid characterization,
- microbial analysis, oxidation state determination of Pu,
- inorganic anions in the brine leachate,
- TIC in the brine leachate,
- TOC in the brine leachate,
- dissolved organic chelators in the brine leachate,
- temperature control by heated glovebox,
- headspace gas sampling from STTP liter-scale test containers,
- headspace gas analyses from STTP drum-scale test containers,
- STTP data management, validation, and reporting, and Quality Assurance Project Plan.

Development of Analytical Methods for Brine Leachate

Analytical methods will be developed for each of the analyses and procedures described in the STTP technical requirements document. The methods to be developed are listed in the "Technical Procedures" section above. Each method will be developed to target the DQOs listed in "Data Quality Objectives" of section g. The on-going development of the methods to fulfill the required analyses and determinations are briefly described in the following sections. The STTP will not conduct speciation analysis but will provide samples for speciation to be completed by other LANL projects.

Filtration to Approximately 1.0μm

The approximately 50-mL brine leachate sample will contain a diversity of soluble cationic and anionic species with a wide range of suspended material. Some of the ionic species will be near saturation at 30°C and will fall out of solution if the temperature is lowered during filtration. Consequently, all filtrations will be conducted in a specially designed, temperature-controlled glovebox. The filtration of the entire sample to 0.8 to 1.2μm will be accomplished by sequential filtration. The primary suspended solids expected to clog the filter paper are precipitated iron hydrates. The pressurized tests will be filtered as described in section d, "Pressurized CO_2 Test Containers."

Filtration to Less than 20 nm

Following the removal of the large particles and suspended solids to 1.0 µm, a portion of the 50-mL sample will be filtered to <20nm according to an Amicon centrifugation method in an Amicon Centriprep 100 centrifuge tube (molecular weight cutoff of 100,000 daltons). The Amicon Centriprep centrifuge tube contains a YM-100 regenerated cellulose filter. Initial experimentation with this method has been successful down to 10 nm. These experiments were conducted with standard Brine A solutions that had been prefiltered to 0.22µm through a 47-mm-diam filter paper. The volume of sample to be filtered--estimated to be 30 to 40mL--will be determined by the needs of each analytical procedure.

Determination of Actinide Alpha Activity

Total high-specific-activity, alpha-active actinide radioisotopes such as ^{239}Pu and ^{241}Am, will be determined by liquid scintillation counting and gamma-ray counting of both fully filtered and coarse-filtered leachate samples. The data from these measurements will be used to determine whether colloids of plutonium and americium are present in the brine leachate. The data will also be used as a screening method to establish the need for more extensive particle-size distribution studies on the filtrate and colloid characterization by SEM and x-ray techniques. The results of this initial counting will provide analysts with the first indication of the contamination-control measures that will be needed for each sample. Experiments to determine the stability of brine leachate samples and the LSC quenching effects resulting from high salt and iron concentrations have been established as part of the methods development.

Rough Concentration Measurement (X-Ray Fluorescence Spectrometry)

The concentration of relatively low specific activity actinides, for example, thorium as ^{232}Th, uranium as ^{238}U, and neptunium as ^{237}Np, and all other elemental constituents such as aluminum, iron, lead, bromine, cadmium, and strontium will be analyzed by either WDXRFS or EDXRFS in both fully filtered and coarse-filtered brine leachate. The analyses will complement and expand on the LSC analyses. Whereas LSC is considerably more sensitive for high-specific-activity actinides, WDXRFS is more sensitive for low-specific-activity actinides and has the added feature of identifying each specific actinide (not isotope) whether it is soluble or suspended. Also, the relative concentration of elemental constituents in the brine leachate will be established by this technique. The results of WDXRFS analyses will be very useful in helping analysts performing subsequent analyses to determine what dilutions may be required and to have up-front knowledge of the potential interferences in an individual sample. Experiments to determine the sensitivity of WDXRFS for actinides and other elemental constituents in Brine A have been successfully conducted. Experiments to determine the stability of brine leachate samples with time will be conducted as part of the methods development for this task. These analyses will also serve as a screening tool to establish the need for more extensive analyses for particle-size distribution and colloid characterization.

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p*c*H Measurements

Th measurement of pH in low-ionic-strength solutions is a rather straightforward determination that uses an inexpensive glass electrode to measure the activity of hydrogen ions. However, the measurement of the activity of the very low concentration of hydrogen ions in nearly saturated brine at neutral pH is very complex. Three methods were investigated by LANL. The first is a modification of the method proposed by Solache-Rios and Choppin and consists of measuring the *concentration* (pcH) rather than the *activity* of hydrogen ions with a glass electrode that has been calibrated by a spectrophotometric method using the pH color indicator cresol red. Preliminary experiments to establish the second ionization constant of cresol red in brine by measuring the absorptivities of the monoprotonated and unprotonated form of the indicator were successful. The second method is proposed by H. Nitsche of Lawrence Livermore National Laboratory. The third and the method chosen is suggested by Andrew Felmy and coworkers of Pacific Northwest Laboratories and published in *Radiochimica Acta,* Volume 48, pages 29 to 35 (1989). Also calibration standards prepared by addition of a known quantity of acid to borate and acetate buffers may be used to calibrate specially designed pH electrodes.

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*E*h Measurements

The measurement of *E*h in a nearly saturated brine solution is expected to have complexities similar to those for the measurement of pcH. The experience gained from the determination of pcH can be transferred to the measurement of *E*h. Specialized *E*h electrodes are to be tested and calibrated by measurement of the relative concentration of a series of oxidation-reduction couples. The effectiveness of different commercial *E*h electrodes in Brine A solution were conducted as part of the methods development for this measurement.

Particle-Size Analysis

The results of LSC and WDXRFS analyses will provide the basis for determining whether it will be necessary to measure the population and distribution of particle sizes in the coarse-filtered and fully filtered brine leachate samples from each test container. Particle-size analyses will consist of:

- determining the extent of particle-size analysis to be conducted based on LSC and WDXRFS,
- determining the particle-size population and distribution of colloids from ~5nm with a particle size analyzer and an image analysis system with SEM,
- studying the particle-population at <10nm and >10nm at certain range increments within the capability of the particle-size analyzer and the filtration apparatus used to filter the brine leachate, and
- performing colloid-characterization measurements on the colloid-bearing samples by a series of techniques to be determined as part of methods development.

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The STTP technical requirements document defines "colloids" as those particles having an effective diameter of between 1 nm and 1µm. Results from preliminary filtration experiments indicate that filtration to 10nm (0.01µm or 100 Å) may be achievable in Brine A solutions. Consequently, measurements of particle-size dispersions and populations from 100 to 10,000 Å (10-1000 nm) will be attempted. Mobil colloidal particles in this size range will be difficult to analyze with standard laser scattering techniques. LANL will study the feasibility of measuring the relative distribution of mobile colloidal particles from 10 to 1000nm using an ultrafine particle-size analyzer incorporating measurement of the Doppler shift of dynamically scattered laser light on particles exhibiting Brownian motion in a filtered brine solution with a determined viscosity. Submicrometer particle size analyzers employing light-scattering techniques tend to work best either with nondispersive colloidal dispersions or with heterodisperse colloidal dispersions having two distinct particle sizes. Therefore, it is anticipated that most of the particle-size distribution measurements will be accomplished with an image analysis system coupled with scanning electron microscopy.

The characterization of colloidal suspensions in this small-particle-size regime will be studied by WDXRFS, EDXRFS, and SEM. To complement these methods, attempts will be made to isolate the mobile suspension of colloids through filtration or centrifugation or both, dissolve the colloids, then determine the concentration of plutonium in the dissolver solution by LSC or ICP-MS.

Analysis of Actinides

Actinides in the fully filtered brine leachate (<20 nm) will be analyzed by ICP-MS, one of the most sensitive means available. However, to determine actinides at the 10^{-10}M level may require preliminary separation of the actinides from the brine to reduce the high salt concentrations that can adversely affect the aspiration and nebulization in the ICP torch. To detect plutonium at the 10^{-10}M level (equivalent to 24 pg/mL or 24 parts per trillion) may require pre-concentration of plutonium and analyses with optimal instrumental conditions achievable. Identifying the optimal conditions for determining thorium, uranium, neptunium, plutonium, and americium in brine leachate samples will be part of the methods development effort for these analytical determinations. The calibration of the ICP-MS instrument with NIST-traceable or New Brunswick Laboratory standards, as available, is a major part of the methods development. High-purity americium as the metal or oxide will be used as a secondary standard for americium analyses.

Analyses of Elemental Analytes

The analytes to be determined for the brine leachate samples are iron, lead, aluminum, magnesium, and calcium. These analytes will be determined by ICP-AES and/or ICP-MS. The instrument to be used for analysis of brine leachate elemental constituents will perhaps incorporate a state-of-the-art charge-injection detector (CID) that is designed to analyze and store the emission spectra from all elements in the samples. The spectra of all the elements may be recalled later if a need arises to study the effect of other elements that may be a significant influencing variable. Attempts will be made to analyze the elemental constituents directly in the brine without preliminary preparation. However, an on-line pre-concentration step may be used for analysis of iron, lead, and aluminum. The STTP technical requirements document specifies 100ppb as a lower limit of detection.

Analyses of Rare-Earth Surrogate for Americium-241

Neodymium will be added to most test containers as part of the loading procedure. Addition of neodymium as an americium analogue will mitigate the ALARA concerns of handling high levels of ^{241}Am. Also, addition of a rare-earth element in lieu of americium will lower the contamination-control concerns and the eventual source term during waste disposal. Neodymium will be analyzed by either ICP-MS or ICP-AES, whichever proves to be more sensitive in a high-brine environment having the interferences expected from the complex matrix. If a drum-scale test container holds 40 gal. of brine, addition of 10g of soluble neodymium will result in a concentration ~66ppm. Addition of ~33mg of neodymium will yield a similar concentration in liter-scale test containers holding 500mL of brine. Neodymium will be added as neodymium chloride salt.

Analyses of Inorganic Anions and Carbonate

The STTP technical requirements document discusses the necessity to analyze the brine leachate for free fluoride, nitrate, phosphate, sulfate, and carbonate anions in the fully filtered leachate (<20nm). The massive concentration of chloride in the samples certainly complicates the analyses of the listed anions. Ion chromatography is the technique that has been selected for analyzing these anions at the 1.0 ppm level. If carbonate cannot be analyzed by an ion chromatograph, carbonate will be determined by the total inorganic carbon analyzer.

Analysis of Total Inorganic Carbon (TIC)

TIC analyses will be performed on the fully filtered leachate to determine the total quantity of the free and complex carbonate. Carbonate is an inorganic radical and a chelating (complexing) agent for actinides. A study of the complexing strength of carbonate compounds conducted as part of a separate experiment is available to SNL for establishing the affinity of actinides for carbonate at different pH's. TIC will be determined with a carbon analyzer.

Analysis of Total Organic Carbon (TOC)

A carbon analyzer will be used to perform TOC analyses on both the fully filtered (<20nm) and coarse-filtered (<220nm) leachate. The presence of significant concentrations of TOC will indicate the presence of organic chelating compounds that will be available to complex actinides. Analyses of TOC will provide a basis for comparing soluble organic chelators with the sum of TIC and TOC.

Analysis of Soluble Chelators

The STTP technical requirements document identifies 14 organic chelators that are of interest to study the behavior of actinides exposed to chelators. These ligands have been selected because they are:

- present in the original waste matrix,
- added as spikants or enriching agents, and
- produced by microbial degradation of cellulose.

The 14 organic chelators that may be added to the STTP brine leachate samples are discussed in "Actinides" of section d.

Analyses of these chelating compounds in a nearly saturated brine solution is a challenging analytical task. Efforts will focus on determining the applicability of high-pressure liquid chromatography, liquid chromatography-mass spectroscopy, capillary electrophoresis, isotachophoresis, and anion exchange pretreatment methods followed by one of these methods. The presence of calcium, magnesium, aluminum, and iron in high concentrations is expected to fill the ligand groups of all these chelators, so most of the chelating compounds are expected to be in complex and neutral states rather than uncomplexed, charged states. These analyses will be conducted only on fully filtered brine leachate. The DQOs for these analyses are only target DQOs because of the current uncertainties in the measurement techniques available. The technical requirements document has set a target of 1 ppm with a precision of ±20%. On-going experiments indicate that a target of 20 to 100 ppm may be more realistic.

Speciation Studies

Speciation studies, or analysis of the oxidation or complexed state of plutonium, listed in the STTP technical requirements document may be conducted if the results from other analyses show an unusual *Eh* measurement or abnormally high plutonium solubility. LANL has established a methodology to perform speciation studies of select STTP samples that have high Pu concentrations. The oxidation state concentration in STTP samples will be determined by photoacoustic spectroscopy.

Characterization of Microorganisms in Brine Leachate

If a test container generates a significantly high concentration of microbially produced gases, a special sample passed through special filters will be taken to determine the presence of an unusually high population of halotolerant or halophilic bacteria. These analyses will be conducted according to procedures developed at Brookhaven National Laboratory.

Archival Samples

The volume of sample to be extracted from each test container (except the pressurized test containers) is ~50 mL. The large number of analyses to be performed on these samples exhausts or nearly exhausts the entire volume.

Data Management

The data management practices for maintaining uniform and consistent data will be applicable to the compilation of data packages discussed in "Data Package Compilation for Brine Leachate and Gas Analysis" of section g. The data from analyses of brine leachate samples will be retrievable and will be organized in a manner that will furnish all the information required to complete a data package. A principal objective of the data-accumulation process is to provide the experimenter (SNL) with all of the data required while not including unnecessary information. However, most of the nonessential information not included in the data packages will be retained retrievably in the STTP files by the project leader. STTP data management will be according to the *"STTP Data Reduction, Validation, and Reporting Procedure,"* CST-STP-QAP5-017, latest revision.

II. (j) Regulatory Requirements

All regulatory requirements to conduct the STTP have been addressed diligently and forcefully to ensure that the project was not delayed by failure to obtain the necessary permits or to comply with applicable LANL, DOE, federal, and state regulations. The STTP management team has vigorously pursued a course of action to ensure that all permitting requirements and applicable regulations have been met. The team has taken an active role in generating the necessary documents and communications to promote knowledgeable decisions in determinations of compliance with applicable environmental and safety permits. The status of applicable permits and other reports is summarized, following.

Environmental Safety and Health Questionnaire

The ES&H Questionnaire (#93-0058) for the STTP was completed on March 2, 1993. The ES&H questionnaire for adding hoods and modifying laboratories in the CMR has also been completed. The ES&H questionnaire checklist contacts were completed on May 5, 1993.

Modified Environmental Safety and Health Questionnaire

The original ES&H questionnaire was upgraded to include the modifications made to the STTP technical requirements document and the methods to accomplish the goals of the STTP for the purpose of enhancing radiological and environmental safety.

National Environmental Standards for Hazardous Air Pollutants

The documentation for the National Environmental Standards for Hazardous Air Pollutants (NESHAPS) has been completed, and the STTP is in compliance with the requirements.

Documentation was completed that conclusively showed that waste characterization and test container loading at the WCRRF and the tests and analyses in the CMR Building will not increase radioactive emissions relative to the baseline year of 1989 (when NESHAPS came into effect) or a baseline average of the years 1989 through 1992 (CLS-1/92-818, "STTP Radioactive Source Term Relative to 1989 Baseline for NESHAPS Determination). Further documentation was provided to LANL's Environmental Management Group to illustrate that the chemical reactions occurring within the brine in the STTP test containers would not generate radioactive gases (CLS-1-92-598).

The nongeneration of radioactive gases in the STTP test containers could therefore classify the STTP as a zero-release experiment for gaseous radioactive emissions. That only nonradioactive gases will be generated in the STTP test containers is demonstrated in CLS-1-92-598, *"Additional Information Requested for STTP NESHAPS Determination."*

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The notification memo with the determination that a NESHAP application was not required was received by STTP management on December 21, 1992, EM-8:92-3810, "NESHAPS Determination for STTP Project."

Safety Analysis Report/USQD

The STTP was initially granted permission to submit a graded SAR specific to the STTP rather than incorporate the STTP operations into the SAR for the CMR Building. More recently, the STTP was recommended to submit the documentation for an Unreviewed Safety Question (USQ). This recommendation stemmed from the reduction in the number of test containers required for the STTP and thereby a reduction in the radioactive source term. The USQ addressed transport of the brine-filled test containers from the WCRRF, if required, and the design of the enclosures for the liter-scale and drum-scale experiments in the basement of Wing 9. The seismic rating of the basement of Wing 9 is 0.2, whereas the seismic rating for the main-level floor structures is 0.02. An STTP USQ was completed for the WCRRF and the CMR Facility. Both USQs resulted in a determination (USQD) that the safety evaluation did not constitute a USQ.

LANL RCRA Federal Facilities Compliance Agreement

Completion of the LANL RCRA Federal Facilities Compliance Agreement is a LANL milestone was negotiated with the EPA and completed on March 15, 1994.

STTP and the State of New Mexico

The objectives, goals, and operations of the STTP were presented to the New Mexico Environmental Department in August, 1992. After discussing the possibility that the STTP might be a treatability study, the state regulators and LANL came to an agreement that the STTP was not a treatability study but that when the test period of the experiment begins, LANL will provide the state progress reports according to the format currently used for a treatability study. A letter from LANL senior management to the permit section coordinator of the New Mexico Environmental Department was transmitted to verify the verbal agreements made.

National Environmental Policy Act

In November, 1992, a modified ES&H questionnaire was completed that included the many changes made to the STTP to enhance radiological (ALARA) and environmental safety and that mitigated the consequences of accident scenarios. A determination of categorical exclusion was not received, and STTP management was notified in January, 1993 to begin the necessary documentation of an environmental assessment.

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LANL's Environmental Management Group has selected a consulting agency to complete the required documentation for an environmental assessment. STTP management has prepared an augmentation document that details the conduct of the STTP to help in expediting the document. An environmental assessment document was completed and reviewed by the LANL Environmental Review Committee on June 2, 1993. The environmental assessment document was submitted to the Los Alamos Area Office and to DOE-Albuquerque for review.

The NEPA process, including extensive reviews of the Environmental Assessment document by DOE-Los Alamos Area Office, DOE-Albuquerque Operations, and DOE-Headquarters, was completed with a Finding of No Significant Impact on January 24, 1995.

Chronological Events for the Actinide Source-Term Waste Test Program (STTP)

III. (a) Chronological Origin and Implementation of the Actinide Source-Term Waste Test Program (STTP); Background of the Tests

March 1989

DOE submitted a No-Migration Variance Petition to the EPA under 40 CFR 268.6 to place a limited amount of untreated hazardous waste subject to the RCRA land disposal restrictions in the WIPP for purposes of testing and experimentation for five years.

November 14, 1990

The EPA grants DOE a Conditional No-Migration Determination to allow DOE to place waste in the WIPP for the purpose of conducting tests or experiments to demonstrate the long-term acceptability of the facility.

Conditions

- All wastes tested must be retrievable
- Flammable mixtures of gases in headspace of test containers is prohibited
- Bin experiments must have carbon filters
- Others

WIPP Performance Demonstrations

Experimental Needs

- Amount of gas generated in waste by:
  - Corrosion
  - Microbial Decomposition
  - Radiolysis
- Effect of brine on:
  - Gas Generation
  - Solubility of Actinides
- Effect of influencing variables on:
  - Gas generation
  - Solubility of actinides

Proposed Demonstrations and Tests

1989-1990

- Bin Scale Tests
  - Dry
  - Wet (Brine)
- Alcove tests
- Laboratory tests with simulated wastes
- Laboratory tests with actual wastes
  - Liter-scale tests with brine
  - Drum-scale tests with brine

National Academy of Sciences supports laboratory tests with actual wastes

1991

Technical requirements for the CH-TRU Waste Solubility/Leaching Program issued by Sandia National Laboratories

- 75 Liter-scale test containers
- 99 Drum-scale test containers

SAND91-2111
Mark Phillips and Martin Molecke

November 1991

Technical requirements for the Contact-Handled Transuranic Waste Source-Term Test Program issued by Sandia National Laboratories

- 75 Liter-scale test containers
- 117 Drum-scale test containers

SAND91-2111
Mark Phillips and Martin Molecke

January 1992

Bid estimates too high, technical requirements modified by Sandia National Laboratories

March 1992	Technical requirements for the Contact-Handled Transuranic Waste Source Term Test Program issued by Sandia National Laboratories • 39 Liter-scale test containers • 24 Drum-scale test containers Relationship of STTP and WIPP Bin Scale Tests (STTP to be conducted in parallel with Bin-Scale Tests and the Laboratory Test Programs) SAND91-2111 Mark Phillips and Martin Molecke
May 15, **Program 1992**	Final proposals for Contact-Handled Transuranic Waste Source-Term due to WPSO and WPIO (Joe Lippis and Arlen Hunt)
August 18, 1992	• Site selection process completed by WIPP Project Integration (WPIO) and Project Site Office (WPSO) • LANL selected to conduct STTP work • Work to commence 10-01-92 (public announcement by John Arthur, III)
October 1992	• DOE/WPIO appoints STTP Representative, Robert Houck • SNL appoints Technical Representative, Mark Phillips • LANL appoints STTP Project Leader, Bob Villarreal
October 8, EPA's **1992**	• U.S. Congress passes WIPP Land Withdrawal Act LWA and reaffirms role as regulator • DOE is to submit CCA to EPA (this removes requirement for no-migration) • Determination provides secretary with flexibility to determine the need for engineered and natural barriers

November 1992	Approval and review chain for STTP documents established by: • WPIO U.S. DOE WPIO Project Director, John Arthur, III • LANL Program Director, James Shipley • LANL Program Manager, Bruce Erdal • SNL/NM Manager, Wendell Weart • DOE/WPIO Chief, Patrick Higgins • SNL/NM Manager, Richard Lincoln • SNL/NM Manager, James Nowak • SNL/NM Representative, Mark Phillips • LANL Group Leader, John Phillips • DOE/WPIO Representative, Robert Houck • LANL Project Leader, Robert Villarreal • LANL PI, Larry Field
December 1992	LANL funded to conduct STTP
December-January 1993	Revised technical requirements, document issued by Sandia National Laboratory • 39 Liter-Scale Tests • 15 Drum-Scale Tests Mark Phillips and Martin Molecke
December 13, 1992	Coordination of responsibility established between SNL and LANL for preparation of STTP plan
October 1992 - January 1993	LANL establishes STTP Work Breakdown Structure - 15 major elements

October 1992 - February 1993

LANL commences preparation of regulatory documentation

- ES&H Questionnaire
- NEPA Determination
- Environmental Assessment
- SAR Review
  - CMR
  - Size Reduction Facility
- NESHAPS FFCA
- RCRA FFCA
- USQ
- STTP Management Plan
- STTP Test Plan
- STTP QA Project Plan

October 1992- October 1993

FY '92 STTP preparatory activities (Calendar Year 1993)

- Initiate 15 WBS elements
- Completed STTP Test Plan (7-27-93)
- Completed STTP Management Plan (7-28-93)
- EA submitted (seven times to Headquarters)
- Design of experiments finalized

October 21, 1993

DOE announces that radioactive waste testing with actual wastes will be conducted at Los Alamos National Laboratory and other sites rather than the WIPP site

October 1993

1) NAS Panel recommends design of STTP experiment and test containers should be for 10-12 years

2) Technical Requirements for the Actinide Source-Term Waste Test Program (Final) Issued by Sandia National Laboratory

- 39 Liter-Scale Tests
- 15 Drum-Scale Tests

SAND91-2111
Mark Phillips and Martin Molecke

December 9, 1993	DOE appoints George Dials, Manager of Carlsbad area office
January – October 1994	• Transfer of management of STTP from DOE WPIO - WPSO to DOE-CAO • Technical lead - SNL • Management chain to Experimental Programs Manager - CAO • Implementation of STTP - LANL • SNL representative - Chris Craft • CAO manager - Richard Lark • Selection of waste drums from LANL- inventory completed (SNL approval) • Preparation of Size Reduction Facility for characterization and loading of waste complete • Design and fabrication of environmental enclosures complete • Design and fabrication of liter-scale and drum-scale tests complete • Design and procurement of analytical equipment with gloveboxes complete • Development of analytical methodologies on-going • Readiness review of Size Reduction Facility initiated (SNL oversight) • Readiness review of test containers initiated (SNL oversight) • Readiness review of pressurized test containers initiated (SNL oversight) • Readiness review of CMR enclosures initiated (SNL oversight) • Readiness review of analytical installations and methods initiated (SNL oversight) • All documentation completed <u>"except EA"</u>
April 6, 1994	• STTP goals, objectives, activities, and status presented to full panel of National Academy of Sciences, New Mexico EEG, New Mexico Environmental Department, State of New Mexico, and DOE Headquarters • LANL - SNL Presentation
December 1994	All elements of STTP WBS completed
January 23, 1995	STTP environmental assessment approved - no significant impact documented
January 20, 1995	LANL receives authorization to initiate STTP from CAO (Dick Lark)

February 1995	Shipment of waste to Waste Characterization, Reduction, and Repackaging Facility • TA-54 Inventory **(02-01-95)** • CMR Building **(02-03-95)** • TA-55 Inventory **(02-15-95)**
March 23, 1995	• Commenced core drilling • Completed loading of liter-scale test containers • Added brine to liter-scale test containers • Transported LS test containers to CMR • Added Innoculum to liter-scale test containers
March 29, 1995	Commenced liter-scale tests
May 9, 1995	• Commenced characterization of heterogeneous waste for drum-scale tests • Completed loading of drum-scale tests • Transferred drum-scale tests to CMR • Added Innoculum to drum-scale tests
May 10, 1995	Commenced drum-scale tests
May 26, 1995	Completed first data package of liter-scale tests
June 19, 1995	Completed first data package of drum-scale tests
November 2, 1995	Plan for the utilization and interpretation of Actinide Source-Term Waste Test Program data issued by Sandia National Laboratories
Remainder of 1995	Conducted sampling and analysis of brine and headspace gas for all test containers
April 1996	• Completed first year of STTP sampling and analysis activities • Received revised Technical Requirements Document from SNL • Continued sampling and analysis

June, July, August 1996:

- Prepared new test plan for the STTP
- Presented results of first year of STTP tests to CAO-manager
- CAO Experimental Programs and STTP assigned to Butch Stroud
- Continued to conduct sampling and analysis

December 1996

Sandia National Laboratory submits "Report on Comparison of TRU Waste Tests from the STTP with the SNL WIPP Actinide Solubility Submodel"

February – March 1997

- LANL adds MgO to pressurized liter-scale test container No. 28
- LANL conducts analyses of pretest conditions and posttest results

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April 1997

- Test results and status of STTP presented to CAO-manager
- Second year of sampling and analysis completed
- Data trends of STTP results compiled and presented to CAO and SNL

May 15-16 1997

- Data and results from STTP sampling and analysis presented to National Academy of Sciences panel in Washington D.C.
- Included New Mexico EEG
- Included results of MgO addition to STTP pressurized test container No. 28
- NAS requested special session for STTP experiments and results
- SNL presented comparison of STTP data with latest actinide solubility sub-model

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III. (b) Details of the Actinide Source-Term Waste Test Program (STTP)

The STTP consists of:

15	Drum-scale tests with heterogeneous wastes (combustibles, lab wastes, metal, etc.)
33	Liter-scale tests with homogeneous wastes (sludges, cemented or solidified wastes, pyrochemical salts, etc.)
6	pressurized Liter-scale tests are 60 bar with homogeneous wastes

Drum-scale tests:

- 65 gallon all titanium vessels
- Double O-ring purgeable lid

Liter-scale tests:

- 3-liter all titanium vessels
- Double O-ring purgeable lid

Pressurized Liter-scale tests:

- 2-liter all titanium vessels
- 60-bar tests (870 psig) with$C0_2$
- Sampling pressure @ 60 bar

The STTP is an extensive and dynamically designed test to:

- Provide time-sequential quantitative measurements of mobile actinide (TH, U, Np, Pu, Am) concentrations in WIPP brines that have been in continual contact with actual CH-TRU wastes;
- Determine the influence of additive chemical variables on the concentration of mobile actinides in STTP test containers, including influences of gas generation, speciation, and microbial activity;
- Determine relative gas accumulation concentrations in headspace of test containers as a result of corrosion, microbial activity, and radiolytic degradation of waste and brine; and
- Allow comparison with the hypotheses of the Actinide Solubility and Colloid Characterization models developed from controlled laboratory tests.

III. (c) Projected Chronological Chemical Conditions in the WIPP Repository for 500 Years

Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2150	150	**IV. WIPP Creep Closure Period**	
		1. Administrative controls cease. 2. Early panels 70% closed from creep closure. 3. Late panels >50% closed from creep closure. 4. Compaction of non-cemented drums on going. 5. MgO sacks crushed open. 6. Salado Brine seepage continues. 7. Repository remains dry. 8. Porosity disequilibrium exists between disposal rooms and panels. 9. Permeability decreases because of deformability of rock salt and compacted waste and other materials.	1. MgO reacts with brine seepage by four mechanisms. 2. Corrosion rate of mild steel drum levels off. 3. Oxygen is depleted by corrosion of metals. 4. Headspace gas is primarily N_2, H_2, N_2O, CH_4, and VOCs. 5. CO_2 reacts with $Mg(HO)_2$ to form $MgCO_3 \bullet 3H_2O$ and Mg Oxychloride nodules. 6. CO_2 reacts with MgO to form physico chemical weak mono and bidentate complexes. 7. Salado Brine salts continue to precipitate/ crystallize and accumulate as hardened mass. 8. Water acts as catalyst to form $MgCO_3 \bullet H_2O$. 9. Microbial activity is limited and Produces CO_2 and CH_4 10. Radiolysis processes are limited and produce limited H_2 and CO_2. 11. Alpha activity degradation of organics produces H_2 and CO_2. 12. No solubility of actinides occurring. 13. Repository pressure increases but void volume is small. 14. Anhydrite interloads provides diffusion path for H_2 15. Effect of swelling of MgO reactions noticeable $MgO \rightarrow Mg(OH)_2 \rightarrow MgCO_3 \bullet 3H_2O$. 16. Overall degradation from all processes is slow. 17. Less than 12.0% of MgO has reacted with brine @ in-leakage rate of 4 m^3/disposal room/yr. for 50 years

Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2600	500	**(V.) WIPP Solidification Period (W/O Brine Intrusion)**	
		1. Dynamic creep closure complete 2. Non-cemented drums compacted 3. Cemented drums encased 4. Salado Brine seepage continues 5. MgO dispersed 6. Porosity at equilibrium 7. Permeability minimal 8. Repository remains dry 9. Tortuosity prevents intra-room communication 10. Intra-repository sites develop with no communication with overall repository	1. MgO – brine reaction continues to maintain dry repository 2. Mild steel drums continue to corrode non-uniformly 3. H_2 with N_2 is prevalent gas $H_2 > N_2 > N_2O > CH_4$ 4. CO_2 absorbed by $Mg(OH)_2$ 5. Salado Brine salt solidifies 6. Water continues to be catalyst information of $MgCO_3 \bullet 3H_2O$ 7. Microbial activity increases slowly in dry condition; produces CO_2 8. Radiolysis increases slowly in dry conditions 6. Alpha degradation produces CO_2 7. Chemical degradation is slow 8. No solubility of actinides 12. Cementitious material is degrading producing CO_2 13. Basicity of repository is increased 14. Anhydrite interbeds continue to provide diffusion path for H_2 9. Repository pressure due to all gases increases because of small void space 16. Swelling of MgO $\longrightarrow$ $MgCO_3 \bullet 3H_2O$ decreases void space 17. Iron corrosion begins to impact available void space 18. Less than 15% of MgO reacted with brine 19. ^{241}Am has gone through one half-life and reduced source term 20. Particle size of waste form remains large 21. No colloids will form in this high ionic strength condition 22. Shear strength of compacted waste is high

Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2600	500	**(V_a) WIPP Solidification Period**	**(W/Brine Intrusion)**
		1. Dynamic creep closure complete 2. Non-cemented drums compacted 3. Cemented drums encased 4. MgO is dispersed 5. Porosity is at equilibrium 6. Permeability is minimal 7. Tortuosity retards intra-repository communication 8. Human intrusion scenario results in brine intrusion into repository from Castile	1. Brine diffuses into available void volume 2. Infused brine reacts with MgO resulting in greater swelling and decreased porosity and permeability 3. Castile Brine infusion yields $Mg(OH)_2$ and salt 4. Radiolysis becomes active in producing H_2 and CO_2 over hundreds of years 5. Microbial activity increases and accelerates degradation of cementitious solids yielding more basic system (kinetics of hundreds of years) 10. Only part of repository will be inundated and release of pressure will be localized 11. Corrosion of mild steel drums will accelerate 12. Chemical degradation will be accelerated 13. ^{241}Am has gone through one half-life 14. Actinides that solubilize will precipitate and be adsorbed on $Mg(OH)_2$ 15. Void space will be essentially nonexistent

Introduction

This report provides a flowsheet of the projected chemical conditions within the WIPP disposal rooms, panels, and repository on a chronological and sequential basis for 500 years. The chemical conditions in the repository will be dependent on the physical changes that are occurring to the repository because of dynamic creep closure and the effect of added MgO on Salado formation brine in-leakage and how these processes influence the chemistry of the waste on a long-term basis.

The chronological and projected chemical conditions are sequentially discussed from the time the waste is generated and stored in 55-gallon drums and standard waste boxes at the generator sites to eventual placement, entombment, and degradation according to physical changes to the repository and overall chemical degradation of the waste. The flowsheet is sequentially arranged in six sections covering 500 years from time of closure of the loaded panels.

Repository Reference Parameters[1]

- 8 panels
- 4 entry shafts equivalent to 2 panels
- 7 disposal rooms per panel
- Lithostatic pressure = 14.8 mPa
- Repository storage volume = 436,000 m^3
- Excavated volume of one panel = 46,097 cm^3
- Number of drums in one panel = 86,000
- Design volume of waste in repository – 1.76×10^5 m^3
- Volume of one drum = 0.21 m^3
- Mass of Fe in containers - 2.61×10^7 kg
- Density of Salado Brine - 1.23 gm/cm^3
- Weight of MgO to be added to repository[2] = 85,600 tons where 1 ton = 2000 pounds
- Weight of MgO to be added to 1 panel[3] = 8560 tons
- Brine inflow rate into Salado Disposal Rooms - 4 m^3/room/yr. for first 50 years (maximum)
- Brine inflow rate into Salado Disposal Rooms after 50 years = <0. 1 m^3/room/yr
- Dynamic creep closure rate = 50% of void volume in 50 years
  = 90-100% of void volume in 100 years

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[1] Premliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992, SAND92-0700.
[2] R. Vann Bynum, et.al., Implementation of Chemical Controls Through a Backfill System for the Waste Isolation Pilot Plant (WIPP).
[3] Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992, SAND92-0700.

Waste Stored at Generator Sites

TRU Waste at Sites

Transuranic (TRU) waste historically generated by defense-related activities is stored in 55-gallon drums and Standard Waste Boxes (SVv'Bs) in both above ground storage enclosures or temporarily buried in storage pits at the generator sites throughout the DOE complex.

The wastes destined for the WIPP must be TRU waste that meets the specifications of the WIPP Waste Acceptance Criteria document. In general, the waste can be categorized as heterogeneous waste, homogeneous (solidified) wastes, or metallic wastes which includes the mild steel 55-gallon drum container.

Chemical Degradation/ Corrosion

Chemical degradation of the waste commences immediately upon emplacement in storage locations at the generator sites but these reactions are very slow and are barely noticeable as evidenced by the limited quantities of evolved gases that are vented through the carbon composite filters placed on the containers. Corrosion of the internal surface area of the drums containing moisture such as drums with Portland Cement, Envirostone, or other solidification agents will initiate corrosion during the storage period at the generator sites. Above-ground managed storage will result in drums that are less corroded or have been repackaged during the storage period. Drums stored in earthen burial sites are expected to be considerably more corroded and perhaps are more susceptible to severe corrosion during the storage period.[4]

Microbial Activity/ Headspace Gas

Microbial activity in the individual drums is on-going for aerobic microbes but this is a very minor degradation activity. Radiolysis and alpha degradation of organics is ongoing but also very limited during this storage period. The headspace gas composition of the storage drums is air that has differing concentrations of H_2, $C0_2$, and evolved VOCs. The headspace gas is vented through carbon composite filters or other venting arrangements. The time period the different waste containers reside at the generator sites can be less than 10 years for newly-generated waste or up to 30 years for legacy waste that may have had to be repackaged to meet WIPP Waste Acceptance Criteria.

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[4] Pit-9 at INEEL and underground burial locations at LANL (TA-54) are examples of buried storage locations.

Waste Emplacement in WIPP Commences

Waste Emplacement/ MgO Addition

Waste transport to WIPP will be via TRUPACT-II shipments from generator sites for loading into the WIPP Disposal Rooms. At the WIPP, the waste drums and SWBs will be emplaced in a waste container array within the disposal rooms with MgO sacks or packs throughout the waste stacks. A description of the methodology for emplacing supersacks (4000 lbs.) and minisacks (25 lbs.) is given in the document reference in footnote #2.

Of note is that supersacks will be emplaced on top of waste stacks so those sacks will be crushed open when the roof of the disposal rooms "caves in" due to dynamic creep closure. Waste will be emplaced in a sequential manner so some panels will be fully loaded while others will be in the process of loading through the entry shaft elevators.

Salado Brine Seepage

Salado brine seepage will continue throughout this process as the Disturbed Rock Zone will continue to release brine to the disposal rooms. Once a panel is completely loaded and an operational seal is placed in the entry to that panel, creep closure and the waste degradation process unique to that panel will begin.

Headspace Gas

The headspace gas of the sealed panel will be air with some addition of evolved gas from the emplaced waste containers. The initial pressure in the panel will be near atmospheric for the WIPP, which is 0.101 mPa.

MgO Antibacterial

The addition of excess MgO will maintain the panel in a dry condition and the MgO will retard microbial activity because it has been reported to be anti-bacterial and would inhibit the activity of facultative anaerobes.[5, 6] The inhibitory activity of the MgO has been studied and reported to be due to active oxygen sites on the MgO rather than only basic conditions.

Corrosion

Corrosion of the mild steel drums would increase in panels once a panel is sealed because of the increased moisture levels at the temperature of the repository (30°C) and the ubiquitous presence of chloride.

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[5] J. Sawai, et.al., "Detection of Active Oxygen Generated From Ceramic Powders Having Antibacterial Activity," Journal of Chemical Engineering of Japan, Vol. 29., pp. 627-733. (1996).

[6] J. Sawai, et.al., "Evaluation of Growth-Inhibitory Effect of Ceramics Powder Slurry on Bacteria by Conductance Method," Journal of Chemical Engineering of Japan, Vol. 28., pp. 288-293. (1995).

WIPP Entry Shafts Sealed: WIPP Closed

WIPP Closure

The WIPP is expected to be fully loaded in approximately 50 years followed by sealing of the 8 panels and entry shafts. Once loading of the repository is complete and each panel has been sealed with an operational seal, the 4 entry shafts will be closure-sealed so the repository will be permanently closed.

Creep Closure

Each panel will be at a different stage as the process of geologic creep closure of the massive salt rock begins to heal and isotropically, but not uniformly, close in on the waste stacks. The panels that were filled early in the loading process and were sealed with operational seals would be closing at a rate given as a contraction of 50% of the excavated volume in 50 years. Consequently, some panels would be at approximately 40% contraction while others would be commencing dynamic creep closure.

Repository Setting

The repository as a whole would remain dry because of the excess MgO. Brine seepage from the Salado Disturbed Rock Zone would continue as seepage inflow into the repository at a rate given as $4 m^3$ per disposal room per year for 50 years and $< 0.1\ m^3$ per year thereafter. Assuming the $4 m^3$ per year per disposal room for 50 years, the calculated quantity of brine in the repository after 50 years would be:

$$(4\ m^3/yr)\ (7\ \frac{rooms}{panel})\ (8\ \frac{panel}{repository}) = 224\ m^3/yr/repository$$

For 50 years:

$$(224)\ (50) = 11{,}200\ m^3 \text{ Salado brine in repository}$$

This is equivalent to:

$$(11{,}200\ m^3)\ (1\times10^6\ \frac{3m^3}{m^3}) = 1.12\times10^{10}\ cm^3 \text{ brine in repository after 50 yrs}$$

The composition of Salado Brine (Brine A) has been reported by Martin Molecke.[7,8]

Continued on next page

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[7] Martin Molecke, "Test Plan" WIPP Bin-Scale CH-TRU Waste Tests," SNL Report, p.16, January, (1990).

[8] M. A. Molecke, "A Comparison of Brines Relevant to Nuclear Waste Experimentation, " SAND 83-0516, (1993).

The concentration of salts in Brine A is approximately 305 gm/liter of solution, consisting of about 45% $MgCl_2$, 33% NaCl, 19% KCl, and 2% Na_2SO_4. Consequently, for each liter of solution that reacts with MgO, there is a resulting salt deposit of 305 gm. The quantity of water available to react with MgO is approximately 695 gm/liter. For a brine in-leakage of 4m³ /disposal room/year for 50 years, the quantity of crystallized salt would be $(11{,}200\ m^3)(0.305) = 3416\ m^3$ of crystallized salt.

Addition of MgO

The weight of MgO added to the repository has been given as 85,600 tons, and the weight added to each panel is given as 8,560 tons. The density of the MgO was measured to be 3.51 gm/cm³, which agrees with the theoretical density 3.58 gm./cm³. The calculated volume of MgO in the repository is:

$$(85{,}600\ \text{tons})\,(2{,}000\ \text{lb/ton})\,(453.59\ \text{lb}) = 7.76\times 10^{10}\ \text{gm}$$

This is equivalent to 1.93×10^{9} mole in the repository.

$$V = 7.76\times 10^{10}\ \text{gm}/3.58\ \text{gm/cm}^3 = 2.17\times 10^{10}\ \text{cm}^3 = 21{,}691\ \text{M}^3$$

WIPP Creep Closure Period

Reaction of MgO

There are many different ways that Salado brine can contact MgO in the WIPP disposal rooms. The four major ways that are described are given below and elaborated on in the enclosed report, "Effectiveness of MgO for Controlling PCO_2 in WIPP Including Phase Diagrams."

Process 1
Salado brine contacting the MgO by free fall droplets from the roof

Process 2
Salado brine contacting the MgO by wicking or capillary action through salt or other crushed waste.

Process 3
MgO contacting Salado brine by dropping as small pellets into a pool of brine.

Process 4
Reaction of MgO with moisture in the WIPP void volumes from vapor pressure of water at 30°C above available brine or water retained in brine A/MgO reaction products.

These four contact processes will result in different reaction products and reaction kinetics and will influence the capability of reacting with available CO_2 to form $MgCO_3$, leading to
$MgCO_3 \bullet 3H_2O$.

Reaction Process 1

Reaction Process 1 will yield the following reactions and products:

$MgO + \text{Brine A} (MgCl_2, NaCl, KCl) \xrightarrow{H_20} Mg(OH)_2$
$+ 5\ Mg(OH)_2 \bullet MgCl_2 \bullet 8\ H_20$
$+ 3\ Mg(OH)_2 \bullet MgCl_2 \bullet 8\ H_20$
$+ 5\ MgO \bullet MgCl_2 \bullet 13\ H_2O$ (metastable product in basic solution[9,10])

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[9] Chuanmei Zhang and Dehua Deng, "Research on Water Resistance of Magnesium Oxychloride Cement 1: The Stability of the Reaction Products of Magnesium Oxychloride Cement and Water," J. Wuhan University Technology, Materials Science Edition (1994).

[10] E. S. Solov'eva, B. I. Smirnov, E. E. Seaglova, "Kinetics of the Development of Crystallization Structures During Hardening as Illustrated by Hydration of Binder-Sorel Cement" USSR, Usp. Kolloid. Khim., pp. 235-8, (1973).

The formation of the above reaction products would be accompanied by inclusion of $MgCl_2$, NaCl, and KCl and $NaSO_4$ salts that would crystallize on absorption of water by the MgO. The resultant mass on the pellet surface would be highly porous and be available to react with available CO_2 but not with the same efficiency as pure $Mg(OH)_2$. $MgCO_3 \bullet 3H_2O$ (nesquehonite) will form upon exposure to moisture saturated atmospheres.[11] LANL has conducted a test by dripping brine into an excess of MgO powder and observed similar results.

Reaction Process 2

The reactions occurring during Process 2 would be similar to those of Process I at the surface of the MgO, but would change as water with decreased salt concentration (because of the crystallization of salts at the surface of the MgO) penetrates into the MgO. The reaction front would progress into the bulk MgO forming $Mg(OH)_2$ that would be available to react with CO_2

Reaction Process 3

Process 3 would result in super- saturation of the brine pool with crystallization of the excess salts. The $Mg(OH)_2$ and sorel cement products would sink to the bottom of the brine and solidify. The resultant basic solution would be available for reaction with CO_2, but the magnesium oxychloride solid would require less magnesium-rich brine that allows the formation of $MgCO_3$. This reaction would retard the kinetics of the reaction products with CO_2.

Reaction Process 4

The reaction occurring as a result of Process 4 would yield relatively pure $Mg(OH)_2$ and would make very efficient use of MgO for ultimate absorption of CO_2. The vapor pressure of water at a repository temperature of about 30°C (86°F) would be high enough to penetrate the solid reaction products resulting from Processes 1, 2, and 3.

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[11] D. M. deCastellar, A. Traveria, J. M Tura, and F. C. Lorente, "Nesquehonite ($MgCO_3 \bullet 3 H_2O$) Efflorescence on the Surface of Magnesium Oxychloride Polishing Bricks and Calcite Nucleation Inhibition as an Effect on High Halite Concentration," Neues Jahrb. Mineral, Monatsh. Vol. 8, pp. 337-343 (1996). Journal in English.

Hadspace Gas

The headspace gas in the repository during the WIPP closure period would be principally air depleted in O_2 and newly-generated H_2, evolved VOCs, and some CH_4. Only a low level of carbon dioxide would be generated because of the dry conditions leading to retardation of corrosion and microbial activities in the repository.

Microbial activity would be inhibited by the loading of MgO.(5,6) The rates of CO_2 production would be considerably lower with MgO addition than the projected rates without MgO.[12, 13] The absence of water in the repository because of MgO addition would limit the radiolytic gas generation processes. The major radiolytic processes would be in the waste drums and would result in low generation of H_2, CO_2, N_2O, and CH_4 from alpha bombardment of carbonaceous materials producing H_2 and CO_2,[14] alpha bombardment of high nitrate concentrations producing N_2O,[15] low concentrations of CH_4 from alpha degradation of organic materials,[16] and via bacterial (microbial) methanogenesis.[17]

The production of CO_2 via methanogenesis could result from three classes of methanogenic carbonaceous substrates that are metabolized by anaerobic microbes. The generation of CH_4 from the carbon sources is maximized by conversion of CO_2 to CH_4 by reaction with H_2. With MgO present in the repository, the ambient concentration of CO_2 will be reduced to very low levels and methanogenic CH_4 generation would also be reduced.

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[12] Douglas Caldwell, et. al., "Rates of CO_2 Production From Microbial Degradation of Transuranic Wastes Under Simulated Geologic Isolation Conditions," SAND 87-7170, January (1988).

[13] L. H. Brush Memorandum to M. S. Tierney, "Likely Gas-Generation Reactions and Current Estimates of Gas Generation Rates for the Long-term WIPP Performance Assessment," June 18 (1993).

[14] Eugene Mroz, personal communication, preliminary results from Gas Generation/Matrix Depletion Experiment, March (1997).

[15] Lisa Pansoy-Hjelvik, Memorandum to Robert Villarreal, "Denitrification of N_2O Production," March 18, (1997).

[16] Eugene Mroz, personal communication, preliminary results from Gas GenerationiMatrix Depletion Experiment, March (1997).

[17] Lisa Pansoy-Hjelvik, Memorandum to Robert Villarreal, "Methanogenesis," March 18, (1997).

MgO Volume

The percentage of MgO contacted with Brine A is calculated for 50 years by assuming a Salado in-leakage rate of $4M^3$ per disposal room/year and dividing by the total weight of MgO added to the repository. The Salado brine is approximately 30.5% soluble salt and 69.5% water. The reactions that occur during contact with Salado brine can be summarized as follows:

$$\mathrm{MgO} + \mathrm{H_2O}\ (\text{in Brine A}) \rightarrow \mathrm{Mg(OH)_2} + \text{other reaction products (reaction 2)}$$

$$\mathrm{Mg(OH)_2} + \mathrm{CO_2} \rightarrow \mathrm{MgCO_3} + \mathrm{H_2O}\ (\text{reaction 3})$$

$$\mathrm{MgCO_3} + \mathrm{H_2O} \rightarrow \mathrm{MgCO_3} \bullet 3\mathrm{H_2O}\ (\text{reaction 4})$$

The weight of the MgO added to the repository is 7.76×10^{10} gm.

The volume of brine that enters the repository for 50 years is calculated to be $1.12 \times 10^{10}\,\mathrm{cm}^3$.

This total volume will remain fairly constant after 50 years, and the additional in-leakage into the repository can be considered insignificant.

Assuming $1.12 \times 10^{10}\,\mathrm{cm}^3$ of brine contains 69.5 % water, the available water is $7.78 \times 10^9\,\mathrm{cm}^3$. In reaction 2, one mole of MgO (MW = 40.30) reacts with one mole of H_2O (MW = 18) to form one mole of $Mg(OH)_2$ (MW = 58.30). The ratio of the mass of H_2O to MgO is 18/40.30 = 0.45, and this relative mass would be theoretically reacted to form $Mg(OH)_2$. However, laboratory tests conducted at LANL showed that MgO reacted with water resulted in an uptake of 220% more water than the initial mass of MgO.[18] This hydrated $Mg(OH)_2$ reaction product could lose the physico-chemically bound water through vaporization at a repository temperature of 27-30 °C. The temperature of the repository is not expected to increase beyond that range for any length of time.[19]

Assuming the available water for reaction with MgO is $7.78 \times 10^9\,\mathrm{cm}^3$ and not considering the 220% uptake that occurs, the percentage of MgO that is reacted in the repository is $\frac{7.78 \times 10^9}{7.76 \times 10^{10}} \times 100 = 10\%$. This percentage should not increase for a 500 year period because of the insignificant in-flow that occurs after 50 years.

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[18] Jason Lashley, LANL Memorandum to Robert Villarreal, "Magnesium Oxide Experiments in Preparation for Addition to an Actinide Source-term Waste Program (STTP) Test Container," March 17, (1997).

[19] David Bennett, Yifeng Wang, and Tim Hicks, "An Evaluation of Heat Generation Processes for the WIPP," SNL Memorandum, August 20, (1996).

WIPP Solidification Period (W/O Brine Intrusion)

After 150 years, the dynamic creep closure of the WIPP Waste Disposal Rooms is essentially complete. After 500 years, all panels have arrived at maximum closure due to dynamic creep closure of the bulk salt rock. The non-cemented drums containing heterogeneous wastes are crushed and compacted while the cemented drums are encased or surrounded by salt. The closure has resulted in the inclusion of what was headspace gas into an integrated porosity at elevated pressure. MgO added to the repository is now integrated into the waste salt residues from reaction of Salado Brine with MgO, and salt granules from the creep closure process. Salado Brine seepage has abated because of lithostatic pressure equilibration and continued slow generation of gases from degradation of the waste. The repository remains dry because of the continued up-take of water from the brine by the MgO. The permeability of the repository is decreased and the tortuosity of the waste/salt/MgO and other reaction products prevents intra-room connectedness. Intra-room sites develop that do not have communication with the overall repository.

The reaction of MgO with any residual brine will continue by Process 2 and Process 4, but the much-retarded inflow of Salado Brine will maintain a dry repository. If the Salado Brine inflow continues at a rate of 5% of the original 4m^3/disposal room/year for an additional 50 years, the overall increase in total brine inflow would be <5% and the overall reaction-depletion of MgO would be < 15%.

The mild steel drums and metallic waste forms will continue to corrode with areas in the repository having more or less corrosion depending on the available oxygen and brine in the repository. The corrosion of the mild steel drums and other mild steel waste forms can progress by two major pathways depending on availability of brine and O_2 as follows:

$$2\,Fe + O_2 \rightarrow 2\,FeO$$
$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$$

The mass of Fe in the mild steel drums is reported as 2.61×10^7 Kg.(1)

If all the Fe in the repository were converted to $Fe(OH)_2$, the increase in volume of Fe to $Fe(OH)_2$ will be from $3.32 \times 10^3\ M^3$ to $1.22 \times 10^4\ M^3$ or an increase of 368%. The volume increase in the repository is from an Fe volume of 0.76% of the total evacuated storage volume to 2.8%. The Fe present in the waste is approximately 7% by volume after conversion to $Fe(OH)_2$.

The gas composition in the porosity of the disposal rooms would be expected to be primarily H_2, N_2, N_2O, and CH_4. All CO_2 generated by microbial and radiolytic processes would be totally reacted by the $Mg(OH)_2$.

Continued on next page

The soluble salts in the Salado Brine that diffuse into the interstices of the MgO pellets will crystallize as the water in the brine reacts with the MgO to form $Mg(OH)_2$. This swelling of MgO to $Mg(OH)_2$ and eventually $MgCO_3$ with a concomitant swelling due to salt precipitation and sorel cement phase will reduce the number of MgO spheres (pellets) within a given volume in the repository. Water in the Salado Brine will continue to act as a catalyst in the presence of CO_2 in the sequential reactions from $MgO \rightarrow Mg(OH)_2 \rightarrow MgCO_3 \rightarrow MgCO_3 \bullet 3H_2O$.

Microbial activity will remain very slow in a dry repository condition in a highly basic environment. Radiolysis will be limited to the waste matrix, which will be fairly dry due to the desiccant effect of MgO. The degradation of waste will be very slow because of the lack of brine in the waste as free water. Direct contact of alpha-emitting actinides with organic waste forms will generate CO_2 gas at a very limited rate. Chemical degradation of the waste will be retarded because of the presence of MgO. Because there is no free brine in the repository, there are no concentrations of actinides that can accumulate at any level. The moisture inherently present within the cementitious material will lead to supporting microbial degradation of the cement. Degradation of cementitious material will provide $Ca(OH)_2$ that will be available for reaction with CO_2 and will be a source of a strong basic media that will inhibit anaerobic bacteria and precipitate elemental salts including actinides provided brine was available. The anhydrite interbeds continue to provide a diffusion outlet for H_2 gas but the repository pressure would increase significantly because of the small pore size of the gas space within the waste. Less than 15% of the MgO is calculated to be reacted based on calculations of a Salado Brine inleakage rate of $4M^3$/room/yr. for 50 years and 0.02 M^3/room/yr. for an additional 50 years. After 500 years, the ^{241}Am activity will be reduced by greater than 50% because over one half-life of ^{241}Am ($t_{1/2}$ = 432 yr.) will have passed. This will reduce the source term of the repository significantly. No colloids or polymers of Pu will form for transport in this repository condition because of the lack of water (Brine A) due to reaction with MgO. The particle size of the waste will remain large with a dry repository and the compressive strength of the waste will be high because of compacted waste and waste degradation product mass.

WIPP Solidification Period (With Brine Intrusion)

The physical condition of the repository after 500 years including an intrusion scenario that infuses brine into the repository would be similar to the condition without brine intrusion. However, introduction of brine from a lower-lying WIPP formation or any other location would significantly change the chemistry of the repository. Brine would diffuse into the available porosity of a disposal room. The tortuosity of interconnectedness would be significant and may limit the repository area or volume that would be affected by an infusion of brine. If the brine intrusion is Castile Brine, the low $MgCl_2$ brine would react with MgO more effectively and efficiently relative to the Salado Brine. The repository volume affected by the brine intrusion would react with any MgO that was available for reaction and yield $Mg(OH)_2$ that would diffuse through the porosity of the brine-affected zone. Solubilization of actinides and other elemental salts will result in precipitates of the salts in the highly basic media of $Mg(OH)_2$ and $Ca(OH)_2$ (from cement). An injection of Castile Brine into the porosity of the repository at this time would lead to immediate contact with the crystallized and powdered salt within the MgO, $Mg(OH)_2$, and $MgCO_3$ matrix and re-solubilization of those salts. The resulting brine mixture would be more like a Salado Brine that would be very viscous. In less than 5 years, the low viscosity of the high ionic strength brine would lead to plugging of pore spaces within the brine-affected zone. This viscosity and plugging process has been observed in the Actinide Source-term Waste Test Program (STTP) experiments conducted at Los Alamos National Laboratory.[20, 21] The high ionic strength brine solutions will lead to increased radiolysis, microbial activity, corrosion, and chemical degradation. All of these activities will result in a more and more viscous solution in the repository that will eventually plug up the porosity of the repository.

Any further brine intrusion scenarios would not have a significant impact on the brine-affected zone because of the low permeability and porosity and high tortuosity in the repository. The formation of actinide colloids would be essentially non-existent at these very high ionic strength brine solutions and low actinide concentration as evidenced by data obtained from the STTP.(20, 21) Any packets of solubilized actinides that might exist in the repository for any unexplained situation would result in the actinides being adsorbed by the precipitated $Mg(OH)_2$ that has not been exposed to CO_2.

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[20] Robert Villarreal and Mark Phillips, "Test Plan for the Actinide Source-term Waste Test Program, "CLS I -STP SOP5-012/0, May (1993).

[21] Data Compilations from STTP Experiments, Reported by Los Alamos National Laboratory to Sandia National Laboratories and DOE, Carlsbad Area Office, (1995, 1996, 1997).

III. (d) Effectiveness of MgO for Controlling PCO_2 in WIPP, Including Phase Diagrams

Purpose and Scope

A backfill of MgO has been proposed for WIPP primarily to control the partial pressure of CO_2 in the repository over time at low levels (<10^{-3} atmospheres) (Vann Bynum et al., 1997). High partial pressures of CO_2 could potentially cause waters in the repository to attain low pmH values. This could have negative consequences for the transport of radionuclides, particularly the actinides. The MgO would likely be emplaced in sacks stacked on top of the waste and beside it.

The Peer Review Panel charged with evaluating WIPP technical work has raised questions concerning the effectiveness with which MgO would maintain low CO_2 Partial pressures in WIPP after closure. In particular, the Panel is concerned that CO_2 will form relatively impermeable reaction rims on the MgO pellets emplaced in the repository. If such rims were to form, it is conceivable they could restrict the quantity of MgO available for reaction with CO_2.

This paper, will discuss the mechanisms and kinetics by which CO_2 could react with MgO or its hydrated forms. The discussion of mechanisms will be based on phase diagrams formulated for the $MgO-H_2O-CO_2$ system. The kinetics discussion will be based on conceptual models for the reaction of WIPP brines with MgO pellets, a literature review of pertinent kinetics data and available experimental data.

Characteristics of MgO Pellets

Although final decisions regarding the form and characteristics of the MgO to be emplaced in the repository have not been made to our knowledge, some assumptions and estimates regarding these parameters had to be made to carry out the analysis. These assumptions and estimates were based largely on information supplied to Dr. David Janecky (LANL) by David R. Wilson of National Magnesia Chemicals, Moss Landing California.

The following is a transcript of the information supplied by National Magnesia Chemicals on the MgO they could supply:

IDENTITY:	GRADE OOHB
DESCRIPTION:	A chemical grade granular magnesium oxide featuring high purity, very low reactivity and high bulk density. Produced from seawater at Moss Landing California in a rotary kiln.

Continued on next page

APPLICATIONS: Grade OOHB is an excellent magnesium source for the manufacture of magnesium salts. Also used in production of fused MgO for heating elements, manufacture of heat resistant glass and other ceramics. Granular grades are used in filtration beds for water treatment and pH control.

CHEMISTRY:	Ignited Basis (%)	TYPICAL	SPECIFICATION
	Magnesium Oxide (MgO) (by difference)	98.5	97.5 minimum
	Calcium Oxide (CaO)	0.3	1.0 maximum
	Silica (SiO_2)	0.4	0.6 maximum
	Iron Oxide (Fe_2O_3) maximum	0.2	0.31
	Aluminum Oxide (Al_2O_3) maximum	0.04	0.06
	Sulfate (SO_3) maximum	0.0	0.10
	"As Is" Basis (%)		
	Loss on ignition (including Cl)	0.2	0.5 maximum
	Chloride (Cl) maximum	0.0	0.02
PHYSICAL PROPERTIES:	Surface Area (m^2/g)	< 2	1-2
	Citric Acid Activity (CAA) seconds	> 1500	
	Acid Insolubles (%)	0.07	
	Loose Bulk Density (lbs/ft^3) ($1.4\ g/cm^3$)	90	
	Tyler Sieve Analysis - Standard Sizing	− 3/8, 3/8 × 10 and - 10 mesh	
	Special Sizes available upon request		

Continued on next page

SHIPPING:	Bulk - available in rail carload or truckload quantities Bagged - packed in multiwall paper bags including polyethylene moisture barrier. Net weight - 50 pounds (22.68 kg). There will be less than 0.1 % hydration during shipment.
HANDLING PRECAUTIONS:	Magnesium oxide is by nature hygroscopic and should be stored in a dry place. Exposure to moisture may cause caking. Bulk storage should be protected from the atmosphere. Material should be used within six months. Seller warrants that this product meets the specifications listed. Seller makes no other warranties, expressed or implied, with respect to this product or its use.

MgO-Fluid Contact Modes

Once MgO has been emplaced in a given room within the repository and the room has been sealed, there are several scenarios by which brines and gases might interact with the MgO. In the undisturbed scenario, the brine interaction could involve four separate contact modes including (1) a vapor phase mode, (2) a drip mode, (3) a wicking mode and (4) a saturated mode. In a human intrusion scenario involving drilling of a well into the Castille Formation, the most likely contact mode would be the saturated mode.

The first three modes are more likely to occur during the early history of a room while the last mode could only occur after the room had been flooded. The vapor phase mode is most general because all the MgO pellets in a room will be subject to this contact mode. Note that this mode involves only H_2O and CO_2 and not the other dissolved components of the brine. The drip mode involves drips of Salado brine from the ceiling of a room onto the bags of MgO pellets. This mode would likely be localized in a limited portion of a given room but this portion could be anywhere in the room. The wicking mode involves contact of the MgO pellets with a reservoir of liquid. It could occur as a result of contact of the pellets with brine emanating from the walls or floor of a room. It could also occur in relation to the drip and saturated modes. The saturated mode involves partial or complete flooding of a room. In the undisturbed case, the flooding would likely involve Salado brine. In a human intrusion scenario involving drilling into the Castille Formation, the flooding would more IdKely involve a Castille brine. Because these brine compositions are quite distinct, they may have different impacts on $MgO/H_2O/CO_2$ reaction efficiencies.

Phase Relations Assuming Different Contact Modes

Before the kinetics of the reactions with emplaced MgO can be discussed, the possible phases that could form under repository conditions must be identified. One way to identify these phases is to use the results of laboratory experiments with MgO and appropriate brine and vapor compositions.

Continued on next page

The work with MgO-brine reactions carried out at Sandia National Laboratory (Krumhansl et al., 1997) has identified primarily two sets of solid phases depending on the brine composition used in the experiments. When the Castille brine is used in the experiments, the phases identified are primarily $Mg(OH)_2$ (brucite) and $MgO\text{-}CO_3\text{-}H_2O$ phases such as nesquehonite ($MgCO_3 \bullet 3H_2O$), hydromagnesite ($3MgCO_3 \bullet Mg(OH)_2 \bullet 3H_2O$) and dypingite ($4MgCO_3 \bullet Mg(OH)_2 \bullet 5H_2O$). When the Salado brine is used in the experiments, the phases formed are a function of the partial pressure Of CO_2. At low CO_2 partial pressures, phases common to Sorel cement are formed. These are hydrated magnesium hydroxychlorides with compositions such as $5Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$ and $3Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$.

At higher partial pressures of CO_2, the phases formed are similar to those identified in the experiments with Castille brine.

Another way to identify the phases that could form in the repository environment is to calculate phase stabilities on the basis of thermodynamic data. These calculations are generally summarized in the form of phase diagrams in which the stability field for each phase is plotted in terms of two dominant chemical variables. The stability fields are calculated under the assumption of an equilibrium condition. Metastable phases can also be plotted by assuming they are a surrogate for the equilibrium phase.

For experiments involving the Castille brine and the Salado brine at partial pressures of CO_2 that are above atmospheric, a useful phase diagram is one for the $MgO\text{-}H_2O\text{-}CO_2$ system in which the variables are the Log (fH_2O) and Log (fCO_2). This phase diagram is also appropriate for the vapor phase contact mode.

Figure 1 shows the phase equilibria in the system $MgO\text{-}CO_2\text{-}H_2O$ as a function of Log (fH_2O) and Log (fCO_2) at 25 °C and 1 bar. This figure indicates that so long as periclase (MgO) remains present and equilibrium is maintained the partial pressures of both CO_2 and H_2O should remain very low in the repository. Reaction of periclase with CO_2 and H_2O in this environment produces brucite and magnesite. Once the periclase has been consumed the brucite and magnesite will begin to react with CO_2 and H_2O to produce hydromagnesite. The Log (fCO_2) and Log (fH_2O) increase as this reaction progresses. Eventually, the Log (fCO_2) will be buffered at approximately $10^{-4.6}$ and the Log (fH_2O) will be approximately $10^{-2.5}$ or less as long as brucite remains.

Figure 2 shows the region of Figure 1 around the region of liquid water or brine stability. Once the magnesite has been consumed a liquid phase can appear. At this point, reaction of CO_2 with brucite to produce hydromagnesite will continue with the equilibrium fugacity of CO_2 near $10^{-4.6}$. Once the brucite is consumed, the fugacity of CO_2 can increase and reaction of hydromagnesite with CO_2 and H_2O can proceed to produce nesquehonite. The fugacity of CO_2 at equilibrium during this reaction is highly dependent on the fugacity of H_2O, but it should be below 1 bar. Thus high CO_2 pressure would not be expected until complete conversion to nesquehonite.

This latter set of reactions most closely approximates the conditions under which the laboratory experiments with Castille brine were carried out.

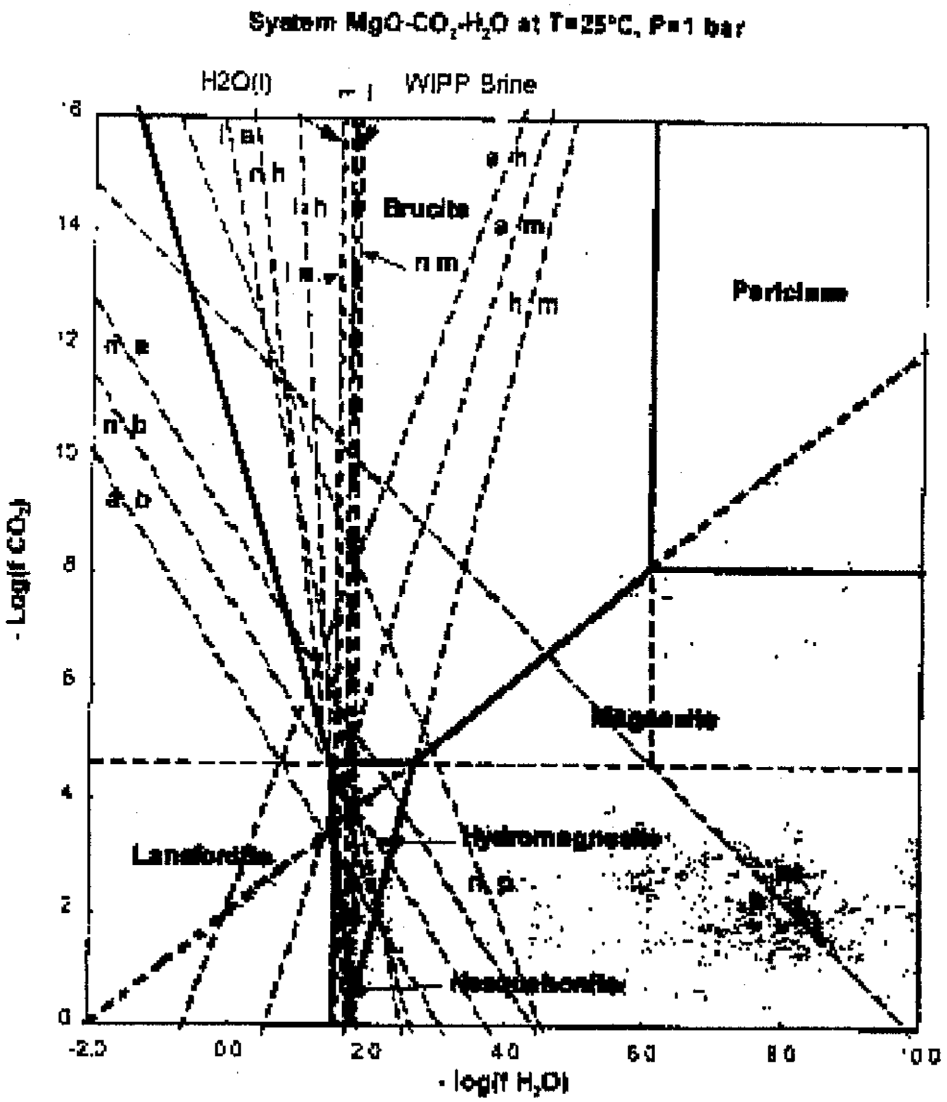

Figure 1. Data for phases in the system MgO-CO_2-H_2O

	Formula	Symbol	Delta G_f	Reference
H2O (g)	H_2O		-54525	supcrt92
CO2 (g)	CO_2		-94254	supcrt92
Artinite	$Mg_2CO_3(OH)_2{:}3H_2O$	a	-609472.03	Langmuir 97
Brucite	$Mg(OH)_2$	b	-198921.17	Langmuir 97
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2{:}4H_2O$	h	-1396991.3	Langmuir 97
Lansfordite	$MgCO_3{:}5H_2O$	l	-525581.72	Langmuir 97
Magnesite	$MgCO_3$	m	-241381.33	Langmuir 97
Nesquehonite	$MgCO_3{:}3H_2O$	n	-412379.09	Langmuir 97
Periclase	MgO	p	-136086	supcrt92

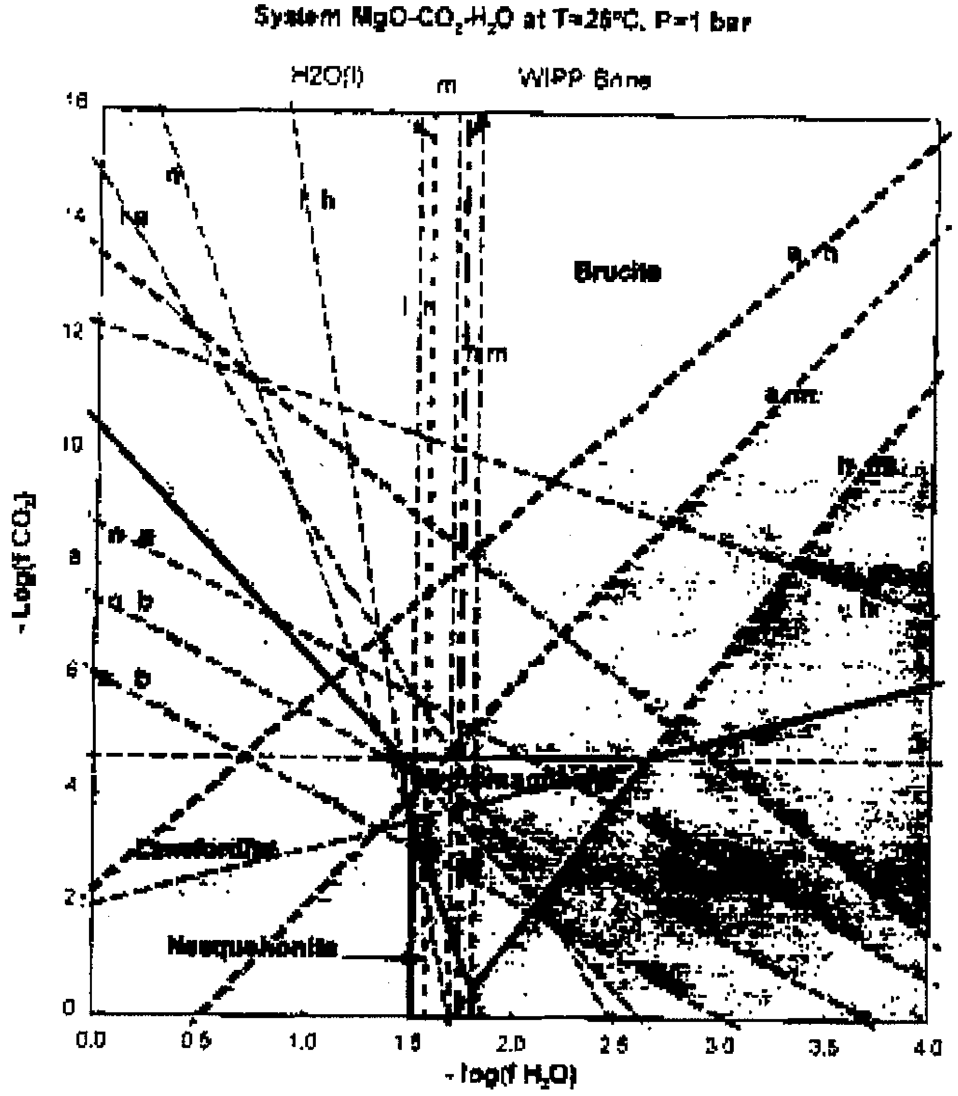

Figure 2. Mass of CO_2 and H_2O consumed by formation of phase from MgO

	Phase Formula Weight	gH2O/g MgO	g CO2/g MgO
Artinite	196.137	.90	0.55
Brucite	58.049	0.45	0.00
Hydromagnesite	466.281	0.45	0.88
Lansfordite	174.118	2.25	1.10
Magnesite	84.043	0.00	1.10
Nesquehonite	138.088	1.35	1.10
Periclase	40.034	0.00	0.00

Reaction Kinetics

Based on the equilibrium phase relations and on the amount of MgO to be emplaced per room, there should be sufficient MgO to absorb all the CO_2 produced by the degradation of organic components emplaced in the repository and maintain the partial pressure of CO_2 at acceptably low levels. However, the Peer Review Panel has questioned whether all the MgO to be emplaced will be accessible to CO_2. In particular, the Panel has questioned whether reaction rims could form on the MgO pellets that would preclude or at least greatly inhibit access of CO_2 into the interior of the pellets. Hypothetically, several different types of reaction rims could form depending on the $MgO/H_2O/CO_2$ contact mode. Each of these rims could have a somewhat different impact on CO_2 diffusion rates.

In the vapor phase contact mode, the hypothetical reaction rims would likely consist initially of brucite and subsequently of hydromagnesite or magnesite. In the drip contact mode, the hypothetical reaction rims may be brucite followed by Sorel cement phases or possibly only Sorel cement phases. In the wicking contact mode, the phases that could form the rim will depend on the composition of the brine that is wicked into the MgO pellets. If the brine is a Salado brine, the phases will be similar to those produced in the drip contact mode. If it is a Castille brine, the phases formed would likely be similar to those produced in the vapor phase mode although the proportions of phases may be different. For the saturated contact mode, a similar situation pertains depending on whether the repository is flooded by Salado or Castille brine.

The vapor phase contact mode is the least likely to restrict CO_2 diffusion into the pellets because this mode only involves the addition of H_2O and CO_2 to the pellets. Literature data suggest that the conversion of MgO to $Mg(OH)_2$ involves a four step dissolution/reprecipitation process (Smithson and Bakhshi, 1969) as follows:

(1) "Initially water vapor is chernisorbed on the MgO and then physically adsorbed to form a liquid layer on the surface of the solid."

(2) "This layer of water reacts with the MgO to form a surface layer of $Mg(OH)_2$."

(3) "The $Mg(OH)_2$ subsequently dissolves into the water layer."

(4) "As the water layer becomes saturated with $Mg(OH)_2$, precipitation will take place with nuclei forming at the interface between the chemically and physically adsorbed water at points where active sites occur on the MgO surface."

According to Feitknecht and Braun (1967), the $Mg(OH)_2$ crystals that form in this process are needle-like and grow outward perpendicular to the MgO surface. This results in a high porosity rim, which should not inhibit CO_2 diffusion.

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Unfortunately, similarly detailed studies have not been identified in the literature regarding the conversion of $Mg(OH)_2$ into hydromagnesite or magnesite. Therefore, the degree to which a reaction rim of these materials would inhibit CO_2 diffusion into a pellet cannot be adequately evaluated on the basis of literature data alone. Experimental data are needed on the permeability of these reaction rims.

The drip contact mode is complicated by the fact that in addition to the phase changes discussed for the vapor phase contact mode, salts will be deposited from the brine in the intrapellet pore space. This will very likely cause the permeability of the pellets affected by this contact mode to be less than the permeability of the pellets affected only by the vapor phase contact mode and also less than the pellets affected by the wicking or saturated contact modes. The reason is that as Salado brine drips onto the pellets and the water in the brine is taken up by the MgO to produce $Mg(OH)_2$, the brine remaining in the pellets becomes supersaturated with halite (NaCl) and other salts originally present in the brine. This eventually results in the precipitation of these salts in the intrapellet pore space further decreasing the permeability of the pellets. The extent of the permeability decreases resulting from this contact mode can only be determined through experiment. Such experiments should involve dripping Salado brine onto pellets in a column under an atmosphere with a low CO_2 partial pressure. The drip rate should be slow enough so that free liquid does not break through the pellet mass.

Experiments in which the pellets are submersed in Salado brine will not provide the proper data on the drip contact mode because in such experiments the salts are not constrained to precipitate in the intrapellet pore space. The salts can precipitate anywhere that there are suitable crystallization nuclei and conditions most favorable for crystallization. In addition, the saturated experiments do not result in the same net transfer of salt to the pellets unless all the liquid in the experiments is taken up by the MgO. The saturated experiments would, however, provide useful data on reaction rim formation in the saturated contact mode. A critical parameter in these experiments would be whether Salado or Castille brine is used.

Recommendations for Additional Experimental Work

The experiments currently ongoing or planned by Sandia National Laboratory (Krumhansl et al., 1997) address many of the issues relating to the diffusion rate of CO_2 into the pellets and other issues may have been addressed by experiments for which the results have yet to be reported. However, several issues remain to be addressed. These include:

(1) In the vapor phase contact mode experiments carried out by Sandia, it is reported that "a cohesive mass has formed that is 1.5% by weight carbon (not CO_2)." The pellets used in these experiments should be sectioned to determine where the carbon is located in the pellets. The question is whether or not CO_2 has access to the interior of the pellet as the hydration and carbonation reactions proceed inside the pellet.

(2) The diffusion rate of CO_2 into pellets modified by drip contact mode exposure must be determined. This could be accomplished by slowly dripping Salado brine onto pellets in a column under an atmosphere with a low partial pressure of CO_2. After some period of time the gas permeability of the pellets must be measured possibly using the pH rebound technique (Krumhansl et al., 1997).

(3) Thickness of reaction rims. The reaction rims formed in the experiments carried out by Sandia may not be as thick as the rims that may ultimately form in the repository environment, hindering evaluation of CO_2 fixation limitations and kinetics. One way to enhance the reaction rim formation rate to test its impact is to perform the experiments under moderately elevated temperatures, which increases MgO hydration reaction rates. Following development of reaction rims, addition of CO_2 to the reaction vessel will allow monitoring of its loss from solution as a function of time due to reaction with the Mg phases. The mineralogy and structure of the altered MgO pellets can be determined at the end of the experiments and combined with the solution information to evaluate the impact of altered rim formation. A drawback to this approach is that the phase assemblage and the textures formed may differ from those formed under repository conditions, and only saturated reaction conditions can be quickly investigated. However, these experiments will provide critical constraining information on the question of how rim formation impacts CO_2 fixation during saturated brine interactions.

Conclusions

In order to bound the effectiveness of MgO in buffering the partial pressure of CO_2 in the WIPP repository, phase relations and kinetic data are required. Because there will likely be different contact modes between MgO and brine/vapor including a vapor phase, a wicking, a drip and a saturated mode, different phase stability and reaction kinetic data will be required. An analysis of thermodynamic data for the system $MgO/H_2O/CO_2$ has identified the phases that will be stable or metastable in the contact modes involving a vapor phase or Castille brine. Thermodynamic data are not adequate to evaluate phase stabilities in contact modes involving the Salado brine composition.

An evaluation of literature data on the kinetics of MgO vaporibrine reactions indicates that only limited pertinent data are available. The available data relates primarily to the MgO-$Mg(OH)_2$ reaction. This result emphasizes the need for appropriate laboratory experiments. Recommendations for several additional experiments are presented. These include drip mode experiments and the possibility of enhancing the reaction rim formation rate by performing experiments at somewhat elevated temperatures.

STTP Chronological Events:

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THE ACTINIDE SOURCE-TERM WASTE TEST PROGRAM (STTP)

Final Report

Prepared for the DOE-Carlsbad Field Office

Summer 2001

VOLUME II

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Volume II

Selection of Wastes for the Actinide Source-Term Waste Test Program (STTP)

I. Selection of Wastes

The technical requirements for the STTP were detailed in the Sandia National Laboratories document, “Technical Requirements for the Contact-Handled Transuranic Waste Source-Term Test Program,” SAND91-2111. The primary criteria for waste to be selected for the STTP tests were determined by the test matrix for the STTP and the additives added to specific liter-scale and drum-scale tests. The test matrix is given in Table 1 and Table 2 of section III. (a). The principal criteria applied to all tests were as follows:

1) For the 15 drum-scale tests, the entire contents of a standard 55-gallon waste drum of a specified Transuranic content code (TRUCON code) must be used for each of the drum-scale tests;

2) For the 39 liter-scale tests, a portion of the homogeneous (Solidified, sludge, or salt) waste must be obtained from a different drum for each test. That means that 39 waste drums must be sampled so that each test will have a unique waste and no test will be from a single waste drum; and

3) Each waste drum used for the drum-scale tests and sampled for the liter-scale tests must have at least 5 grams of ^{239}Pu. Five grams of ^{239}Pu per 210 liter of brine will give a concentration of 2.38 X 10^{-2} gm/L or approximately 1 X 10^{-4} M solution of ^{239}Pu if the Pu were to dissolve completely.

The Waste drums containing the available TRUCON codes were selected from the inventory of waste drums already present at Los Alamos National Laboratory. The wastes were located at TA-54, TA-55, and CMR Building. A preliminary list of waste drums that met the TRUCON code requirements and the 5 gm specification was devised and a final selection was made based on TRUCON code, ^{239}Pu content, and access to the waste drums.

Loading of Test Containers for the Actinide Source-Term Waste Test Program (STTP)

II. (a) Loading of Test Containers: Introduction

This section documents the method used to prepare, package, and label the actinide isotopes requested for the WIPP Actinide Source-Term Waste Test Program (STTP). The following table summarizes the sources that were requested as well as the quantity of each nuclide needed.

Table 1. Number of Containers Containing Each Actinide

Number of Containers	*^{232}Th*	*^{238}U*	*^{237}Np*	*^{241}Am*
15	5g	5g	5g	0
41	75mg	75mg	75mg	0

The original actinide starting materials include:

1) High purity depleted uranium metal, which had a purity of about 100.0%. The metal's I.D. is CLS-1-LC314.

2) Reagent grade (96.2% $Th(NO_3)_4 \bullet 4H_2O$) thorium nitrate from Baker and Adamson Products, General Chemical Division, Allied Chemical Corporation.

3) High purity (88.11% Np) neptunium oxide from sample NMT-3-ERP6947CF2S.

4) High purity (99.26% Np) neptunium metal from sample NMT-3-ERP6749T2BC.

In some cases it was not possible to prepare the requested level of material in the container because of limitations caused by the total amount of starting material in possession.

Each of the starting actinide material was treated as follows:

1) Two thorium nitrate master solutions were prepared. An accurately weighed portion of thorium nitrate was dissolved in water for each solution. The lower concentrated solution was filtered into a calibrated 100ml volumetric flask. The higher concentrated solution was filtered into a calibrated 250ml volumetric flask. Using a "Rainin" pipettor, equal portions of about 75mg of the lower concentrated solution were added to 41, 5 dram glass vials having pop-top caps, and equal portions of about 5g were added to 15, 4oz wide mouth, screw cap jars.

   Two portions of each master solution were sent for analysis by IDMS (Isotope Dilution Mass Spectrometry). The concentration as determined by IDMS was used to calculate the thorium content for each master solution.

Continued on next page

2) Two uranium master solutions were prepared. Uranium metal was dissolved in concentrated nitric acid with a trace of hydrofluoric acid. The lower concentration solution was transferred to a calibrated 100ml volumetric flask while the higher concentration solution was transferred to a calibrated 250ml volumetric flask. Using a "Rainin" pipettor, equal portions of about 75mg of the lower concentrated solution were added to 5-dram vials containing the 75mg of thorium. About 5g of the higher concentrated uranium solution were added to the 15, 4oz jars containing the 5g of thorium. Two portions of each master solution were sent for analysis by IDMS (Isotope Dilution Mass Spectrometry). The concentration as determined by IDMS was used to calculate the uranium content of each master solution.

3) Accurately weighed portions of neptunium oxide were dissolved using the sealed-reflux dissolution system (LA-5776). The resulting solutions were combined into a calibrated 100ml volumetric flask. Using a "Rainin" pipettor, equal portions of about 70mg were added to the same 5-dram vials containing the thorium and uranium. With all the actinides added to the vials, the solutions were left to air dry to near dryness. The neptunium concentration was determined by coulometry.

4) Fifteen accurately weighed portions of neptunium metal, each weighing 5.00g ± 0.05g were dissolved in a 100ml beaker using concentrated hydrochloric acid and hydrofluoric acid. The resulting solutions were quantitatively transferred with water to the 15 jars containing the 5g portions of thorium and uranium. The solutions were allowed to air dry to near dryness.

Table 2 shows the amount of thorium, uranium, and neptunium in each 5-dram container.

Table 2. Amount of Neptunium, Thorium, and Uranium in Each Source Container

Container No.	***^{*232}Th***	***^{*238}U***	***^{**237}Np***
NTU75-1 to 41	78.9mg	80.4mg	65.2mg

[*] The calculations for this value are found in LA notebook #5768, page 67.

[**] The calculations for this value are found in LA notebook #5768, page 68.

Table 3 shows the amount of neptunium, thorium, and uranium in each 4oz jar.

Table 3. Amount of Neptunium, Thorium, and Uranium in Each Source Container

Container No.	***^{237}Np***	***^{232}Th***	***^{238}U***
NTU 5-1 to 15	4.97g	4.77g	4.97g

Note: the headers print markers: *237Np, **232Th, **238U.

[*] The calculations for these values are found in LA notebook #5768, page 75.

[**] The calculations for these values are found in LA notebook #5768, pages 71-73.

II. (b) Loading of Liter-Scale Test Containers

The loading of the liter-scale test containers occurred at the LANL Waste Characterization, Reduction, and Repackaging Facility. The Pyrochemical salt waste, including MgO-Y_2O_3 crucible, chloride salts, and calcium oxide, was comminuted at LANL's TA-55. Added to the titanium test vessels was 800 to 1,340g of the Pyrochemical salt waste. Figure 1 is a flowchart of the process used for loading the liter-scale test containers (refer to page 9 for Figure 1).

Listed below are summaries of the appropriate influencing variables for the Pyrochemical salt test containers.

L25, 26, and 27:

Comminuted waste: 1,338g; 1,315g; 1,315g
Fe mesh: ~110g
Nd: 45mg; Th, U, and Np: 75mg each
Brine: solid ratio = 2:1

L28, 29, and 30: (pressurized)

Comminuted waste: 907g; 907g; 930g
Fe mesh: ~55g
Nd: 30mg; Th, U, and Np: 75mg each
Brine: solid ratio = 2:1
CO_2 at 60 bars (870 psig)

L31, 32, and 33:

Comminuted waste: 1,315g; 1,315g, 1,338g
Fe mesh: ~110g
Nd: 45mg; Th, U, and Np: 75mg each
Brine: solid ratio = 2:1
Bentonite: brine equilibrated; 120g each

Continued on next page

L34, 35, and 36:

Comminuted waste: 862g; 885g; 885g
Fe mesh: ~110g
Nd: 45mg, Th, U, and Np: 75mg each
Brine: solid ratio = 3:1

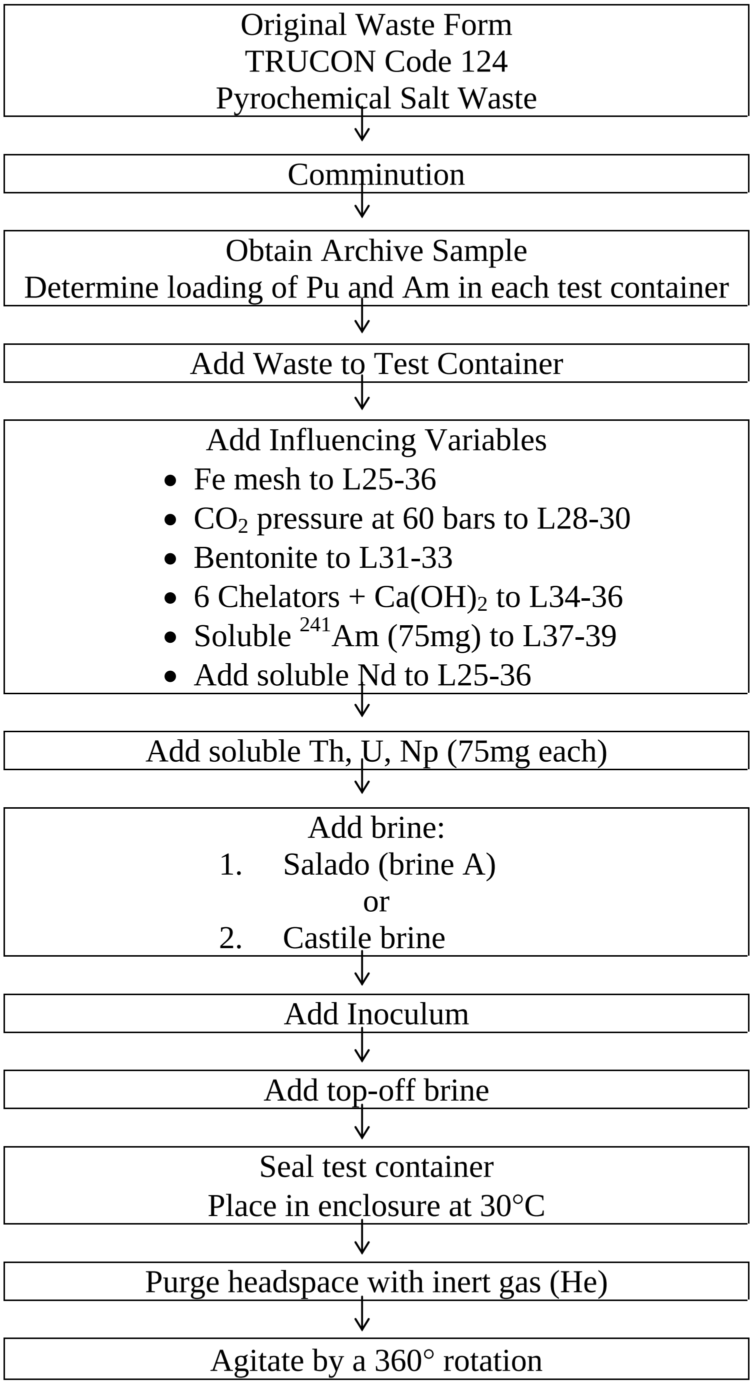
Chelators added:	Acetamide	100ppm
	Sodium acetate	139ppm
	Ascorbic acid	101ppm
	Trisodium citrate dihydrate	154ppm
	Oxalic acid dihydrate	143ppm
	Ammonium thiocyanate	148ppm

$Ca(OH)_2$: 96g each

L37, 38, and 39:

Comminuted waste: 1,315g; 1,338g, 1,338g
Fe mesh: none
Nd: 45mg; Th, U, and Np: 75mg each
Brine: solid ratio = 2:1
^{241}Am added: 75mg as soluble salt

Figure 1.
Flowchart of process used for loading Pyrochemical salt tests.



After loading the test containers with all the influencing variables and Brine A or Castile brine, the containers were transferred to the Chemistry and Metallurgy Research (CMR) nuclear facility. At the CMR approximately 100-150cc of inoculum containing microbes from the WIPP environs were added.

The inoculum consisted of WIPP brine combined with anaerobic brine-containing sediments from around the WIPP. The brine extract from a combination of WIPP brine and WIPP sediments were allowed to settle, then decanted and added to all the test containers. A portion of top-off brine was added to each test container to adjust total volume, leaving a headspace volume of 5 to 12%. The inoculum used for the STTP contained organic colloids, organisms, and microorganisms. The inoculum was maintained in an anaerobic condition. The inoculum was expected to represent an initial reducing condition to the test containers.

After the test containers were loaded with all the additives including inoculum and brine, they were sealed to maintain the anaerobic condition for the length of the testing. Any oxic conditions that might develop from radiolysis would have to overcome the initial reducing condition of the test container's contents.

II. (c) Loading of Drum-Scale Test Containers

The STTP Drum-Scale Test containers will each contain the contents of a single waste drum and several additives as illustrated in Figures 2 and 3 (pages 12 and 13). There will be 15 drum-scale test containers; twelve to be loaded with TRUCON Code 116/216 (combustibles) waste types and three will be loaded with TRUCON Code 117/217 (metals) waste types. Two drum-scale test containers will be designated as QA/QC blank Brine A and Castile Brine containers.

Each set of triplicate experiments will include two drum-scale test containers with Brine A and the third test container will be filled with Castile Brine. Nonradioactive additives will be added prior to attachment of the DS test containers to the Waste Characterization, Reduction, and Repackaging Facility (WCRRF) glovebox. The quantities of actinides to be added are given in the following table (Table 4):

Table 4. Loading of STTP Drum-Scale Test Containers

TRUCON Code 116[*] (Combustibles)

Test Container	***Brine Type***	***Additives***
D1	Brine A	
D2	Brine A	
D3	Castile Brine	
D4	Brine A	10kg Brine – Equilibrated Bentonite
D5	Brine A	10kg Brine – Equilibrated Bentonite
D6	Castile Brine	10kg of Non-Equilibrated Bentonite
D7	Brine A	Chelating Agents
D8	Brine A	Chelating Agents
D9	Castile Brine	Chelating Agents
D10	Brine A	$NaNO_3/NaH_2PO_4$
D11	Brine A	$NaNO_3/NaH_2PO_4$
D12	Castile Brine	$NaNO_3/NaH_2PO_4$

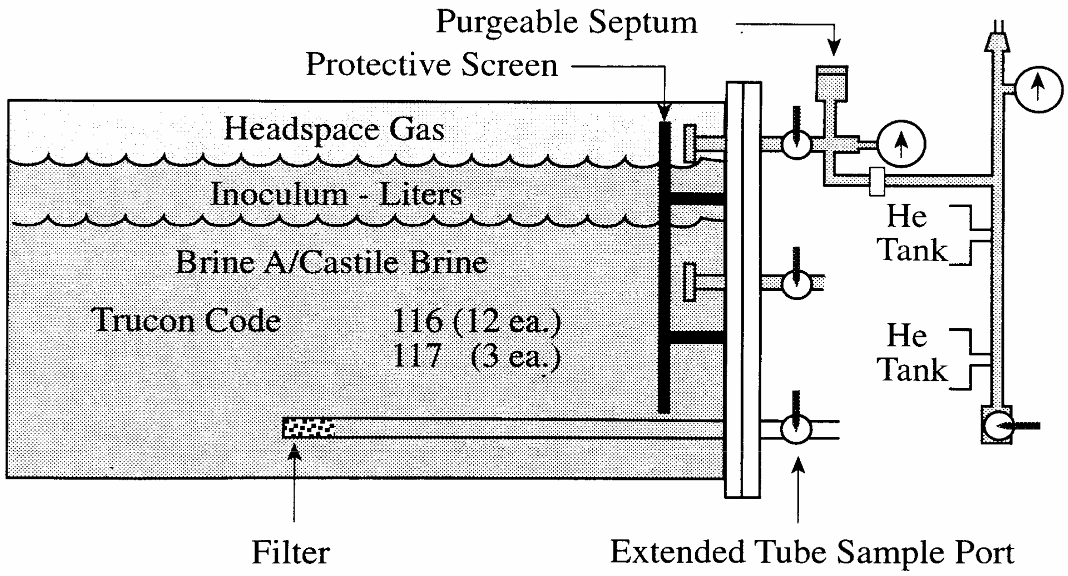
TRUCON Code 117[**]

D13	Brine A	Metals
D14	Brine A	Metals
D15	Castile Brine	Metals
D16	Brine A	Blank
D17	Castile Brine	Blank

[*] Fe mesh and added actinides (D1 – D5)
[**] $NdCl_3$ added (D1 – D17)

Figure 2.

Layout of Loaded Drum-Scale Test Container



Given: Volume = 65 gal = 246 liters
Headspace Gas Volume = 12% - Inoculum = 29.5 L - Inoculum
Inoculum = ~5% (~12.3 L)
Min Free Volume > 40 gal = > 151.4 liters

Neodymium chloride (D1 thru D17)
Add 6.42 gm $NdCl_3$ per each DS test container
Add 6.42 gm $NdCl_3$ to 2 ea QA DS test containers

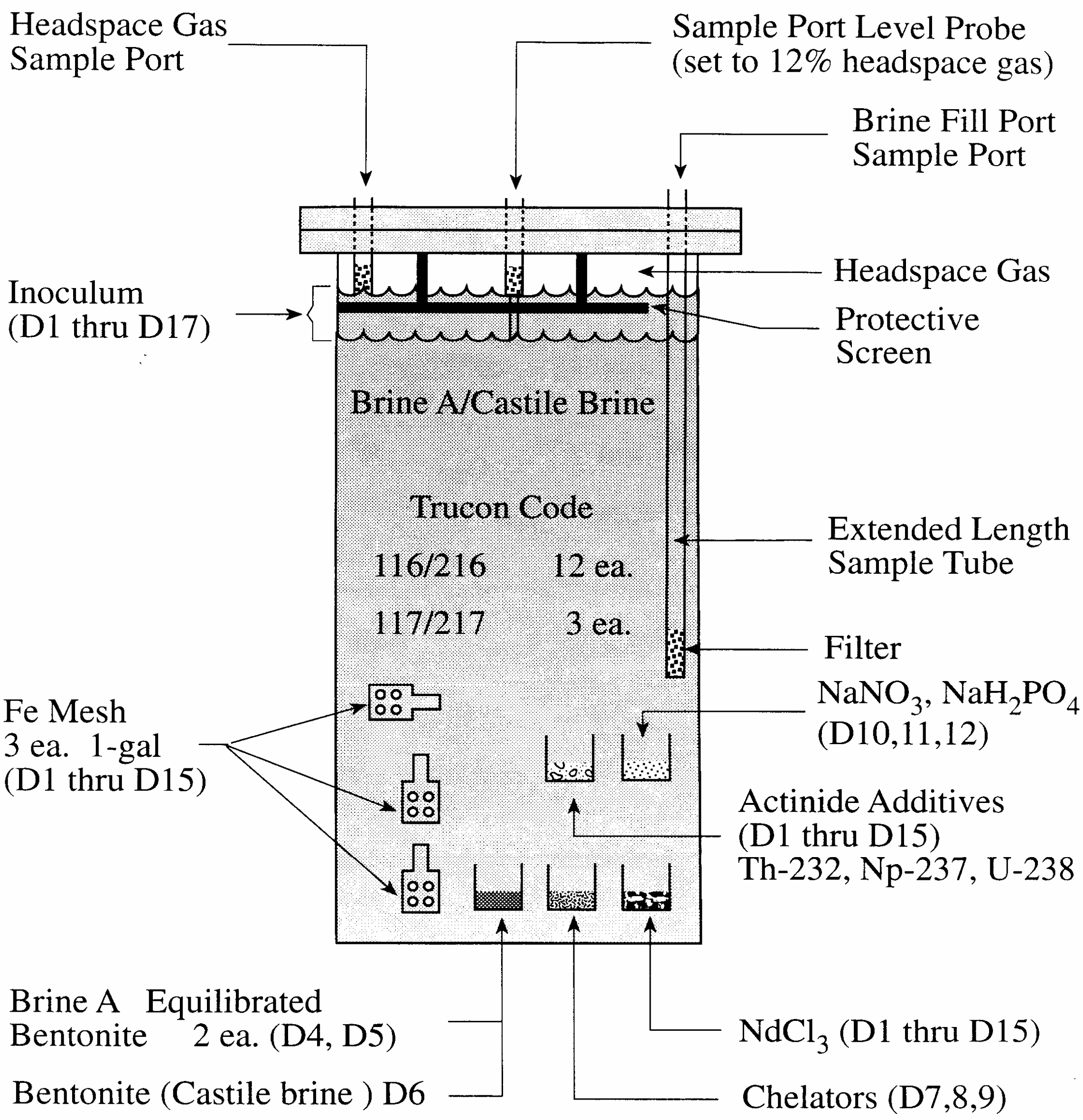
Chelators (D7,D8,D9)
Add low-MW major chelators 100-200 mg/L
Add High-MW minor chelators 30-50 mg/L

Brine-Equilibrated Bentonite
Add 10 kg Brine A - Equilibrated Bentonite D4, D5
Add 120 kg of non-equilibrated Bentonite to D6

Microbial Fertilizer
Add 0.01 M $NaNO_3$ to D10, D11, D12
Add 0.01 M $NaH_2PO_4 \bullet H_2O$ to D10, D11, D12

Actinides
Add ~ 5gm Th-232, U-238, and Np-237 to D1 thru D15

Figure 3.
Illustration of STTP Drum-Scale Test Container Loading



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CST-94-2050

II. (d) Calculation of Concentration of Chelators in STTP Liter and Drum-Scale Test Containers

The following chelators were added to three liter-scale and three drum-scale test containers.

Liter-scale test containers with added chelators and 96.2 gm of $Ca(OH)_2$ are:

L-34 Oxygen sparging Pyrochemical salts
L-35 Direct oxide reduction Pyrochemical salts
L-36 Direct oxide reduction Pyrochemical salts

The concentration of chelators added to the liter-scale test containers assume a brine volume of 2000 ml.

The drum-scale containers with added chelators are D7, D8, and D9, which are loaded with TRUCON Code 116/216, combustibles. The concentration of chelators added to the drum-scale test containers assume a brine volume of 200L.

Chelator	***LS 34 (mg)***	***LS 35 (mg)***	***LS 36 (mg)***
Acetamide	200	200	202
Sodium Acetate	277	276	277
Trisodium Citrate Dihydrate	308	307	311
Oxalic Acid Dihydrate	285	288	286
Ascorbic Acid	201	202	198
Ammonium Thiocyanate	295	294	295

Chelator	***D 7 (mg)***	***D 8 (mg)***	***D 9 (mg)***
Acetamide	30.2	30.2	30.3
Sodium Acetate	42.0	42.0	42.0
Trisodium Citrate Dihydrate	46.6	46.6	46.6
Oxalic Acid Dihydrate	43.3	43.3	43.3
Ammonium Thiocyanate	44.4	44.4	44.4

Calculations for Liter-Scale Test Containers

Acetamide

$$\frac{(200\ \mathrm{mg})\,(1000\ \mathrm{ug/mg})}{2000\ \mathrm{ml}} = 100\ \mathrm{ppm}$$

Sodium Acetate

$$\frac{(277\ \mathrm{mg})\,(1000\ \mathrm{ug/mg})}{2000\ \mathrm{ml}} = 139\ \mathrm{ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(308\ \mathrm{mg})\,(1000\ \mathrm{ug/ml})}{2000\ \mathrm{ml}} = 154\ \mathrm{ppm}$$

Oxalic Acid Dihydrate

$$\frac{(285\ \mathrm{mg})\,(1000\ \mathrm{ug/mg})}{2000\ \mathrm{ml}} = 143\ \mathrm{ppm}$$

Ascorbic Acid

$$\frac{(201\ \mathrm{mg})\,(1000\ \mathrm{ug/mg})}{2000\ \mathrm{ml}} = 101\ \mathrm{ppm}$$

Ammonium Thiocyanate

$$\frac{(295\ \mathrm{mg})\,(1000\ \mathrm{ug/mg})}{2000\ \mathrm{ml}} = 148\ \mathrm{ppm}$$

Calculations for Drum-Scale Test Containers

Acetamide

$$\frac{(30.2\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 151\ \text{ppm}$$

Sodium Acetate

$$\frac{(42.0\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 210\ \text{ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(46.6\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 233\ \text{ppm}$$

Oxalic Acid Dihydrate

$$\frac{(43.3\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 217\ \text{ppm}$$

Ammonium Thiocyanate

$$\frac{(44.4\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 222\ \text{ppm}$$

II. (e) Addition of Influencing Variables

Addition of Actinides to STTP Test Containers

The waste streams added to the STTP test containers were all from the Los Alamos National Laboratory inventory of wastes. The criteria for waste drums to be used for the STTP matrix is that each waste drum must contain at least 5 grams of Pu. ^{241}Am should accompany the total Pu but a criteria is not established for Am. There is no criteria to limit the quantity of ^{240}Pu and ^{241}Pu. There is no need to include waste containing ^{238}Pu because of the added difficulty in handling, sampling, and analyzing samples with the very high radioactivity levels of ^{238}Pu. The chemical effects expected to result from ^{238}Pu in the wastes will be induced by addition of about 75 mg of ^{241}Am to six different liter-scale test containers. Because the WIPP is expected to have wastes contaminated with Th, U, and Np, all the liter-scale and drum-scale tests are spiked with soluble salts of these actinides. Neodymium was also added to select test containers as a chemical analogue or surrogate for ^{241}Am.

The following is a list and description of the added actinides and neodymium:

Neodymium

Neodymium was added as $NdCl_3$ directly to the test containers at the WCRRF. The glass vial containing the $NdCl_3$ was not added to the test container.

Thorium

Thorium was added as a water solution of $Th(NO_3)_4 \bullet 4H_2O$ to a glass vial containing other actinides. The glass vial was placed in each test container. The Th was 99.99% pure and was present as ^{232}Th.

Uranium

Uranium was added as a nitric acid solution from a high purity specimen of depleted U metal (100%). The metal was dissolved in 16 N HNO_3 heated with a trace of HF. An aliquot of the U solution was placed in a glass vial containing other actinides. The glass vial was placed in each test container. The U was ^{238}U.

Neptunium

Neptunium was added as a Np salt solution after dissolution of NpO_2 by a sealed reflux dissolution system. Concentrated HCl with a few drops of HNO_3 and HF was used to dissolve the NpO_2. Aliquots of the dissolved oxide were added to glass vials containing other actinides. An aliquot of the solution was placed in a glass vial with other actinides. The glass vial was placed in each test container. The Np was ^{237}Np. The Np solution from the dissolved NpO_2 was added to each liter-scale test container, the Np added to the drum-scale tests was dissolved from specimens of Np metal. The metal was dissolved in concentrated HCl with a few drops of HNO_3 and HF. The 15 specimens of Np metal weighed 5 gm.

Continued on next page

Americium

Americium was added as an Am solution after dissolution of AmO_2 in 0.5 ml 12 N HCl with two drops 16 N HNO_3 and two drops of HF. An aliquot of the solution was placed in a glass vial and evaporated to damp dryness. Each of the six glass vials had a radiation reading of about 800 mR/hr β, γ at contact. The AmO_2 was about 82.2% Am and remainder Pu. The vials with Am were added to each select test container along with the vials containing the other actinides.

Table 5. Actinides Added to STTP Liter-Scale Test Containers

Test Containers	*Nd (mg)* [*]	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	45	75	75	75	0
4, 5, 6	30	75	75	75	0
7, 8, 9	45	75	75	75	0
10, 11, 12	0	75	75	75	75
13, 14, 15	45	75	75	75	0
16, 17, 18	45	75	75	75	0
19, 20, 21	45	75	75	75	0
22, 23, 24	45	75	75	75	0
25, 26, 27	45	75	75	75	0
28, 29, 30	30	75	75	75	0
31, 32, 33	45	75	75	75	0
34, 35, 36	45	75	75	75	0
37, 38, 39	0	75	75	75	75

[*] Nd added as $NdCl_3$ for a concentration of about 15 mg/L for nonpressurized tests, assumption of 3L; 15 mg/L for pressurized tests, assumption of 2L.

Table 6. Actinides Added to STTP Drum-Scale Test Containers

Test Containers	*Nd (mg)* [*]	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	3.69	5	5	5	0
4, 5, 6	3.69	5	5	5	0
7, 8, 9	3.69	5	5	5	0
10, 11, 12	3.69	5	5	5	0
13, 14, 15	3.69	5	5	5	0

[*] Nd added as $NdCl_3$ for a concentration of about 24.37 mg/L, assuming 151.4 L (40 gal).

Addition of Mixed Inoculum to STTP Test Containers

A batch of mixed inoculum was prepared for addition to each of the 39 liter-scale tests and 15 drum-scale tests. The inoculum consisted of a mixture of ingredients sampled from the WIPP site that contained a diverse mixture of halotolerant microorganisms that survive in the surfacial and supersaline conditions of the WIPP environments. The components making up the mixed inoculum batch are found in the table below.

Table 7. Components of the Mixed Inoculum Batch

Component	***Quantity %***	***Liters/drum***
Lake Brine and sediment mixture	20 %	1.06
Muck-pile salt solution	30 %	1.59
G-seep Brine	50 %	2.65
	Total	5.30

The inoculum solution was to be added to the test containers to establish and maintain an anaerobic environment. The anaerobic environment was established by purging the mixed inoculum for 30 minutes with N_2. The mixed inoculum was continually mixed and maintained under a N_2 atmosphere prior to addition to the liter-scale and drum-scale tests. About 100-150 ml of inoculum was added to the liter-scale tests, and about 5.3 liters was added to the drum-scale tests. For the pressurized liter-scale tests, 80-100 ml of inoculum was added to each of the 6 pressurized tests. The quantity of chemical reducing agents added as part of the inoculum injection was not known.

Addition of Fe to STTP Test Containers

An important parameter that could have a significant effect on the Redox potential in the repository is the presence of iron from the mild steel 55-gallon drums containing the waste. The STTP experiments were designed to be conducted in Ti vessels because high ionic strength brine was expected to dissolve to different degrees many of the proposed containment vessels that might be used to contain the experiments with brine at 30 °C for up to 5 years. Because titanium was not dissolved by the synthetic Brine A and Castile Brine formulations, a means of trying to determine the effect of Fe in the mild steel drums had to be tested. Consequently, all test containers were fabricated from Ti metal and a high surface area mesh was added to each test to simulate the amount of Fe that would be present if the waste were in a 55-gallon drum. The corrodable surface area in a 55-gallon drum was calculated to be about 4 m^2. To simulate this surface area of Fe, an Fe mesh with wire strands of a small diameter and therefore a large surface area was procured and prepared by Sandia National Laboratory for addition to the STTP test containers. The procured material was a No. 10 mesh made with 20 gauge wire and procured from Aggregate and Mining Supply Company of Albuquerque, New Mexico. The material came in rolls three feet wide and had a nominal analyses of elements as follows:

Fe	98.453 %
C	0.679 %
Mn	0.620 %
Si	0.230 %
P	0.012 %
S	0.006 %

It was determined that 2748 in^2 of this mesh would provide about 4 m^2 of surface area in a 55-gallon or 210-liter test drum. For the liter-scale vessels, about 39.25 in^2 would be required. The Fe mesh was cut in approximately 1.25 inch width and 30.0 inch length sections, with a target mass of 102.01 g selected to provide the necessary surface area for the experiments in three liter-scale test containers. This amounted to 39.25 in^2 with an average weight to surface area ratio of 2.599 g/in^2. These cut samples were packaged in 4 ounce Qorpak polypropylene jars with one inch diameter holes cut on the top and bottom of each jar to allow inflow and outflow of brine.

The Fe mesh for the 6 pressurized test containers with a two-liter volume were cut to a target mass of about 68 g and placed in 2-ounce Qorpak polyethylene jars.

The Fe mesh prepared and packaged for the drum-scale tests were cut into 6 pieces that were 36 inches by 12 inches plus one additional piece that was 12 inches by 12.9 inches for a target surface of 2748 square inches. The target weight of Fe mesh was about 7142 g to achieve about 4 m^2 of corrodable steel surface. The accumulated Fe mesh sections were placed in a 5 gallon polyethylene bucket that had 5-inch diameter holes cut in the top and bottom to allow flow of brine through the Fe mesh.

Continued on next page

A spectroscopic analysis of the Fe mesh with a Wavelength Dispersive X-ray Fluorescence Spectrometer showed an average constituent analysis of five wires, giving the following data:

Fe	95.4 %
Zn	1.5 %
P	1.43 %
Mn	1.28 %
Si	0.29 %
Cr	0.14 %
C	not analyzed

The presence of zinc was disturbing because it might be a galvanizing constituent or a protective layer. A surface analysis was performed to determine the property of the zinc in the wire by Auger Electron Spectroscopy. The zinc was determined to be a loose protective layer that was discontinuous over the Fe based wire strands. Corrosion on the unprotected Fe strands was visible where the zinc layer was very thin (~200 angstroms) and did not provide total protection of the wire.

II. (f) Nitrates in STTP Waste Solutions

A concern has been raised concerning the oxidative strength of nitrates in STTP wastes. This memo responds to that concern. Nitrates can be considered to be oxidants when they are in solid form or in concentrated acid solutions. Nitrates in dilute solutions or in neutral basic solutions are very weak oxidants or are not oxidants at all unless heated in the presence of strong reductants.

STTP waste does not contain concentrations of nitrates in solid form. The samples from the test containers contain varying concentrations of nitrates according to Table 8.

Generally, there is an average of 7 to 8 samples taken each week from the STTP test containers. Taken as a whole, the average concentration of nitrates in 50-ml samples taken from STTP test containers is about 4150 μg/ml or ppm. The amount of nitrates that would be disposed of, without consideration of dilution, would be as follows:

$$\frac{\left(50\ ml/_{sample}\right)\left(8\ ^{sample}/_{week}\right)\left(4150\ ^{\mu g}/_{ml}\right)}{1\times10^{6}\ ^{\mu g}/_{gm}} = 1.7\ gm\ \ per\ \ week$$

Analyses of elemental analytes and actinides requires that the samples be acidified with nitric acid (HNO_3) to assure the actinides and elemental analytes are solubilized and remain stable or do not precipitate. Consequently, each sample is acidified by adding concentrated nitric acid (16N) to a final concentration of 2N HNO_3. A total of 200 to 250 ml of 2N HNO_3 results from analyses of each sample for ICP-MS and ICP-AES analyses of samples. This results in generating about 2 liter of 2N HNO_3 waste per week. 2N HNO3 is considered to be a dilute acid relative to concentrated nitric acid (16N) and does not have appreciable oxidative strength at that concentration. If the samples are added to the CMR outflow of waste water, the dilution is such that there is no oxidative strength of the resultant solution. In summary, the nitrates and nitric acid solutions to be disposed of from STTP waste solutions are:

1.) 1.7 gram of nitrates in solution per week

2.) About 2 liter of 2N HNO_3 per week

3.) There are essentially no solid nitrates to be disposed as waste from STTP samples

Table 8. Nitrate Concentrations in STTP Waste Solutions

Liter-Scales:

LITER-SCALE NUMBER	CONCENTRATION, µG/ML
L01	200
L02	600
L03	1,000
L04	200
L05	600
L06	2,000
L07	200
L08	800
L09	1,000
L10	200
L11	700
L12	1,000
L13	100
L14	100
L15	200
L16	100
L17	13,000
L18	1,000
L19	36,000
L20	30,000
L21	32,000
L22	36,000
L23	30,000
L24	32,000
L25	<100
L26	<100
L27	<100
L28	<100
L29	<100
L30	<100
L31	<100
L32	<100
L33	<100
L34	<100
L35	<100
L36	<100
L37	<100
L38	<100
L39	200

Drum-Scales:

DRUM-SCALE NUMBER	CONCENTRATION, μ/G/ML
D1	<50
D2	<50
D3	<50
D4	<50
D5	<50
D6	150
D7	<50
D8	800
D9	500
D10	100
D11	<50
D12	500
D13	<50
D14	<50
D15	200

II. (g) Evaluation of Hydrogen as a Potential Hazard in STTP Test Containers

Summary

Safety assessment of hydrogen in headspace of STTP test containers

An assessment of the details of gas generation in STTP test containers has resulted in a conclusion that a hazard does not exist for rapid combustion or an explosion to occur in the headspace of the test containers due to the reaction of H_2 and O_2 or N_2O. The conditions for the reactions to occur are not present when consideration is given to the following influencing parameters:

- volume of reactant gas – very small (30 cc max. in LS and 120 ml max. in DS)
- concentration of reactant gas – unbalanced
- stoichiometry – unbalanced fuel to oxidant ratio
- pressure – low to ambient
- temperature – 30 ^{O}C
- ignition sources
  - continuous: none
  - single spark: none
- presence of moisture – 31 torr over pool of brine

The thermodynamic or thermochemical reactions governing the combination of H_2 with O_2 or N_2O were calculated to show that the total amount of energy theoretically available for release under optimal conditions and stoichiometry would be about 0.09 kcal for liter-scale test containers and 0.36 kcal for the drum-scale test containers. The dilute concentration of oxidant will favor non-propagation of the reaction. Titanium does not spark when contacted by other metals and the large volume of highly conductive brine does not allow a static charge to develop in the test containers. The test containers are purged with He at least once a year and for some test containers is the predominant gaseous component in the headspace. The pressure of each test container is released before each sampling event.

Consideration of the major influencing parameters show that the combustion of H_2 and oxygen or some other oxygen containing gas is highly unlikely and even if a reaction was to occur the theoretical energy available for release within the test container headspace would be easily contained. The hazard associated with the hydrogen gas generation in the headspace of the STTP test containers is predictable, contained, and will not result in spread of contamination or present a hazard to the samplers.

Introduction

This section provides a discussion on the generation and accumulation of hydrogen in the headspace of STTP test containers and the potentiality of hydrogen as a hazard or non-hazard under the conditions of the experiments.

Hydrogen is generated within the test containers by four major processes:

- radiolysis of water molecules in brine;
- radiolytic decomposition of organics dissolved in brine;
- radiolytic degradation of solid organic materials; and
- corrosion reactions of brine on metals including electrolytic enhancement of corrosion.

The first three processes are the result of the energy given off by the decay of radioactive actinides entrained in the waste or dissolved in the brine. The most prevalent actinides with high specific activity in transuranic wastes destined for the WIPP are ^{238}Pu, ^{239}Pu, and ^{241}Am. The specific activity of the three most active actinides is dependent on the half-life of the particular radioisotope according to the following equations.

$$dn/dt = N\lambda$$

where dn/dt = decay rate as a function of time
N = number of atoms
λ = decay constant of specific radioisotope
where $\lambda = 0.693 / t_{1/2}$
$t_{1/2}$ = half-life of radioisotope
N = Avogadro's number/gm-atomic weight

For $^{239}\text{Pu}: t_{1/2} = 2.410 \times 10^4$ annum

$$dn/dt = \frac{(6.02\times10^{23})(0.693)}{(239)(2.410\times10^{4})(365.25)(1440)}$$

$$= 1.38 \times 10^{11} \text{ disintegrations/min/gm}$$

For $^{241}\text{Am}: t_{1/2} = 432.7$ annum

$$dn/dt = \frac{(6.02\times10^{23})(0.693)}{(241)(432.7)(365.25)(1440)}$$

$$= 7.60 \times 10^{12} \text{ dis/min/gm}$$

For $^{238}\text{Pu}: t_{1/2} = 87.7$ annum

$$dn/dt = \frac{(6.02\times10^{23})(0.693)}{(238)(87.7)(365.25)(1440)}$$

$$= 3.80 \times 10^{13} \text{ dis/min/gm}$$

Continued on next page

The primary radioactivity in STTP test containers arise from ^{239}Pu and ^{241}Am because ^{238}Pu containing waste was not included in the STTP test matrix. However, the specific activity from ^{239}Pu and ^{241}Am is high enough to generate radiolytically produced gases in the test containers. Radiolytically produced gases include H_2, CO, CO_2, CH_4, N_2O, ethane, and ethylene. Very small and insignificant quantities of O_2 and N_2 are generated that accumulate in the headspace. Oxygen is known to be generated as free radicals but recombination reactions preclude significant quantities of oxygen from accumulating in the headspace as oxygen in a standard state. Liter-scale test containers No. 36, 39, 38, 26, 27, and 37 are high activity test containers that show generated O_2. The primary source of oxygen is from air originally present in the headspace or solubilized in the brine. Also, air can be introduced as part of the brine and gas sampling that is conducted on each test container. However, the greatest concentration of gases in the headspace are generally H_2, CO_2, CO, and N_2O. The N_2O is highest in test containers that contain very high concentrations of nitrate. The highest concentrations of H_2 are from test containers that have a high concentration of soluble organics and high radioactivity such as ^{241}Am.

Hydrogen from corrosion is primarily shown in drum-scale tests (DS 13, 14, and 15) selected because of their metal content.

Hydrogen, oxygen, and other gases in the headspace of an STTP test container can be considered to be in their standard state because they exist in their most stable form as molecules of O_2, H_2, CO_2, H_2O, etc. and at a pressure of almost 1 atmosphere and 30 °C. To determine the energy evolved from a reaction of stoichiometric quantities of H_2 and O_2, the reactants which are H_2 and O_2 are considered to react to form the product in a straight-chain or one-step path as in the following reaction.

$$H_2\,(g) + 1/2\,O_2 \rightarrow H_2O\ (\ell)$$

The standard enthalpies of formation, or more common, standard heats of formation of the reactants are combined to form the product of the thermochemical reaction which is liquid H_2O. The standard enthalpy change for this reaction at 25 °C and about 1 atm is the standard heat of formation of $H_2O_{(l)}$. Calculation of the energy evolved from the thermochemical reaction according to Hess's Law Equation gives the following result.

Given:

The standard Enthalpy of Formation (ΔH°_f) for:

$$H_2(g) = 0.00\ kcal/mol$$

$$O_2(g) = 0.00\ kcal/mol$$

$$H_2O(\ell) = -68.32\ kcal/mol$$

Continued on next page

$$\Delta H^\circ = \left[Sum\, of\ \Delta H^\circ{}_f\ of\ products - sum\, of\ \Delta H^\circ{}_f\ of\ reactants\ \right]$$

For Reaction:

$$2H_2 + O_2 \rightarrow H_2O(\ell)$$

$$\Delta H^\circ = \left[1mol\,(\frac{-68.32kcal}{mole}) \right] - \left[2mol\,(\frac{0.00kcal}{mole}) + 1mol\,(\frac{0.00kcal}{mole}) \right]$$

$$= -68.32\ \tfrac{kcal}{mole}\ per\ mole\, of\ H_2O\ formed$$

For Reaction:

$H_2 + N_2O \rightarrow H_2O + N_2$

$$\Delta H^\circ = -88\, kcal/mol$$

From the above calculation for H_2 and O_2 and assuming standard conditions, the reaction is exothermic by

–68.32 kcal/mol.

Because the reaction is at near standard conditions and it is assumed to be a one step reaction, the standard entropy change (ΔS°) from the standard entropy of formation does not need to be considered.

The STTP test containers have an internal volume of approximately 3 liters and were loaded with enough brine, waste, and other influencing variables to leave a headspace volume of 5 to 10% of the total volume of the test container. Assuming the headspace volume is 10% then the volume is

(3000 mL)(.10) = 300 mL

The vapor pressure of water at 30 °C is 31.82 torr. To determine the partial pressure of each gas in the headspace of the test container would require subtration of the influence of the vapor pressure of H_2O.

$$P_{o2} = P_{total} - P_{water}$$

Continued on next page

The atmospheric pressure at Los Alamos is about 570 mm Hg therefore the partial pressure of O_2 is

$$\begin{aligned} P_{O_2} &= 570\, torr - 31.82\, torr \\ &= 538.2\, torr \end{aligned}$$

Correcting for volume

$$V_2 = V_1 \left(\tfrac{P1}{P_2}\right)$$

$$V_2 = V_1 \, \frac{538.2}{570}$$

$$V_2 = 0.94 V_1$$

The partial pressure of $H_2O(g)$ is about 6% of the total gas pressure in the headspace of a test container.

Conditions of Flammability

The hazard associated with containing an ignitable gas or mixture of gases is governed by the conditions, which enhance or suppress the possibility of ignition or uncontrolled rapid reaction. The conditions or parameters that influence the possibility and intensity of an ignition are described below.

Volume of Gas

The energy expelled by igniting a volume of gas is governed by the volume of gaseous components that will react and the kinetics of the reaction. The potential flammability of a gas or mixture of gases is a safety concern when the gas(es) support propagation of a flame and provide conditions that promote a high speed of flame propagation. The energy released from exothermic reactions is given in thermodynamic terms as kjoul/mol or kcal/mol. The greater the number of moles of a gas, the greater the energy released and alternatively, the smaller the volume, the less the energy released.

Stoichiometry

The rate of reaction of a mixture of gases is controlled by the fuel to oxidant ratio. The ratio of fuel (H_2) to oxidizing media (O_2 or N_2O) influences the combustibility of the gas mixture. If too much fuel is present, the fuel rich mixture may combust but flame propagation rate will be slow.

Continued on next page

If too little fuel is present, the lean flammability limit will have a higher threshold of ignition and the flame propagation rate will be limited. If the fuel (H_2) and oxygen (O_2) concentrations are optimal (stoichiometric) at 2 mole of H_2 and 1 mole of O_2, then ignition can occur with a single spark rather than a continuous spark source and flame propagation is maximized. However, impurity gases such as N_2, CO, CO_2, and H_2O (g) can upset stoichiometric ratios and make gaseous mixtures less likely to ignite and combust.

Pressure

The pressure of a container containing ignitable gases has a great influence on the rate of reaction because the concentration of gases is greater within a given volume. The higher the pressure, the greater the number of reactant molecules and the greater the energy that can be released from a single source. Reactions that occur at high pressures create the greatest “shock’ wave during the reaction because of the greatest potential energy available for reaction in a confined space. Reactions occurring at ambient pressure are generally slower unless the stoichiometry of the mixtures are near perfect on a mole to mole basis.

Temperature

The temperature of a gas can influence the rate of reaction of two gases by maintaining a stoichiometric mixture and providing a convection of ideal gases with molecules with higher or lower kinetic velocity. The higher the temperature for a given volume and mass of gas, the greater the pressure of the gases and reaction between gases is more rapid and complete. Temperatures higher than about 500 ^oC will have a decided influence on increasing reaction rates while temperatures less than 100 ^oC will generally have a lesser influence on the reaction rate of gases. The Kelvin temperature of a gas is directly proportional to the average kinetic energy of its molecules and hence the reaction rate in a fixed volume. If pressure and temperature are at near ambient conditions, the rate of reactions are slowed and stoichiometry becomes a greater factor in the combustibility of gases.

Ignition Sources

Sources of ignition can be considered to be of two types; single spark or continuous spark. Single spark ignition sources can be a spark initiated because of a discharge between positively and negatively charged items, especially in a dry atmosphere. Striking two metals together can also create a single spark. A continuous can spark result from an electric current arcing between two conductive contacts or a sporadic arc between contacts. The presence of water in an enclosed system tends to ground out or eliminate the possibility of arcing between two contacts due to static electricity because water is a good conductor of electricity. In the case of STTP, brine is an excellent conductor of electricity and eliminates sparking due to static electricity.

Continued on next page

Presence of Moisture

The presence of moisture mitigates the possibility of ignition in gaseous mixtures because it eliminates the possibility of ignition from a single spark and maintains a cooling effect on any heated surface. Also, moisture has a vapor pressure that dilutes and upsets achieval of a stoichiometric gaseous mixture. The presence of moisture within an enclosed gas system will mitigate the possibility of ignition and eliminate flame propagation because of the cooling effect of the partial pressure of moisture especially if the moisture arises from a relatively large volume of water.

STTP Liter-Scale Test Containers

The STTP Liter-Scale test containers are all-titanium metal vessels that have a total volume of 3 liters. The test containers have been loaded with comminuted homogeneous wastes, namely, Portland cement, Envirostone, and Pyrochemical salt wastes. Certain test containers have added influencing variables such as Fe mesh, chelators, $Ca(OH)_2$, and ^{241}Am. After addition of Brine A or Castile brine, the test containers were topped-off with an inoculum brine mixture containing microbes from the WIPP site. The remaining headspace in the liter-scale test containers is about 5-10% of the total volume or 150 to 200 ml. The gas composition measured in the headspace of the liter-scale test containers after the headspace has been purged and several weeks have elapsed is given in Table 9 on page 32.

As shown in Table 9, the concentration of gases generated due to radiolysis dilutes and replaces the air atmosphere gases that were soluble in the brine in equilibrium with the headspace. The concentration of H_2 predominates in most liter-scale test containers except where N_2O predominates in test containers that contain high nitrate in the brine solution. The concentration of O_2 and nitrogen is depleted to less than 10% except for LS 36 and 39. A classic method for determination of O_2 in the headspace of an enclosed container has been to add an excess of H_2 and initiate a reaction between H_2 and available O_2 by providing an intermittent spark until most of the O_2 was consumed in the following reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

I have conducted this type of analysis many times and generally tried to maintain a volume of 0_2 less than 50 ml. An intermittent spark source was required to complete the reaction. In STTP test containers, the total volume of O_2 is generally less than 1% of the 150-200 ml headspace volume or between 1-2 ml. One test container (LS 36) was measured to have about 15% O_2 or 22 to 30 ml. The number of kilocalories calculated for this reaction is about 68 kcal/mol. With one mole of O_2 equal to 22.4 liters, the energy released for the reaction of 30 ml of O_2 with excess hydrogen under ideal conditions and a continuous spark would be:

$$68{,}000\,cal/mole)\left(\frac{30\,cc}{22{,}400\,\frac{cc}{mol}}\right) = 91\,cal$$

Continued on page 33

Table 9. Headspace Gas Analysis for all Test Containers

LS	**PU Total G**	Solution Activity (100 ev/min)	**H_2** (vol. %)	**O_2** (vol.%)	**N_2** (vol.%)	**CO_2** (vol.%)	**N_2O** (vol.%)	**NO_3** (ppm)	**TOC** (ppm)	**pcH**
L01	0.017	1E11	0.8	0.03	0.3	<0.1	<0.1	200	40	8.9
L02	0.105	6E10	3.9	0.64	2.2	<0.1	0.1	600	40	10.5
L03	0.124	1E11	7.2	0.57	3.8	0.1	<0.1	1000	50	13.0
L07	0.026	1E11	1.2	0.16	1.1	<0.1	<0.1	200	30	8.9
L08	0.118	6E10	1.8	0.03	0.2	<0.1	<1.0	800	70	9.4
L09	0.108	6E10	3.4	0.17	0.5	<0.1	<0.1	1000	60	13.0
L10*	0.021	1E12	**32.5**	1.50	0.2	<1.0	0.2	200	40	8.9
L11*	0.131	6E10	**22.2**	0.90	2.0	0.1	0.1	700	40	10.4
L12*	0.107	6E10	**~30.0**	1.20	0.3	<0.1	<0.1	1000	50	13.0
L13	**3.386**	1E11	**56.6**	0.20	0.5	404	<0.1	100	**4300**	7.2
L14	**3.468**	2E12	**37.4**	0.04	0.4	2.7	0.6	100	**4400**	7.3
L15	**0.041**	2E11	**3.0**	0.01	2.6	0.5	<0.1	200	**1300**	7.1
L16	0.618	5E12	61.6	0.06	0.6	0.7	2.5	100	400	7.8
L17	1.474	7E10	7.7	0.05	2.4	0.3	**20.4**	**13000**	300	7.8
L18	2.591	6E10	--	0.09	1.3	0.4	>1.0	1000	400	7.6
L19	0.508	3E11	15.8	0.10	5.9	1.8	**32.0**	**36000**	700	8.1
L20	0.080	6E10	2.9	0.06	2.0	0.4	**20.0**	**30000**	400	7.2
L21	0.250	1E11	7.3	0.02	4.1	0.2	**19.0**	**32000**	320	8.0
L22	0.233	4E11	6.1	0.15	6.0	0.6	**39.0**	**36000**	480	7.0
L23	0.500	6E10	8.0	0.06	6.4	0.9	**31.3**	**30000**	400	7.3
L24	0.309	6E10	12.7	0.02	25.0	0.2	**22.5**	**32000**	350	7.5
L25	0.381	8E11	13.0	0.08	0.8	<0.1	0.2	<100	20	7.8
L26	1.044	7E14	72.7	5.40	0.6	<0.1	0.1	<100	30	7.8
L27	3.400	1E15	65.2	4.80	5.0	<0.1	<0.1	<100	60	10.8
L31	0.806	2E11	32.7	0.80	1.5	<0.1	0.5	<100	30	9.0
L32	**4.083**	3E14	**44.6**	2.00	1.0	<0.1	<0.1	<100	30	8.9
L33	1.151	1E12	34.5	2.20	2.5	<0.1	0.3	<100	30	9.7
L34	2.004	3E11	28.6	0.66	2.2	0.1	1.1	<100	60	8.8
L35	0.451	1E13	20.9	0.07	1.7	<0.1	<1.0	<100	50	8.3
L36	**11.130**	3E14	**69.9**	14.90	0.2	<0.1	<0.1	<100	120	11.0
L37*	**4.333**	2E11	**50.0**	4.70	0.2	<0.1	<0.1	<100	20	7.7
L38*	2.736	1E11	51.3	8.70	0.2	<0.1	<0.1	<100	30	7.7
L39*	**4.482**	7E14	**45.6**	11.90	0.3	0.1	<0.1	200	40	9.8

* Am added to test container

This amount of energy is quite small and would not present a hazard. The assumption that this reaction would occur presupposes optimal conditions and a continuous or intermittent spark. The conditions in the STTP liter-scale test containers are not optimal because there are other gases in the mixture including water vapor from the brine at 30 ^{O}C. The partial pressure of $H_2O(g)$ at 30 ^{O}C is about 31.8 torr in the headspace of the test containers. The test containers are totally fabricated from titanium metal which does not spark when brought in contact with another metal so the potential for an ignition source is not present.

Seven liter-scale test containers contain a high concentration of N_2O from the radiolytic decomposition of nitrate. Typically, for test containers that have high N_2O content (up to 39%), the oxygen concentration is very low (<0.1%) and the H_2 concentration ranges from about 3% to 16%. This would make available about 8 to 40 ml of H_2 to react with excess oxidant.

The reaction kinetics of the reaction of H_2 with N_2O is slower than with O_2 but the total energy released is greater. The total energy released when a stoichiometric concentration of H_2 reacts with N_2O to form H_2O is about 88 kcal/mole. For 40 ml of H_2, the total energy released would be about 157 cal. The reaction of H_2 with O_2 or N_2O would result in an initial energy release and a subsequent negative pressure. A test conducted by STTP analysts consisted of dissociating a quantity of H_2O into a stoichiometric quantity of H_2 and O_2 in the headspace of a liter-scale test container and applying a direct electrical spark, which resulted in a small pop and a negative pressure. This actual test provided the samplers with an example of a worst case reaction under the most ideal conditions for the reaction to occur. The actual conditions in a test container do not favor stoichiometric ratios and the presence of brine and water vapor without a spark source makes this potential hazard quite innocuous if it should happen to occur and quite improbable because of the non-ideal conditions.

Drum-Scale Test Containers

The STTP Drum-Scale test containers are fabricated from titanium metal with a total volume of about 65 gal (246 liter). The test containers have been loaded with a mixture of heterogeneous wastes including combustibles (DS 1 through 12) and metals (DS 13, 14, 15). DS 4, 5, and 6 have added brine equilibrated bentonite, DS 7, 8, and 9 have added chelaters, and D 10, 11 and 12 have added sodium nitrate and phosphates as influencing variables. The drums were filled with Brine A or Castile brine and topped off with a microbial inoculum brine mixture. The headspace volume after addition of all additives is approximately 17.2 liters or about 7% of the total volume. The present gas composition in the headspace of the drum-scale test containers after the headspace has been purged with He and allowed to set for several weeks shows that O_2, CO, and N_2O are all less than 0.7%. The concentration of H_2 predominates in the headspace of the drum-scale test containers but the highest oxygen concentration is 0.7% (120 ml) and most drums are at <0.3% (52 ml). As with the discussion on liter-scale test containers, the amount of H_2 that is stoichiometrically available to react with O_2 is very small and in the drum scale test containers the oxygen concentration is diluted so ignition will not occur.

Continued on next page

Also, the drum-scale test containers are filled with brine and maintained at 30 ^{O}C, which results in water vapor (g) being present in the headspace with a partial pressure of about 31.8 torr. The drum-scale test containers are totally fabricated from titanium metal, which does not tend to spark when brought in contact with another metallic object. The headspace of each test container is purged with He at least once a year. The pressure developed in the headspace of the drum-scale test containers is released to less than 2 psig each week or prior to sampling. The remaining very low concentration of oxygen (<0.7% or $< 7 \times 10^{-3}$ mole)will not result in propagation of a H_2 and O_2 reaction and require several ignition events to react the O_2 with the excess H_2.

Test Matrix for the
Actinide Source-Term Waste Test Program (STTP)

III. (a) Test Matrix

Overview of the STTP Test Matrix

Liter-Scale:

L01-L12	Portland Cement	12 containers
L13-L24	Envirostone	12 containers
L25-L39	Pyrochemical Salt	15 containers

Drum-Scale:

D01-D12	Combustibles	12 drums
D13-D15	Envirostone	3 drums

* Most containers filled with Brine A (Salado formation brine).
* Containers divisible by 3 (L03, L06, etc.) contain Castile Brine

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Table 1. STTP Liter-Scale Test Matrix

	L-01	L-02	L-03		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic process sludge	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	L-04	L-05	L-06		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge with CO_2	
Brine	A	A	CASTILE	Portland Cement	10:1 / 3:1 / 2:1
	L-07	L-08	L-09		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge without Fe	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	L-10	L-11	L-12		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge w/o Fe; Am-241 added	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	L-13	L-14	L-15		
TRUCON	112/212	112/212	112/212	Absorbed organic liquids	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1

Continued on next page

	L-16	L-17	L-18		
TRUCON	113/213	113/213	113/213	Absorbed aqueous laboratory waste	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	L-19	L-20	L-21		
TRUCON	114/214	114/214	114/214	Cemented inorganic particles	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	L-22	L-23	L-24		
TRUCON	126/226	126/226	126/226	Cemented organic sludge	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	L-25	L-26	L-27		
TRUCON	124/224	124/224	124/224	Pyrochemical salts	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	L-28	L-29	L-30		
TRUCON	124/224	124/224	124/224	Pyrochemical salts with CO_2	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	L-31	L-32	L-33		
TRUCON	124/224	124/224	124/224	Pyrochemical salts with brine – equilibrated bentonite	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	L-34	L-35	L-36		
TRUCON	124/224	124/224	124/224	Pyrochemical salts with $Ca(OH)_2$ and chelators	
Brine	A	A	CASTILE		3:1 / 3:1 / 3:1
	L-37	L-38	L-39		
TRUCON	124/224	124/224	124/224	Pyrochemical salts without Fe; Am-241 added	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1

Table 2. STTP Drum-Scale Test Matrix

	D-01	D-02	D-03	
TRUCON	116/216	116/216	116/216	Combustibles
Brine	A	A	CASTILE	
Waste (lbs)	43	59.1	47.2	
Total (lbs)	740.2	728.4	720	

	D-04	D-05	D-06	
TRUCON	116/216	116/216	116/216	Combustibles and brine – equilibrated bentonite
Brine	A	A	CASTILE	
Waste (lbs)	72.6	85.5	76.6	
Total (lbs)	765	723	746	

	D-07	D-08	D-09	
TRUCON	116/216	116/216	116/216	Combustibles with chelators
Brine	A	A	CASTILE	
Waste (lbs)	122.6	51.55	56.65	
Total (lbs)	783.4	726	720.6	

	D-10	D-11	D-12	
TRUCON	116/216	116/216	116/216	Combustibles and sodium nitrate/phosphates
Brine	A	A	CASTILE	
Waste (lbs)	66.4	48.6	66.4	
Total (lbs)	728	754.6	717	

	D-13	D-14	D-15	
TRUCON	117/217	117/217	117/217	Metals
Brine	A	A	CASTILE	
Waste (lbs)	171.4	136.8	162.2	
Total (lbs)	867.4	846.2	860	

III. (b) Composition of Brines

Table 3. Composition of Brine A and Castile Brine

Compound	*Brine A (g/L)*	*Castile Brine (g/L)*
$MgCl_2 \bullet 6H_2O$	292.10	3.86
NaCl	100.10	261.64
KCl	57.20	7.23
Na_2SO_4	6.20	23.70
$Na_2B_4O_7 \bullet 10H_{2}0$	1.95	6.00
$CaCl_2$	1.66	1.33
$NaHCO_3$	0.96	0.00
NaBr	0.52	1.13
LiCl	0.125	0.00
RbCl	0.027	0.00
$SrCl_2 \bullet 6H_2O$	0.015	0.00
KI	0.013	0.00
$FeCl_2 \bullet 6H_2O$	0.0125	0.00
CsCl	0.00125	0.00

III. (c) Liter-Scale Test Matrix

Portland Cement: L01-L12

Test Container	Description of Contents	Ratios
L01, L02, L03	Solidified aqueous inorganic sludge	10:1 / 2:1 / 2:1
L04, L05, L06	Solidified aqueous inorganic sludge with CO_2, (pressurized)	10:1 / 3:1 / 2:1
L07, L08, L09	Solidified aqueous inorganic sludge without Fe	10:1 / 2:1 / 2:1
L10, L11, L12	Solidified aqueous inorganic sludge without Fe, ^{241}Am added	10:1 / 2:1 / 2:1

Envirostone: L13-L14

Test Container	Description of Contents
L13, L14, L15	Adsorbed organic liquids
L16, L17, L18	Absorbed aqueous laboratory waste
L19, L20, L21	Cemented inorganic particulates
L22, L23, L24	Cemented organic sludge

Pyrochemical Salts: L25-L39

Test Container	Description of Contents	Ratios
L25, L26, L27	Only Pyrochemical salts	
L28, L29, L30	Pressurized with CO_2 to 60 bars, 870 psig	
L31, L32, L33	Brine equilibrated with bentonite	
L34, L35, L36	Added $Ca(OH)_2$ and chelators	3:1 / 3:1 / 3:1

III. (d) Summary of Portland Cement Liter-Scale Tests

Summary of all Liter-Scale Tests, Excluding Pressurized Containers (L04-L06)

Actinides (Th, Np, Pu, U, and Am) and Nd remained very low (typically <20 ppb), except for L07 where Np increased from 4 to 310 ppb and is currently at 264 ppb. Pu, typically <20 ppb, reached a high of 40 ppb (in July 1997). In liter-scale 10, Np ranged from 20-45 ppb and Pu started at 26 ppb but decreased to 11 ppb. For TOC tests, TOC readings were very low (≤ 100 ppm). pcH tests where the highest of all the liter-scale tests (6.9 – 13.2).

Summary of Liter-Scale Pressurized Containers L04-L06

Nd, Th, Np, and Am remained less than 30 ppb, except liter-scale 04, which started at 421 ppb and then dropped. U was high and stayed high, the following chart illustrates this:

- L04: 10,000-15,000 ppb
- L05: 320-700 ppb
- L06: 2,900-4,900 ppb

pcH was comparable to the non-pressurized test containers. It ranged from 7.0-7.9.

III. (e) Summary of Envirostone Liter-Scale Tests

Nd, Th, Np, and Am typically were less than 10 ppb with Am always maintaining 3 ppb. The U count was the highest in Envirostone test containers than all the other liter-scale test containers (170 – 27,000 ppb). Np was also the highest in Envirostone test containers (7753 ppb). Pu was typically low (less than 20 ppb for L17 – L24) with the exception of L13-L16 in which Pu was up to 1700 ppb. pcH was also typically low with the narrow range of 6.4 – 8.6. All tests were neutral to slightly basic (pcH 6.8 – 8.2) and U solubilized from 10 to 20000 ppb whereas Th and Nd did not solubilize. Pu and Am did not solubilize to > 1100ppb. Most tests were <10 ppb. Pu was incorporated into 16% of colloids filtered and Fe identified on 27% of the filters. Organic solvents increased the population of particles by a factor of 100 and increased Pu-bearing colloids but not Th, Np, and U. High nitrate waste yielded 20-40 v/o N_2O in headspace but did not increase Pu concentrations. Envirostone test tended to be reducing as evidenced by presence of green ferrous chloride in sludge. Fe mesh was not fully available to brine because of compaction.

III. (f) Summary of Pyrochemical Salt Liter-Scale Tests

The Pyrochemical salt liter-scale tests are characterized by high Pu loadings with a high radiolytic degradation of brine and low Fe. All tests were basic (pcH 7.7-11.3). Three non-pressurized tests had high peak Pu (L26, 27, 36) concentrations (up to 14% of inventories) and one test (L26) showed high Eh and low Fe concentrations, meaning a prominent oxidizing environment was displayed. Bentonite had relatively low soluble Pu and low Fe concentrations but higher Pu and Fe colloidal populations. Chelators with $Ca(OH)_2$ were not effective in solubilizing actinides in Brine A and were more effective in Castile Brine (only in liter-scale tests, drum-scale tests showed solubilization in both brines). Soluble Am added to L37, 38 and 39 precipitated and did not resolubilize, in fact six tests resulted in cemented solids. Fe in Pyrochemical salt tests was effective in maintaining a non-oxidative environment. Comminution of waste had an important role in Pyrochemical salt waste chemistry and Fe had limited availability to brine because of compaction and cementation.

Overall Assessment of the Actinide Source-Term Waste Test Program (STTP)

IV. (a) Test Results and Interpretation

Results of Observations of Liter-scale Test Containers

Liter-Scale No. 01

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 264 g
Initial Actinide Content: Pu 68 mg/g; Total Pu = 0.018 g
Am 1.12 µg/g; Total Am = 0.296 mg
Brine: Brine A (10:1 brine/solid ratio)
Additives: Fe Mesh, Th, U, Np, and Nd

Soluble Actinide Histories: (4/17/95 – 4/5/99)

Pu - Ranged from < 1 ppb to 6 ppb at end of test.
Am- Was generally < 1 ppb for time period of test.
U - Was generally < 1 ppb for time period of test.
Th - Was < 1 ppb for entire test.
Np - Was generally less than 12 ppb with no trend.
Nd - Was < 6 ppb for entire test; no trend observed.

Other Analyses (nominal):

Typical pcH Range: 8.7 – 9.0
Fe Concentrations: < 1 ppm for entire test.
Other Analytes: Ca 17,000 ppm
K 20,000 ppm
Mg 22,000 ppm
Na 40,000 ppm
TIC/TOC: 20/40 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: No Pu, no Fe, very low Sr with some S
Headspace Gas Content: $H_2 = 0.8$ v/o; $O_2 = 0.03$ v/o

D&D Observations (1-24-01):

Corrosion: No corrosion observed on feedthroughs.
Brine: Clear
Bottom Solids: Approximately 3” of loose cement sludge.
Fe Mesh: Not corroded; black in color.

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Overall Assessment:

Liter-scale test container No. 1 was a Brine A experiment with a 10:1 brine/solid ratio (264 g of solid). The pcH ranged from 8.7 – 9.0 and the D&D process revealed that the brine was clear and that the comminuted Portland Cement was loosely packed at the bottom of the test container (~ 3 inches of compacted solids that was not cemented). There was essentially no actinides, Nd, or Fe that were solubilized in this test. There was no colloids or microprecipitates that contained Pu or Fe on the filter papers. The Fe mesh was coated with a hard black coating that prevented observable corrosion. There was a relatively low Pu and Am inventory (0.018 g and 0.296 mg, respectively) and a very low H_2 content in the headspace of the test container.

Liter-Scale No. 02

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 80 μg/g; Total Pu = 0.105 g
Am 1.41 μg/g; Total Am = 1.86 mg
Brine: Brine A (2:1 brine/solid ratio)
Additives: Fe Mesh, Nd, Th, U, Np added

Soluble Actinide Histories: (4/17/95 – 12/14/98)

Pu - Generally less than 2 ppb; 3 analyses <10 ppb.
Am- Less than 1 ppb.
U - Less than 2 ppb.
Th - Less than 1 ppb.
Np - Less than 1 ppb.
Nd - Less than 2 ppb.

Other Analyses (nominal):

Typical pcH Range: 8.7 – 9.0
Fe Concentrations: < 1 ppm for entire test.
Other Analytes: Ca 17,000 ppm
K 20,000 ppm
Mg 22,000 ppm
Na 40,000 ppm
TIC/TOC: 20/40 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: No Pu, no Fe, very low Sr with some S
Headspace Gas Content: H_2 = 0.8 v/o; O_2 = 0.03 v/o

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D&D Observations (1-24-01):

Corrosion: No corrosion observed on feedthroughs.
Brine: Clear
Bottom Solids: Approximately 3” of loose cement sludge.
Fe Mesh: Not corroded; black in color.

Overall Assessment:

Liter-scale test container No. 1 was a Brine A experiment with a 10:1 brine/solid ratio (264 g of solid). The pcH ranged from 8.7 – 9.0 and the D&D process revealed that the brine was clear and that the comminuted Portland Cement was loosely packed at the bottom of the test container (~ 3 inches of compacted solids that was not cemented). There was essentially no actinides, Nd, or Fe that were solubilized in this test. There was no colloids or microprecipitates that contained Pu or Fe on the filter papers. The Fe mesh was coated with a hard black coating that prevented observable corrosion. There was a relatively low Pu and Am inventory (0.018 g and 0.296 mg, respectively) and a very low H_2 content in the headspace of the test container.

Liter-Scale No. 03

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 93 μg/g; Total Pu = 0.123 g
Am 1.45 μg/g; Total Am = 1.91 mg
Brine: Brine A (2:1 brine/solid ratio)
Additives: Fe Mesh, Nd, Th, U, Np added

Soluble Actinide Histories: (4/17/95 – 2/22/98)

Pu - Generally < 6 ppb and mostly < 2 ppb. No trend observed.
Am – Generally < 1 ppb with no trend observed.
U - Generally < 6 ppb with no trend observed.
Th - < 1 ppb throughout test.
Np - < 1 ppb throughout test.
Nd - < 1 ppb throughout test.

Other Analyses (nominal):

Typical pcH Range: 12.8 – 13.1
Fe Concentrations: < 1 ppm for entire test period.
Other Analytes: Ca 120 ppm
K 8,000 ppm
Mg < 10 ppm
Na 83,000 ppm
TIC/TOC: 30/40 ppm

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Particle Concentration:	10^9 to 10^{11} particles/Liter
Filter Paper-WDXRF:	One filter paper had a barely detectable amount of Pu and 15 of 17 filters had Fe. Most filters had Sr and S.
Headspace Gas Content:	H_2 = 7.2 v/o; O_2 = 0.6 v/o

D&D Observations (4-12-01):

Corrosion:	No visible corrosion on SS feedthroughs; screen was not corroded. Screen about half full of finely divided cement.
Brine:	Castile Brine was fairly clear with slight grayish tinge. Solids in brine settled out readily.
Bottom Solids:	About 8 inches of loose but settled cement and other solids in the bottom of the test container. Color of solids is gray with a consistency of hardened oatmeal.
Fe Mesh:	The Fe mesh was lodged in gray solid material but was pried off. The mesh was in good condition and was not corroded visibly. After rinsing with alcohol, the Fe mesh appeared to be totally untouched by corrosion. The wire was gray in color with shiny ends.

Overall Assessment:

LS-03 was the Castile brine part of the triplet on LS-01, 02, 03. As in LS-01 and 02, LS-03 did not solubilize Pu or any other actinide. There was no soluble Fe detected in this test. The pcH range of 12.8 to 13.1 was high enough to precipitate both Mg and Ca which led to greater solids. There was no soluble Fe detected in any sample during the test period and yet 15 of 17 filters had Fe. There was essentially no Pu detected on the filter papers taken from this test; actually one filter has a barely detectable amount of Pu. The wide range of particle concentrations of 10^9 to 10^{11} was similar to LS-02. There was no corrosion of the SS feedthroughs or the Fe mesh. The brine was clear of suspensions but had a gray color. Any suspensions stirred up were rather quickly settled.

Liter-Scale No. 04 (Pressurized)

Test Characteristics:

Waste:	Portland Cement
Total Waste Weight:	184 g
Initial Actinide Content:	Pu 103 μg/g; Total Pu = 18.95 mg Am 1.27 μg/g; Total Am = 0.233 mg
Brine:	Brine A (10:1 brine/solid ratio)
Additives:	Fe Mesh, Nd, Th, U, Np, 60 Bar (870 psig) CO_2 pressure in headspace.

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Soluble Actinide Histories: (8/28/95 – 9/21/98)

Pu - Pu started at 1.6 ppb and steadily increased to 225 ppb on 9/21/98. Total alpha activity was 15.29 nCi/ml on 9/21/98 and decreased to 0.08 nCi/ml on 5/15/01 (a factor of 191).
Am – Am was less than 0.2 ppb at the beginning of the test, Am-241 total alpha activity decreased from 0.92 (9/21/98) to 0.23 nCi/ml (5/15/01).
U - U concentration of 10,000 ppb at the beginning of the test remained fairly constant and ended up at 8705 ppb at the end of the test.
Th - Th was < 10 ppb for the entire test period. There were no trends observed.
Np –Concentrations of Np were generally less than 21.0 ppm and showed no trend during the entire test period.
Nd - Nd concentrations were < 1.1 ppb for the entire test period.

Other Analyses (nominal):

Typical pcH Range: 7.21 – 7.43
Fe Concentrations: Started at 3.1 ppm and increased to 162.4 ppm at the end of the test.
Other Analytes: Ca 6,000 ppm
K 6,000 ppm
Mg 26,000 ppm
Na 40,000 ppm
TIC/TOC: 1100/70 ppm
Particle Concentration: 1×10^{11} particles/Liter
Filter Paper-WDXRF: No Pu; 1 filter of 4 showed Fe. No Sr identified. No Al identified.
Headspace Gas Content: 60 Bar of CO_2; no other gas analyzed.

D&D Observations (5-9-01):

Corrosion: No corrosion on lid or screen.
Brine: Clear, non-viscous brine with light gray color. Brine level was at the top of the screen.
Bottom Solids: The Fe mesh holder was filled with light gray colored compacted sludge.
Fe Mesh: The Fe mesh was holder was embedded in gray-colored solids. The Fe mesh after washing had a gray-green color. The Fe mesh wire strands were black.

Overall Assessment:

LS-04 was a Portland cement test with 60 Bar (870 psig) CO_2 pressure. The Pu never achieved a high concentration but had a definite upward trend to 255 ppb. U concentrations were relatively high at ~ 10,000 – 11,000 ppm. The Fe concentration started at 3.1 ppm and increased to 162.4 ppm, which is quite high. There was no corrosion observed on the lid, screen, or feedthroughs. There were no colloids or microprecipitates that contained Pu. The pcH did not vary due to CO_2 pressure and had a range of 7.21 to 7.43. This test was a 10:1 ratio brine to solid ratio and only contained 184 grams of waste.

Liter-Scale No. 05 (Pressurized)

Test Characteristics:

Waste:	Portland Cement
Total Waste Weight:	613 g
Initial Actinide Content:	Pu 83.5 μg/g; Total Pu = 51.2 mg Am 0.970 μg/g; Total Am = 0.595 mg
Brine:	Brine A (3:1 brine/solid ratio)
Additives:	Fe Mesh, Nd, Th, U, Np, 60 Bar (870 psig) CO_2, pressure in headspace.

Soluble Actinide Histories: (8/28/95 – 9/21/98)

Pu - Pu started at 1.7 ppb and increased to a peak of 184 ppb with an average of about 15 ppb. Total alpha activity was 0.71 nCi/ml on 9/21/98 and decreased to 0.03 nCi/ml on 5/15/01. There was no rotation during that final period of time.

Am – Am was less than 0.8 ppb during the entire test. Am-241 total alpha activity was < 0.14 nCi/ml on 9/21/98 and was < 0.12 nCi/ml on 5/15/01.

U - U concentration started at 696 ppb and remained quite steady to end up at 479 ppb at the end of the test. No apparent trend was observed.

Th - Th was < 5.1 ppb for the entire test period.

Np - Concentrations of Np were less than 27.0 ppm.

Nd - Nd concentrations were < 0.9 ppb.

Other Analyses (nominal):

Typical pcH Range:	7.0 – 7.44
Fe Concentrations:	Started at 7 ppm and increased to 57.1 ppm. Ended at 16.4 ppm.
Other Analytes:	Ca 12,000 ppm K 25,000 ppm Mg 22,000 ppm Na 40,000 ppm Ni 7 ppm
TIC/TOC:	700/70 ppm
Particle Concentration:	1 x 10^{11} particles/Liter
Filter Paper-WDXRF:	No Pu identified on 3 filters analyzed. One filter showed Fe. No Sr identified.
Headspace Gas Content:	60 Bar of CO_2 pressure.

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D&D Observations (5-10-01):

Corrosion: No corrosion on lid or screen.
Brine: Clear, non-viscous brine with light brown tinge.
Bottom Solids: Yellowish-brown mass that was compact and about 5-1/2 inches in depth.
Fe Mesh: The Fe mesh holder was embedded in solids with a peanut butter texture and color. After rinsing the material of the mesh, the solution had a bluish tint. There was a hard coating on the mesh that was black with a blue tint. No corrosion was visible but the Fe concentration in the brine seemed to imply some corrosion took place at the pcH 7.0 – 7.4 range.

Overall Assessment:

Liter-scale test container LS-05 was a Portland cement test with 60 Bar (870 psig) CO_2 pressure. The Pu did not appreciably solubilize and other actinides remained rather low. The Fe concentration started at 7.0 ppm and increased to 57.1 ppm. There were no Pu colloids or microprecipitates that were filtered out. The pcH did not change significantly (pcH 7.4 – 7.35) during the test period. There was no corrosion observed on the lid, screen, or Fe mesh. LS-5 was the second in a set of three pressurized test containers; LS-4 has a 10:1 brine-to-solid ratio, LS-5 had a 3:1 brine-to-solid ratio and LS-6 had a 2:1 brine-to-solid ratio.

Liter-Scale No. 06 (Pressurized)

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 920 g
Initial Actinide Content: Pu 95 μg/g; Total Pu = 97.4 mg
Am 1.08 μg/g; Total Am = 0.994 mg
Brine: Castile (2:1 brine/solid ratio)
Additives: Fe Mesh, Nd, Th, U, Np, 60 Bar (870 psig) CO_2, pressure in headspace.

Soluble Actinide Histories: (8/28/95 – 9/21/98) then 4/27/01

Pu - Pu started at 25 ppb and peaked at 638 ppb before settling down to 319 ppb on 9/21/98. Pu was at an apparent trend upwards near the end of the test. The alpha activity on 9/21/98 was 28 nCi/ml which decreased to 0.07 nCi/ml (a decrease factor of 400) on 4/27/01. There was no rotation during the last period.

Am – Am was less than 1 ppb (except 1.4 ppb on 1/13/97) for the entire test period. Am total alpha on 9/21/98 was 1.12 nCi/ml and 0.21 nCi/ml on 4/27/01.

U - U started at 2934 ppb and ended up at 3675 ppb. Not much variation and rather low concentrations for a high carbonate system.

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Th - Th was < 3 ppb for the entire test period.
Np –Concentrations of Np were less than 15 ppb for the entire test period.
Nd - Nd was < 4 ppb for the entire test period.

Other Analyses (nominal):

Typical pcH Range: 7.49 – 7.87
Fe Concentrations: Ranged from 2 ppm to 41.4 ppm.
Other Analytes: Ca 1,000 ppm
K 10,000 ppm
Mg 600 ppm
Na 40,000 ppm
Ni 8 ppm
TIC/TOC: 1700/100 ppm
Particle Concentration: 9×10^{10} particles/Liter No correlation with L04 and L05.
Filter Paper-WDXRF: No Pu or Fe identified on 4 of 4 filters.
Headspace Gas Content: 60 Bar (870 psig) of CO_2 pressure.

D&D Observations (4/24/01):

Corrosion: No corrosion on lid or screen.
Brine: The brine was a milky color with no suspensions or crystals. The brine pool was ~ 2 inches deep that led to the top of a brownish-gray soft solid.
Bottom Solids: Brownish-gray soft solid that was compacted and took up about ¾ of the test container.
Fe Mesh: Embedded in a clay-like sludge that was compacted in the Fe mesh holder. The compacted material would have limited brine flow to the Fe mesh. After washing, the Fe mesh did not appear to be corroded and the ends of the wire were shiny. The Fe mesh strands were dark-colored. The Fe concentration in the brine varied from 2 to 41.4 ppm at a pcH around 7.5 – 7.9. This is higher than expected for an Fe mesh that is impacted with solid material.

Overall Assessment:

LS-06 was a Portland Cement test with 60 Bar (870 psig) CO_2 pressure in Castile Brine. LS-4,5,and 6 were a set of three test containers with CO_2 pressure and Portland Cement. LS-4, 5, and 6 had a brine-to-solid ratio of 10:1, 3:1, and 2:1, respectively. This is evident during the D&D because of the increase in bottom solids with the lower ratio. Pu did not solubilize in this test to a high level (638 ppb peak) but was greater than LS-4 and LS-5 as should be expected because of the greater amount of Pu as the brine/solid ratio was smaller. No other actinides were significantly solubilized and Nd, Th, and Np were essentially very low. Nd (< 4 ppb, Th (< 3 ppb) and Np (< 14 ppb). There were no Pu or Fe colloids identified on the 4 filter papers. There was no corrosion observed on the lid, screen, or Fe mesh. The overall observations of the LS4, 5, and 6 is that there was very little solubilization of actinides on these three Portland Cement tests with added CO_2 pressure at 60 Bar (870 psig).

Liter-Scale No. 07

Test Characteristics:

Waste:	Portland Cement
Total Waste Weight:	264 g
Initial Actinide Content:	Pu 94.5 µg/g; Total Pu = 0.025 g Am 1.198 µg/g; Total Am = 0.316 mg
Brine:	Castile (10:1 brine/solid ratio)
Additives:	Th, U, Np No Fe mesh

Soluble Actinide Histories: (4/17/95 – 3/15/99)

Pu -	There were four analyses of 22.9, 40, 10.5, and 14 ppb and the remainder were < 5 ppb. There was no trend of concentrations. Final concentration was 4.1 ppb.
Am -	All analyses were < 1 ppm.
U -	Analyses were generally < 15 ppb with one as high as 20 ppb.
Np -	Started at 3.7 ppb and increased to ~250 ppb.
Th -	Generally < 2 ppb.
Nd -	Generally < 2 ppb.

Other Analyses (nominal):

Typical pcH Range:	8.7 – 8.9
Fe Concentrations:	<2 ppm
Other Analytes:	Ca 14,000 ppm K 21,000 ppm Mg 23,000 ppm Na 44,000 ppm Pb 4 – 5 ppm (last 9 analyses)
TIC/TOC:	12/30 ppm
Particle Concentration:	10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF:	None of the filters had Pu or Fe. Only 3 of 17 had Sr.
Headspace Gas Content:	1.2 v/o H_2, ~ 1.2 v/o O_2. This was the lowest H_2 in STTP.

D&D Observations (3/28/01):

Corrosion:	Corrosion was noted around SS feedthroughs; screen was clean.
Brine:	The brine was colorless with no suspensions or crystals.
Bottom Solids:	About 8 inches of loose muddy solids that could be stirred up; this 10:1 brine to solid test had much liquid left after removal of 1 liter sample. Added AquaSorbe – 2212 to absorb brine.
Fe Mesh:	No Fe mesh added to this test container.

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Overall Assessment:

There was essentially no solubilization of Pu, Am, U, Th, or Nd during the test period. There was a rather consistent 250-300 ppb of Np after 6 months into the test. Np appeared to be more apt to solubilize in 10:1 ratios. This level of Np solubilization is negligible compared to theoretical concentration of 37,500 ppb if the amount added was totally solubilized.

There was corrosion noted on SS feedthroughs on the lid. The screen was not corroded. The brine was clear with no suspensions. The precipitates seemed to settle readily to the bottom and mix with 8 inches of sludge. There was no Fe mesh added to LS-07 and no Fe was detected on any filter paper.

Liter-Scale No. 08

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 88.5 µg/g; Total Pu = 0.117 g
Am 1.095 µg/g; Total Am = 1.45 mg
Brine: Castile (12:1 brine/solid ratio)
Additives: Nd, Th, U, Np
No Fe mesh

Soluble Actinide Histories: (4/17/95 – 3/15/99)

Pu - There were 8 analyses from 10-26 ppb and the remainder were <5 ppb. There was no trend of concentrations.
Am - All analyses were < 0.5 ppb except last analyses was 1 ppb.
U - Analyses were generally < 2 ppb, which is quite low for U. No trend is apparent.
Np - Less than1 ppb for entire test period.
Th - Generally < 1 ppb for entire test period.
Nd - Generally < 2 ppb for entire test period.

Other Analyses (nominal):

Typical pcH Range: 9.1 – 9.5
Fe Concentrations: <1 ppm
Other Analytes: Ca 36,000 ppm
K 30,000 ppm
Mg 2,500 ppm
Na 43,000 ppm
TIC/TOC: 10/50 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: None of the filters had Pu; two of 16 showed Fe. Essentially all showed Sr and S.
Headspace Gas Content: H_2 = 1.8 v/o (2nd lowest in STTP); O_2 = 0.03 v/o.

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D&D Observations (04/03/01):

Corrosion:	No corrosion observed in SS feedthroughs. Screen was clear, had ~1/8-inch of sediment.
Brine:	Clear with grayish coloration; no suspensions or crystals noted.
Bottom Solids:	About 8 inches of solids; 4 inches of loose fluffy solids and then 4 inches of hard solids that may have been cemented.
Fe Mesh:	No Fe mesh added to this test container.

Overall Assessment:

There was essentially no solubilization of Pu or any other actinide in LS-08 at pcH 9.1– 9.5 in a Brine A environment. Most of the Mg precipitated at the pcH range of 9.1 – 9.5. There was no soluble Fe throughout the test nor was there any filterable Pu or Fe (mostly) in LS-08. There was no Fe mesh added. There was about 4 inches of hard solids at the bottom of the test container. The brine was fairly clear for a 2:1 Brine/solid ratio test. There was no corrosion of the SS feedthroughs.

Liter-Scale No. 09

Test Characteristics:

Waste:	Portland Cement
Total Waste Weight:	1320 g
Initial Actinide Content:	Pu 81 μg/g; Total Pu = 0.107 g Am 0.995 μg/g; Total Am = 1.26 mg
Brine:	Castile (2:1 brine/solid ratio)
Additives:	Nd, Th, U, Np No Fe mesh

Soluble Actinide Histories: (4/17/95 – 3/15/99)

Pu -	All results were < 10 ppb except two analyses at 13.0 and 16.3 ppb. Most analyses were < 5 ppb.
Am -	All analyses were < 1 ppb; no trend observed.
U -	All results were < 10 ppb, except one at 13.4 ppb. No trend is apparent.
Np -	Less than 1 ppb, except one result (1.7 ppb).
Th -	Less than 2 ppb for entire test period.

Other Analyses (nominal):

Typical pcH Range:	12.9 – 13.1
Fe Concentrations:	<1 ppm for the entire test period.

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Other Analytes: Ca 150 ppm
K 8,400 ppm
Mg <10 ppm
Na 80,000 ppm
Pb 4 ppm average for last nine results.
TIC/TOC: 15/50 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: No Pu colloids or microprecipitates detected. Seven out of 17 filters had Fe. Twelve out of 17 contained Sr. Although there was < 10 ppm Mg, there was much Mg and Ca in all the filters. The Ca, Mg, and Fe were mostly on the 5 micron filters.
Headspace Gas Content: H_2 = 3.4 v/o; O_2 = 0.17 v/o.

D&D Observations (04/19/01):

Corrosion: No corrosion observed in SS feedthroughs. (Sampling port, level probe, pressure gauge). No coloration was noted.
Screen: No corrosion on the o-ring; ~1/2-inch of gray paste in the screen.
Brine: Clear except for Portland cement suspensions.
Bottom Solids: Loose solids (6-8 inches) that settled readily, no cementation.
Fe Mesh: No Fe mesh added to this test container.

Overall Assessment:

LS-09 was a Castile brine experiment with a 2:1 Brine/solid ratio with a very basic pcH (12.9 – 13.1) that precipitated both Ca and Mg as hydroxides. There was essentially no solubilization of Pu, Am, other actinides and Fe. There was no Fe mesh added to this test but seven of 17 filters contained Fe, perhaps from the ferric sulfate added to the original Portland Cement mix. There was no corrosion of the three SS feedthroughs at the highly basic pcH. There was 6-8 inches of loose solids that probably contained Ca and Mg hydroxides. There was no Pu found in any filter paper. The dilution of Pu within a Ca and Mg hydroxide matrix could have been substantial. The H_2 concentration in the headspace was relatively low (3.4 v/o) and the O_2 was 0.17 v/o.

Liter-Scale No. 10

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 264 g
Initial Actinide Content: Pu 86 μg/g; Total Pu = 0.021 g
Am 1 μg/g; Total Am 0.25 mg
Brine: Brine A (10:1 Brine/Solid ratio)
Additives: Th, U, Np, No Fe mesh added; no Nd addition
Other: ^{241} Am (75 mg) added as soluble salt

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Soluble Actinide Histories:

Pu - Pu concentrations ranged from about 10 to 20 ppb for most of the test. No trend was observed .
Am - Am concentration varied from about 0.3 to 1.9 ppb for the life of the test. No trend was observed.
U - U concentrations ranged from 0.3 to 12 ppb for the lifetime of the test. No trend was observed.
Np - Np concentrations ranged from 20 to 48 ppb for the test and no trend was observed.
Th - Concentrations were generally less than 5 ppb with no trends observed.
Nd - Neodymium was not added to LS 10.

Other Analyses (Nominal):

Typical pcH Range: 8.2 to 8.9
Fe Concentration: There was no Fe mesh added to this test container and Fe was typically less then 1 ppm.
Other Analytes: Ca 13 k
K 23 k
Mg 23 k
Na 40 k
Other: Al, Ni, and Pb < 5 ppm
TIC/TOC: 10/30 ppm
Particle Concentration: 10^9 to 10^{10} particles/L
Filter Paper-WDXRF: No Pu or other actinides identified on 5 micron, 1 micron and < 10 nm filter papers. Sr was not identified on 5 and 1 micron filter paper but was identified on < 10 nm filters. No Fe identified; high Ca and Mg.
H_2 Headspace Gas Content: 32.5 v/o H_2, 1.5 v/o O_2

D&D Observations (2/5/01):

Corrosion: Some corrosion visible around sampling port, level probe, and gauge port. Some rust colored corrosion product on screen and sides of vessel.
Brine: Brine is clear.
Bottom Solids: About 3 to 4 inches of compacted but soft solids that were not solidified.
Fe Mesh: No Fe mesh in LS10.

Overall Assessment:

LS10 was a comminuted Portland Cement test with 75 mg of added Am-241 to increase alpha activity and radiolysis. All actinides and Nd were precipitated immediately in the Portland Cement matrix at pcH 8-9. The added Am-241 was also immediately precipitated in the Portland Cement matrix and did not show an increase beyond 1 ppb during the entire test.

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The presence of the precipitated Am-241 was evident from the H_2 concentration in the headspace in this test container (~ 32.5 v/o H_2) which was higher than similar Portland cement tests w/o Am-241 (typically < 5% H_2). This test exemplified the effectiveness of Portland Cement in immobilizing or precipitating actinides in a high radiolytic environment. The 10:1 brine to solid ratio may have been the reason that the brine was clear and that there was a definite phase separation between the comminuted Portland cement and the brine. Although there was 75 mg of added ^{241}Am equivalent to 37,500 ppb, if totally dissolved, there was no Pu or Am detected on the filter papers indicating that at this brine to solid ratio that there was no Pu or Am colloids or microprecipitates that did not settle to the bottom of the Brine A after each rotation. There was no Fe identified on any filter.

Liter-Scale No. 11

Test Characteristics:

Waste: Portland Cement
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 98 μg/g; Total Pu = 0.129 g
Am 1.195 μg/g; Total Am 1.58 mg
Brine: Brine A (2:1 Brine/Solid ratio)
Additives: Th, U, Np No Fe mesh added; no Nd addition
Other: ^{241} Am (75 mg) added as soluble salt.

Soluble Actinide Histories:

Pu - Pu concentrations less than 5 ppb with 4 exceptions. Low Pu with no visible trend.
Am - Less than 0.5 ppb with no apparent trend.
U - U concentrations less than 3 ppb with no visible trend.
Np - Np concentrations less than 1 ppb with no trend observed.
Th - Concentrations were less than 1 ppb with no visible trend.

Other Analyses (Nominal)

Typical pcH Range: 9.0 to 10.8
Fe Concentration: Generally less than 1 ppm. There was no Fe mesh added to this test container.
Other Analytes: Ca 40,000 ppm
K 30,000 ppm
Mg < 200 ppm (this seems like Castile Brine)
Na 40,000 ppm
Other: Al, Ni, and Pb < 5 ppm
TIC/TOC: 10/40 ppm
Particle Concentration: 10^9 to 10^{10} particles/L

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Filter Paper-WDXRF:	No Pu identified in any filter paper. Seven of 15 filters had Fe; all filters had Sr and S at 5 and 1 micron and < 10 nm filters. High Ca and Mg found on all filters.
H_2 Headspace Gas Content:	22% H_2

D&D Observations (2/6/01):

Corrosion:	SS fittings and feedthroughs were slightly rusted. There was also the appearance of rust around the top of the vessel.
Brine:	Brine is gray color; there was sediment on screen with black particles of rust.
Bottom Solids:	There was approximately 8 inches of very loose gray sludge at the bottom of the test container. Approximately one-inch at the very bottom of the test container was compacted “hard” solid but not cemented.
Fe Mesh:	No Fe mesh in LS11.

Overall Assessment:

LS11 was a typical Portland Cement test at pcH 9.0 to 10.8 that had very low concentrations (< 5 ppb) of all actinides. There was no Fe Mesh or Nd added to this test container but there was 75 mg of Am-241. If all the ^{241}Am added as a soluble salt remained soluble the concentration would have been 37,500 ppb. The Fe concentration was also very low at < 1 ppm. The particle concentration was generally low, 10^9 to 10^{10} particles/liter. No Pu was identified on the filter papers and Fe was identified on the 5 micron filter. All filters (5 micron, 1 micron, 10 nm) showed Sr and S. There was rust observed around the S.S. fittings and feedthroughs. The H_2 was about 22 v/o which was rather low for a test with added Am-241. There was a great deal of sludge in the test container and the Mg was low for a Brine A test. Perhaps the Mg precipitated and led to a higher sludge content but the main reason was that this was a 2:1 brine to solid ratio as opposed to a 10:1 in LS10. Both tests were with Brine A. Mg begins to precipitate as $Mg(OH)_2$ at a pH of about 10.5. The absence of Pu or Am on any filter papers indicates that the Pu did not dissolve initially or that any soluble Pu or Am was immediately precipitated and settled down to the bottom of the test container after each rotation. The sludge was not solidified or cemented but was mostly loose. Overall, the high pcH (9.0 – 10.8) and high sludge content led to a test with essentially no soluble actinides.

Liter-Scale No. 12

Test Characteristics:

Waste:	Portland Cement Solidified dewatered aqueous process sludge
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 81.5 μg/g; Total Pu = 0.108 g Am 1.021 μg/g; Total Am = 1.347 mg

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Brine: Castile (2:1 brine/solid ratio)
Additives: Th, U, Np, and Am-241
No Fe mesh; no Nd added

Soluble Actinide Histories:

Pu - Remained typically <10 ppb.
Other - Nd, Th, Np, U, and Am remained ≤4 ppb throughout the experiment.

Other Analyses (nominal):

Typical pcH Range: 12.7-13.0
Fe Concentrations: <1 ppm
Other Analytes: Ca 200 ppm
K 8,000 ppm
Mg 25 ppm
Na 80,000 ppm
TIC/TOC: 40/50 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: No actinides found on the filter papers. Seven of 13 filters had Fe even though Fe was not detected as a soluble cation. Sr and S were detected on 8 filters.
Headspace Gas Content: ~30 v/o H_2, ~ 1.2 v/o O_2,
<<1% N_2O

D&D Observations (February 1, 2001):

Corrosion: There was a black coating on the lid and O-ring that was hard, (i.e., could not be scratched with a screwdriver). The screen was black, but not impacted.
Brine: The brine was a pale green color, that was clear, (i.e., did not contain sediment.
Bottom Solids: These solids were soft and non-consolidated. The color of the very loose sludge was grayish.
Fe Mesh: No Fe mesh added to this test container.

Overall Assessment:

Liter-scale 12 was the Castile Brine experiment of the set LS 10, 11, and 12. Whereas L10 was an experiment with a 10:1 ratio, L11 had a 2:1 ratio, and L12 had a 2:1 ratio. All three had 75 mg of ^{241}Am added as a soluble chloride complex for a theoretical concentration of 37,500 ppb if the Am remained soluble. The pcH of LS 10, 11, and 12 ranged from 8.2 - 8.9, 9.7 – 10.7, and 12.7 – 13.0, respectively. The Pu and Am were typically less than 5-10 ppb for all three tests and no Fe was identified as a soluble cation. No Pu or any other actinide was found as filterable colloids or microprecipitates. No Fe was found in L10 filters but L11 and L12 filters contained Fe even though Fe mesh was not added to the three tests. There was corrosion of SS feedthroughs in L10 and L11. There was no visible corrosion in L12 (only a black coating). The H_2 content of L10, 11, and 12 was 32.5 v/o, 22.2 v/o, and 30 v/o respectively for the three containers. There was ~1.5, 0.90, and 1.2 v/o oxygen for this three test containers that indicates

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that the ^{241}Am produced this effect. The high pcH in L12 may have been the cause for the very low concentrations of Ca and Mg found in this Castile Brine test. There were about 10^9 to 10^{10} particles per liter in each test.

Liter-Scale No. 13

Test Characteristics:

Waste: Envirostone
80–90 % $CaSO_4$ with 10-20 % melamine-formaldehyde and 0.1% NH_4Cl
Solid Absorbed Organic Liquid Waste
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 2575 μg/g; Total Pu = 3.40 g
Am 1.92 μg/g; Total Am = 2.53 mg
Brine: Brine A (2:1 brine/solid ratio)
Additives: Fe Mesh; Nd, Th, U, Np
Added organic solvents

Soluble Actinide Histories: (5/1/95 – 3/1/99)

Pu - Started at 40 ppb and varied between 10-90 ppb until final concentration of 26 ppb. There did not seem to be a trend.
Am - Generally < 1 ppb except for two results < 2 ppb.
U - Started at 2353 ppb and varied between about 1700 to 6000 ppb and leveled off at 1000 – 2000 with a final result at 1295 ppb. There may have been a trend downward.
Th - Varied between 2 to 24 ppb for entire test with no apparent trend.
Np - < 4 ppb for entire test period; no trend.
Nd - Generally < 5 ppb with no apparent trend.

Other Analyses (nominal):

Typical pcH Range: 7.0-7.2
Fe Concentrations: Started at 14 ppm and increased to 326 ppm after six months and slowly decreased to 35 ppm. Organics seemed to solubilize Fe in this set of tests.
Other Analytes: Ca 1,300 ppm
K 1,200 ppm
Mg 32,000 ppm
Na 41,000 ppm
Pb 4-5 ppm average
TIC/TOC: 60/3,300 ppm
Particle Concentration: 10^{12} to 10^{13} particles/Liter
Filter Paper-WDXRF: Fourteen of 17 filters contained Pu; all filters had Fe; only 2 had Sr. This was a high number of Pu bearing colloids or microprecipitates.

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The Fe in the filters was consistent with the soluble Fe throughout the test.

Headspace Gas Content: H_2 = 56.6 v/o; O2 = 0.20 v/o; CO_2 = 4.4 v/o; TOC = 3300 ppm.

D&D Observations (1-22-01):

Corrosion: No corrosion on lid or screen.

Brine: Clear, with thin layer of suspensions floating atop the brine.

Screen: Yellowish pasty material in the screen.

Bottom Solids: Approximately 4 inches of solids with a consistency of peanut butter that was harder at the bottom but not cemented.

Fe Mesh: The plastic holder was full of greenish-yellow sediment. There was a green color next to the mesh. The compacted sediment washed away readily. The washed wire mesh was black and did not appear corroded and the cut ends were still shiny. The Fe results indicate that there was some dissolution of Fe but it must have been uniform and not noticeable.

Overall Assessment:

LS-13, 14, and 15 had a variety of added organics that had a significant effect on the chemistry of these tests. For LS-13 with Brine A and a pcH that was about neutral to slightly basic, there was relatively low levels of Pu solubilized (10-90 ppb) but the concentration of Pu persisted throughout the test. The concentration of Fe in this test was relatively high and persisted throughout the test period. There was no corrosion of the SS feedthroughs in the lid but a green coloration around the Fe mesh attests to the presence of ferrous chloride in the brine. The presence of organics increased the particle concentration in the brine and Pu and Fe were present in the filter papers, which indicated colloids or microprecipitates of both Pu and Fe. The added organics (TOC = 3300 ppm), resulted in a high H2 content (57 v/o), low O_2 content (0.20 v/o), and measurable CO_2 (4.4 v/o). Of note is that soluble Fe, Pu, and U were correlative in this test.

Liter-Scale No. 14

Test Characteristics:

Waste: Envirostone
80-90% $CaSO_4$ with 10-20% melamine-formaldehyde and 0.1% NH_4Cl

Total Waste Weight: 1,320 g

Initial Actinide Content: Pu 2592 μg/g; Total Pu = 3.42 g
Am 2.54 μg/g; Total Am = 3.35 mg

Brine: Brine A (2:1 brine/solid ratio)

Additives: Fe Mesh; Th, U, Np, and Nd

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Soluble Actinide Histories: (5/1/95 – 4/5/99)

Pu -	Started at 488 ppb and leveled at ~ 150 ppb until 12/2/96 and then decreased to ~ 75 ppb.
Am -	Was generally less than 2 ppb with no trend.
U -	Increased to ~ 5500 ppb after 6 months and then slowly decreased to ~ 1500 ppb at the end of the experiment (4/5/99).
Np -	Ranged from 2-4 ppb for the length of the test. No trend was apparent.
Th -	Ranged from 10-20 ppb for the length of the test. No trend was apparent.
Nd -	Ranged from 5-25 ppb for the length of the test. No trend was apparent.

Other Analyses (nominal):

Typical pcH Range:	6.9 - 7.3
Fe Concentrations:	Ranged from 130 ppm to a high of ~466 ppm after 1 year and slowly decreased to ~ 100 ppm at end of the test.
Other Analytes:	Ca ~1,300 ppm K ~28,000 ppm Mg ~30,000 ppm Na ~40,000 ppm Pb ~3-6 ppm
TIC/TOC:	80/4000 ppm
Particle Concentration:	$3x10^{13}$ to $8x10^{13}$ particles/Liter
Filter Paper-WDXRF:	Pu found on 11 of 15 filter papers; Fe found on essentially all filter papers; Sr found on 4 filter papers and S was on essentially all filter papers. Fe was present in all pore-sized filters.
Headspace Gas content:	H_2 was 37.4 v/o; no other major gases quantified.

D&D Observations (January 18, 2001):

Corrosion:	There was no visible corrosion of the SS fittings or feedthroughs. There was no apparent corrosion on the lid or screen, in fact, it looked new.
Brine:	There were yellowish suspensions above a pool of brine. The liquid was non-viscous. About 1.5 liters was extracted.
Bottom Solids:	The sludge near the bottom was the consistency of peanut butter, probably, powered Envirostone.
Fe Mesh:	The Fe mesh was a dark color without corrosion and the cut ends were still shiny.

Overall Assessment:

This test had the highest TOC of the STTP experiments with a relatively high Pu content (3.42 g) and Am content (3.35 mg) but at a pcH of 6.9-7.3 (about neutral) the Pu was generally less than 200 ppb and Th, U, Np, and Nd less than 25 ppb. Uranium concentrations were as high as 5500 ppb but decreased to ~ 1500 ppb near the end of the test. Am was generally less than 2 ppb. Soluble Fe was prevalent for most of the test at about 100-470 ppm.

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There was no apparent corrosion of the SS feedthroughs or fittings in the headspace of the test containers. The Fe mesh showed no signs of corrosion in the Brine A at pcH 6.9-7.3. Pu was identified on most filter papers along with Fe. The particle concentration in this high organic solution was one of the highest in the STTP at $3\text{x}10^{13}$ to $8\text{x}10^{13}$ particles per liter. Apparently, the high particle concentration was associated with Pu and Fe as colloids or microprecipitates. The high Pu and Am content with TOC of 4000 ppm resulted in a 37 v/o H_2 concentration in the headspace of the test container but this was lower than LS-13 with a TOC of ~ 4000 ppm with a H_2 concentration of ~ 57 v/o.

Liter-Scale No. 15

Test Characteristics

Waste:	Envirostone 80-90% $CaSO_4$ with 10-20% melamine-formaldehyde and 0.1% NH_4Cl
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 31.5 µg/g; Total Pu = 0.042 g Am 0.019 µg/g; Total Am = 0.025 mg
Brine:	Castile (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd Added organic solvents

Soluble Actinide Histories: (5/1/95 – 4/5/99)

Pu -	Started at 57.5 ppb, and leveled at ~ 20 ppb and increased to ~ 165 ppb (peak) and then decreased to a final result of 22 ppb.
Am -	Less than 1.5 ppb for entire test period.
U -	Followed trend of Pu; started at 441 ppb and remained between 300 and 400 until 5/18/98 when the U increased to 2,600 ppb and peaked at 3454 ppb then finally decreased to 1,052 ppb at the end of the test.
Np -	Started at ~ 5,400 ppb, increased to 7753 ppb after 2-3 months and gradually decreased to 60 ppb at the end of the test period.
Th -	Generally < 10 ppb for the entire test period.
Nd -	Started at 544 ppb and slowly decreased to 22 ppb at the end of the test period. This was one of the few tests that solubilized Nd.

Other Analyses (nominal):

Typical pcH Range:	6.8 - 7.1
Fe Concentrations:	Started low at 1-5 ppm and slowly increased to 36 ppm at the end of the test. Mostly in the 20-36 ppm range.
Other Analytes:	Ca ~700 ppm K ~4,000 ppm

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Mg ~1,000 ppm
Na ~88,000 ppm
Pb ~4.5 ppm (final analyses)

TIC/TOC: 40/1,400 ppm

Particle Concentration: 10^{12} to 10^{13} particles/Liter

Filter Paper-WDXRF: No Pu identified on any filter paper. Fe identified on 5 of 14 filters. One filter had a very high Fe concentration (1128) on the 5 micron filter that also showed Th and Nd. This was unique in the STTP and must have been a sample with a large precipitate of Fe hydroxide that scavenged the Th and Nd. There was one high Sr result.

Headspace Gas content: H2 = 3.0 v/o; O_2 = 0.01 v/o; TOC = 1,400 ppm.

D&D Observations (April 19, 2001):

Corrosion: There was no visible corrosion of the SS fittings or feedthroughs. (Sample port, level probe, press gauge). Cream colored material on lid.

Screen: Contained about 2 inches of oatmeal consistency solution. There was no corrosion on the metal o-ring.

Brine: Cream colored brine with oatmeal consistency suspensions.

Bottom Solids: Very loose material about 5-7 inches thick for this 2:1 ratio test.

Fe Mesh: The plastic holder was full of fine loose solids but the Fe mesh after being washed was in good condition. It was gray to black in color with no visible evidence of corrosion.

Overall Assessment:

LS-15 was part of the set of LS 13, 14, and 15 that had added organic solvents in the Envirostone. This test was conducted at pcH 6.8-7.1 which is one of the few tests (except for pressurized tests L28, 29, and 30) conducted at a pcH level on the acid side of neutral. The Pu was not substantially solubilized (up to 165 ppb), Am remained very low (<1.5 ppb) and U followed the trend of Pu and increased to 3,454 ppb and then decreased to 1,052 ppb at the end of the test. Np followed a different trend by starting at 5,400 ppb and then decreasing for the rest of the test period to 60 ppb. Th was < 10 ppb for the entire test period. This is one of the few tests that showed Nd at a starting concentration of 544 ppb. The concentration of Fe was high throughout the test but only 5 of 14 filters had Fe. No filter paper showed Pu. The TOC was 1,400 ppm, but the H_2 in the headspace was low at 3.0 V/o; LS-13 had a H_2 level of ~57 v/o and LS-14 had a H_2 concentration of 37 v/o. There was no corrosion observed on the SS feedthroughs and the Fe mesh did not have observable corrosion.

Liter-Scale No. 16

Test Characteristics:

Waste:	Envirostone 80-90% $CaSO_4$ with 10-20% melamine-formaldehyde and 0.1% NH_4Cl
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 470.0 μg/g; Total Pu = 0.620 g Am 0.25 μg/g; Total Am = 0.330 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd

Soluble Actinide Histories: (5/1/95 – 2/22/99)

Pu -	Concentration initially was at 150-400 ppb for about 2 years and then it went into a steady increase for the remainder of the test. **This was one of the only tests that ended up with Pu increasing, and it increased to about 1,200 ppb.**
Am -	Started at <0.5 ppb for about 2 years and then it increased similar to Pu, to about 3.0 ppb at the end of the experiment.
U -	Started at 14,600 ppb and slowly decreased to 182 ppb during the life of the experiment
Np -	Started at ~100 ppb and increased to ~200 ppb at end of test
Th -	Started at 10 ppb and increased to about 280 ppb at end of test
Nd -	Started at ~20 ppb and increased to ~50 ppb at end of test

Other Analyses (nominal):

Typical pcH Range:	7.3-8.0
Fe Concentrations:	Started very low (<0.1 ppm) and remained low for about 2 years, and then began a slow increase to ~33 ppm at end of test
Other Analytes:	Ca ~1,700 ppm K ~26,000 ppm Mg ~35,000 ppm Na ~40,000 ppm
TIC/TOC:	80/430 ppm
Particle Concentration:	10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF:	Pu, Fe, and $SrSO_4$ identified as colloids or microprecipitates
Headspace Gas content:	H_2 = ~62 v/o; which is relatively high for Envirostone; N_2O = 2.5 v/o. NO_3 was ~ 100 ppm.

D&D Observations (December 19, 2000):

Corrosion:	There was no visible corrosion of the SS fittings or feedthroughs. There was no apparent corrosion of the screen, in fact, it was like new.
Brine:	The brine was tan colored and very cloudy and became thicker near the bottom of the container. Near the bottom the brine had to be scooped out, not poured, because of its high density of solids.

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Bottom Solids: The sludge near the bottom was tan to brown colored, but it was not cemented.

Fe Mesh: The Fe mesh was retrieved and appeared to be totally intact. The Fe mesh holder was totally full of thick sludge that was impacted. There must have been some corrosion or dissolution of the Fe mesh because there was a greenish-black color adjacent to the screen, but only inside the Fe mesh holder. The Fe mesh strands had a black coating that was quite hard. The Fe mesh with its black coating seemed to have retained spring and was not brittle.

Overall Assessment:

This test, L-16, with Envirostone in Brine A at a slightly basic pcH (7.3-8.0) was one of the only STTP tests that was terminated with Pu, Am, Np, Th, and Nd concentrations trends increasing. U was different, it began at 14,983 ppb and trended downwards 182 ppb during the test. The presence of a tinge of green color within the Fe mesh holder indicated that some Fe had dissolved as $FeCl_2$, but was not being released to the brine until near the end of the test. The soluble Fe concentration at pcH 7.3 – 8.0 could have been present as a Fe^{+2} cation.

The high hydrogen concentrations may have been responsible for the corrosion- free SS fittings in the headspace region. The tan color of the brine and suspensions indicate that there was little communication with the Fe mesh and the brine. The brine would have been green colored if there had been more dissolution of the Fe wire. The reason for the eventual increase in all the actinides, except U, is not known. U was high in most of the Envirostone tests, but decreased with time, except L-15. Pu as a filtered colloid or microprecipitate was present along with Fe and $SrSO_4$. Low nitrate concentration gave a low N2O content (<2.5 v/o). The increase in Fe concentration in the brine was concurrent with the increase in all the actinide concentrations. The Fe mesh was not dissolved and had a hard black coating.

Liter-Scale No. 17

Test Characteristics:

Waste:	Envirostone 80 – 90 % $CaSO_4$ with 10-20 % melamine- formaldehyde and 0.1 % ammonium chloride. Solidified absorbed aqueous waste
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 1,140 μg/g; Total Pu = 1.50 g Am 2.05 μg/g; Total Am = 2.706 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd

Soluble Actinide Histories: (5/1/95 – 2/2/99)

Pu - Was always <20 ppb, and typically remained <3 ppb.

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U - Began at 1,300 ppb, increased to a high of 20,000 ppb by July 1995, and then steadily decreased to a low of 270 ppb as of the last sampling, February 1999.
Np - Began at 4 ppb, increased to a high of 25 ppb, March 1996, and then steadily decreased to a low <4 ppb, August 1997 through February 1999.
Other - Nd was typically <10 ppb, and Th and Am were ≤1 ppb.

Other Analyses (nominal):

Typical pcH Range: 7.7-8.0
Fe Concentrations: <1 ppm
Other Analytes: Ca ~2,000 ppm
K ~25,000 ppm
Mg ~30,000 ppm
Na ~43,000 ppm
TIC/TOC: 70/350 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Pu precipitates were found, which appear to be associated with Fe and Ca.
H_2 Headspace Gas Content: ~7.7 v/o H_2; ~ 20 v/o N_2O; NO_3 was ~ 13,000 ppm.

D&D Observations (February 16, 2001):

Corrosion: There was no visible corrosion on the lid, and everything appeared in clean and good condition.
Brine: The brine was tan in color and there were no suspensions or crystals noted.
Bottom Solids: The sludge near the bottom was tan and loose. The solids at the bottom were loose and ‘mushy’.
Fe Mesh: The iron mesh was recovered, and it was in good condition. It was only slightly embedded and there was not much solid material surrounding it. There was a small amount of tan colored material deposited on the Fe mesh screen, which easily rinsed off. After rinsing the screen, it was black with no shiny edges.

Overall Assessment:

LS 17 was a Brine A test with a 2:1 brine/solid ratio at pcH 7.7 – 8.0 that showed essentially no soluble Nd, Th, Np, Pu, and Am but did have high U early in the test (20,000 ppb) which diminished with time to ~260 ppb at the end of the test. The reason for the behavior of U is not known. LS 17 had a high nitrate concentration that yielded an N_2O concentration of ~ 20 v/o in the headspace of the test container. The H_2 concentration of ~ 7.7 v/o was quite low relative to other test containers. There were 14 of 16 filters that contained Pu which was surprising because the soluble Pu concentration was < 3 ppb for most of the test. All filters had Fe which was also surprising because the soluble Fe was generally less than 1 ppm. The Pu and Fe in the filter papers attests to the presence of Pu and Fe bearing colloids or microprecipitates throughout the test. The nitrate in this test container had to be totally soluble in brine but the radiolytic

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production of N_2O was probably from solid or precipitated species of Pu and Am. The activity of 3nCi/ml is about 110 d/s/ml is probably too low to generate 20 v/o of N_2O but a precipitated activity of 1.5 g of Pu and 2.7 mg of Am would be sufficient activity to generate that amount of N_2O. The Fe wire was not corroded in this test.

Liter-Scale No. 18

Test Characteristics:

Waste: Envirostone, 80 – 90% $CaSO_4$ with 10 – 20% melamine formaldehyde and 0.1% ammonium chloride
Solidified absorbed aqueous waste
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 1,970 μg/g; Total Pu = 2.60 g
Am 26.48 μg/g; Total Am = 34.9 mg
Brine: Castile (2:1 brine/solid ratio)
Additives: Fe Mesh; Th, U, Np, and Nd

Soluble Actinide Histories: (5/1/95 – 3/8/99)

Pu - Was typically ≤10 ppb, however spiked to 210-220 ppb on two separate occasions, Oct. 1996 and Aug. 1998.
U - Began at a low of 2,000 ppb, increased to a high of 27,000 ppb by Jan. 1996, and has since steadily decreased to a low of 9,500 ppb as of the last sampling, March 1999.
Np - Began at a low of 14 ppb, increased to a high of 1,600 ppb by Nov. 1995, and has since steadily decreased to typically 19-22 ppb, Aug. 1998 to Jan. 1999.
Other - Nd was typically <5 ppb, Th and Am were typically <3 ppb.

Other Analyses (nominal):

Typical pcH Range: 7.0-7.8
Fe Concentrations: Increased to about 50 ppm after one year and then decreased to <2 ppm for remainder of test.
Other Analytes: Ca ~660 ppm
K ~4,400 ppm
Mg ~900 ppm
Na ~90,000 ppm
TIC/TOC: 40/420 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Twelve of 14 filter papers had significant Pu colloids or precipitates. Two of three filter papers had Np and U precipitates. These precipitates did not appear to be directly related to Fe or Sr precipitates.
Headspace Gas Content: ~50 v/o H_2; 1 –2 v/o N_2O; NO_3 was ~ 100 ppm.

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D&D Observations (January 9, 2001):

Corrosion: There were orange-brown colored solids attached to the lid and screen.

Brine: The brine was clear with suspended clay-like particles that gave the brine a yellow color in appearance.

Bottom Solids: The solids at the bottom of the container were soft and not compacted or cemented.

Fe Mesh: The Fe mesh was surrounded by a black clay-like material that easily rinsed off. After rinsing the mesh, a hard black surface coating was noted. The mesh was still intact.

Overall Assessment:

LS 18 was the test with Envirostone in Castile brine from pcH 7.0 – 7.8 which is just basic. This test had ~ 2.6 g of Pu and 35 mg of Am which is relatively high for Envirostone tests. Soluble Pu and Am were fairly low (< 10 ppb and 1 ppb, respectively) and Fe was generally < 2 ppm after the first year of the test. U generally at the 22,000 ppb level had decreased to about 9,000 ppb near the end of the test. Although the soluble Pu had been low for most of the test, there was Pu in the filter papers indicating that Pu had precipitated or formed colloids that were filtered during the test. The Fe mesh was still intact and black colored and did not dissolve. There was a hard black coating around each strand. The bottom solids were loose and not compacted. The brine was nearly colorless and the crystals throughout the test container had a color like butterscotch in this 2:1 brine/solid ratio test. There did not appear to be corrosion of the lid or feedthroughs.

Liter-Scale No. 19

Test Characteristics:

Waste: Envirostone 80–90% $CaSO_4$ with 10–20% melamine formaldehyde and 0.1% ammonium chloride
Solidified inorganic sludge

Total Waste Weight: 1,320 g

Initial Actinide Content: Pu 380 μg/g; Total Pu = 0.502 g
Am 12.75 μg/g; Total Am = 16.8mg

Brine: Brine A (2:1 brine/solid ratio)

Additives: Fe Mesh; U, Th, Np, and Nd

Soluble Actinide Histories: (5/1/95 – 3/1/99)

Pu - Typically ≤10 ppb throughout the life of the experiment.

U - Began high at 21,000 ppb, increased a little higher to 26,000 ppb in July 1995, and has since steadily decreased to a low of 570 ppb as of the last sampling, March 1999.

Np - Typically varied from 20-45 ppb throughout the life of the experiment.

Nd - Was typically 15 ppb for the first few months of testing and then decreased to <5 ppb for the last two years of sampling.

Other - Th was typically <5 ppb and Am was typically <1 ppb.

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Other Analyses (nominal):

Typical pcH Range: 7.9-8.2
Fe Concentrations: <1 ppm for entire test period
Other Analytes: Ca 1,100 ppm
K 23,000 ppm
Mg 28,000 ppm
Na 50,000 ppm
TIC/TOC: 70/700 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Six of eleven filter papers had low levels of Pu. Essentially all filters had Fe and Sr.
Headspace Gas Content: ~16 v/o H_2; 32 v/o N_2O; 36,000 ppm NO_3

D&D Observations (February 16, 2001):

Corrosion: No corrosion was noted on lid and the screen looked like new. There was a thin orange coating noted around SS sampling port.
Brine: The brine was very clear above the screen, but it was cloudy and yellow colored beneath the screen.
Bottom Solids: The solids at the bottom of the container were a soft sludge.
Fe Mesh: The Fe mesh container was coated with a soft sludge. The inside of the container consisted of a blackened sludge. The Fe mesh was slightly dissolved, and had a very thin hard black coating.

Overall Assessment:

LS 19 was an Envirostone test in Brine A at a pcH of 7.9 – 8.2 and a brine–to-solid ratio of 2:1. Pu did not solubilize to more than 10 ppb during the test period and Am was <1 ppb. There was no corrosion on the lid or SS feedthroughs. The brine above the screen was clear but had a yellowish color below the screen. There had been difficulty in sampling this test container because finely divided waste would plug the sampling needle. The orange color on the lid and the slightly yellow color in the brine may indicate an oxidizing condition for this test container. This test had a high concentration of nitrites (36,000 ppm) and a resulting high concentration of N_2O (32 v/o) that precluded a high concentration of H_2 (16 v/o). Although the soluble Pu concentration was low (0-10 ppb) and Fe was < 1 ppm for this test.

The filtered brine showed Pu and Fe on many of the filter papers indicating the presence of colloids or microprecipitates containing Pu and Fe in the Brine A. The Fe mesh was surrounded by a black sludge and was slightly corroded by the Fe wire strands which were covered with a hard coating.

Liter-Scale No. 20

Test Characteristics:

Waste:	Envirostone Solidified inorganic sludge
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 60.5 μg/g; Total Pu = 79.86 mg Am 7.07 μg/g; Total Am = 9.33mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; U, Th, Np, and Nd

Soluble Actinide Histories:

Pu - Started at 1.3 ppb and peaked at 12.5 ppb with no apparent trend.
Am - Was < 0.8 ppb for entire test.
U - Started at 11,101 ppb and has steadily decreased to a low of 230 ppb on last sample taken (10/18/99).
Th - Was < 2.0 ppb for entire test.
Np - Was generally < 2 ppb for entire test.
Nd - Was < 4 ppb for entire test.

Other Analyses (nominal):

Typical pcH Range:	7.0-7.8
Fe Concentrations:	Started at average of about 80 ppm and ended with about an average of 20 ppm.
Other Analytes:	Ca 1,200 ppm K 25,000 ppm Mg 30,000 ppm Na 50,000 ppm Pb 8 ppm
TIC/TOC:	50/350 ppm
Particle Concentration:	4×10^{10} particles/Liter
Filter Paper-WDXRF:	No Pu or Fe in filters. This is not surprising because Pu concentrations were very low but Fe was actually quite high (20-80 ppm) during the test period.
Headspace Gas Content:	H_2 was 2.9 v/o from a nitrate concentration of 30,000 ppm.

D&D Observations): *No available data.*

Overall Assessment:

This Envirostone test had a very low Pu concentration for the entire test. U started at 11,101 ppb but steadily decreased during the entire test period. The high nitrate concentration resulted in a high N_2O concentration in the headspace. There was no filterable colloids containing Pu or Fe at a pcH of ~ 7.5.

Liter-Scale No. 21

Test Characteristics:

Waste: Envirostone
Solidified inorganic sludge
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 190.0 μg/g; Total Pu = 0.251 g
Am 24.75 μg/g; Total Am = 32.67 mg
Brine: Castile (2:1 brine/solid ratio)
Additives: Fe Mesh; U, Th, Np, and Nd

Soluble Actinide Histories: (5/1/95 – 11/9/99)

Pu - Generally less than 2 ppb, with occasional 8 ppb.
U - Began around 5,000 ppb, and slowly decreased to 750 ppb at the end of testing.
Np - Began at 5,000 ppb and quickly dropped to ~10 ppb after six months, and typically remained <10 ppb.
Am - Typically less than 1 ppb
Th and Nd - Typically less than 1 ppb.

Other Analyses (nominal):

Typical pcH Range: 7.5-8.1
Fe Concentrations: <0.1 ppm
Other Analytes: Ca 600 ppm
K 5,000 ppm
Mg 900 ppm
Na 100,000 ppm
TIC/TOC: 25/300 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: No Pu or actinide precipitates; 3 of 16 filters contained Fe; no Sr but high S in filters.
Headspace Gas Content: H_2 = 8 v/o; N_2O = 19 v/o; NO_3 = 32,000 ppm

D&D Observations (November 9, 1999):

Corrosion: No visible corrosion.
Brine: Clear with an orange tinge.
Bottom Solids: Loose solids.
Fe Mesh: No corrosion; black colored coating.

Overall Assessment:

LS 21 was one of the earliest test containers to be deactivated and decommissioned because it had become so difficult to sample. This was a Castile brine test with a brine to solid ratio of 2:1 as was L 19 and L 20. The pcH of this test ranged from 7.5 – 8.1 which was similar to L 19 and L 20. The brine was clear with an orange tinge and the bottom solids were loose with an orange tinge.

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The Fe mesh had a black coating and did not show signs of corrosion. There was essentially no solubilization of Pu, Am, Th, Nd (< 1 ppm) and U started at ~5000 ppb and decreased to ~750 ppb while Np began at about 5000 ppb and decreased to <10 ppb. There was no soluble Fe (< 1 ppm) detected in this test. There were no colloids or microprecipitates containing Pu or other actinides on filters. Fe was detected on only 3 filters at a low level. H_2 was relatively low at ~ 8 v/o but N_2O was high at ~ 19 v/o (NO_3 was at 32,000 ppm). Overall, this test showed essentially no solubilization of actinides or Fe and the Fe mesh was essentially untouched.

Liter-Scale No. 22

Test Characteristics:

Waste:	Envirostone 80-90 % $CaSO_4$ with 10-20% melamine-formaldehyde and 0.1% NH_4Cl
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 180 μg/g; Total Pu = 0.238 g Am 6.51 μg/g; Total Am = 8.59 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Nd, Th, U, Np

Soluble Actinide Histories: (5/8/95 – 2/22/99)

Pu -	<5 ppb except for one analyses
Am -	<1 ppb except one analyses of 1.4 ppb
U -	Started at 8822 ppb and decreased to ~1100 ppb where it remained for ~3 years and then decreased to 619 ppb.
Np -	Generally < 1 ppb.
Th -	Generally < 1 ppb.
Nd -	Generally < 5 ppb.

Other Analyses (nominal):

Typical pcH Range:	6.8 – 7.2
Fe Concentrations:	Generally 50 to 120 ppb and then down to 16 ppb on last analyses.
Other Analytes:	Ca 2,100 ppm K 26,000 ppm Mg 30,000 ppm Na 46,000 ppm
TIC/TOC:	35/460 ppm
Particle Concentration:	10^{10} to 10^{11} particles/Liter
Filter Paper-WDXRF:	Six of 15 filters had Pu and all filters had Fe. All filters had Sr and S. There seemed to be a collaboration between Pu and Sr.
Headspace Gas Content:	H_2 = 6.1 v/o; N_2O = < 39 v/o; O_2 = 0.15 v/o; NO_3 = 36,000 ppm; TOC = 480 ppm

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D&D Observations (1-24-01):

Corrosion:	No corrosion noted on SS fittings and feedthroughs; no corrosion around screen; screen had ~ ¾ - inch of gold colored sediment.
Brine:	Brine has much sludge and was gold colored but still a liquid with some clarity, but has a light brown color tending to gold.
Bottom Solids:	About 7 inches of a gold colored sludge or mud that was easily stirred.
Fe Mesh:	The Fe mesh was in 3 pieces within the plastic holder. The rinse water was avocado green. This implies a reducing condition and may have been the reason for the high Fe content throughout the test period. Also, the Fe in the filters can be explained from leaching of the Fe wire strands. After rinsing, the Fe mesh was black in color and did not seem to be corroded. The Fe wire strands did not seem to be corroded.

Overall Assessment:

LS-22 did not solubilize Pu (< 5 ppb) over the test period. U was solubilized to a certain extent but other actinides were not. Fe was solubilized during the entire test period at the 50 to 120 ppm level. The 5 micron sized filter papers picked up Fe in all the samples taken (15 each) and Pu at a low level was found in 6 of 15 filters. Both Pu and Fe were found in the 5 micron filters and not the 1 micron or 10 nm sized filters. The TOC at ~460 ppm was higher than most and the particle concentration at 10^{10} to 10^{11} was on the high side of average. There was no corrosion on the SS feedthroughs on the lid or the screen. There was no cemented solids but about 7 inches of loose solids with a consistency of mud. There was a green color around the Fe mesh that indicates some solubilization of Fe as ferrous chloride. The nitrate concentration that was ~ 3,600 ppm led to an N_2O concentration that was much lower or at about 6.1 v/o. The Fe mesh was black and did not appear to be corroded but the green coloration within the plastic holder, which indicates differently.

Liter-Scale No. 23

Test Characteristics:

Waste:	Envirostone 80 – 90 % $CaSO_4$ with 10-20 % melamine- formaldehyde and 0.1 % ammonium chloride. Solidified organic waste
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 380 μg/g; Total Pu = 0.502 g Am 9.55 μg/g; Total Am = 12.61 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd

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Soluble Actinide Histories: (5/8/95 – 3/1/99)

Pu -	<10 ppb except one result at 14 ppb. Generally < 2 ppb. No trend observed..
Am -	< 0.5 ppb entire test period.
U -	Started at 1767 ppb and increased to a peak of 6247 ppb after 2 months and then decreased steadily to a final result of 261 ppb.
Np -	Generally < 1 ppb except 7.2 and 1.7 ppb.
Th -	Generally < 1 ppb except 2.6 ppb. No trend observed.
Nd -	Generally < 5 ppb for test period. No trend observed.

Other Analyses (nominal):

Typical pcH Range:	7.0 – 7.4
Fe Concentrations:	10 to 102 ppm with an average of ~50ppm and a final at 3.2 ppm.
Other Analytes:	Ca ~2,700 ppm K ~28,000 ppm Mg ~36,000 ppm Na ~60,000 ppm Pb 3-12 ppm.
TIC/TOC:	30/480 ppm
Particle Concentration:	10^{10} to 10^{11} particles/Liter
Filter Paper-WDXRF:	Pu found in 6 of 12 filters. Fe was found at high levels in all 12 filters in the 5 micron filters and to a lesser extent in the 10 micron filters. Sr was found on 9 of 12 filters and correlation is made with the Pu filters..
H_2 Headspace Gas Content:	H_2 = 8.0 v/o; N_2O = 31.3 v/o; N_2 = 6.4 v/o; NO_3 was 30,000 ppm; TOC = 400 ppm.

D&D Observations (April 12, 2001):

Corrosion:	Fairly clear of corrosion, perhaps discoloration at SS feedthroughs.
Brine:	Gold colored brine pool about 6 inches in depth.
Screen:	No corrosion; thin coating; easy to remove.
Bottom Solids:	There was about 6 inches of loose solids that could be easily stirred. Solids are gold colored.
Fe Mesh:	The iron mesh was easily removed and totally exposed to brine pool. Fe wires were black colored and appeared to be in good shape.

Overall Assessment:

There was little solubilization of Pu (< 2 ppb) over the test period and Pu was found as colloid or microprecipitation on 6 of 12 filter papers. U was solubilized to a peak of 6,247 ppb after two months and gradually decreased to 261 ppb at the end of the test period. The other actinides did not solubilize. The concentration of Fe at pcH 7.0-7.4 in the Brine A was quite high (10 to 102 ppm) and all filters had Fe. Pu seemed to correlate with Sr on the filters. This was a high nitrate concentration test with NO_3 at 30,000 ppm and N_2O at 31.3 v/o. There was essentially no corrosion of the SS feedthroughs and the Fe wire was not impacted like most other Fe wire holders. The bottom solids were not cemented and quite loose and easily stirred.

Liter-Scale No. 24

Test Characteristics:

Waste: Envirostone
80 – 90 % $CaSO_4$ with 10-20 % melamine- formaldehyde and 0.1 % ammonium chloride.
Solidified organic sludge
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 231 μg/g; Total Pu = 0.305 g
Am 8.19 μg/g; Total Am = 10.8 mg
Brine: Castile Brine (2:1 brine/solid ratio)
Additives: Fe Mesh; Th, U, Np, and Nd

Soluble Actinide Histories: (5/8/95 – 2/2/99)

Pu - Generally <5 ppb with one result of 16 ppb.
Am - All results < 0.7 ppb.
U - Began at 1,575 ppb and varied between 1,500 and 2,000 ppb and then decreased slowly to 267 ppb.
Np - Started at 730 ppb and decreased to <5 ppb for the remainder of the test period.
Nd - < 1 ppb for test period.

Other Analyses (nominal):

Typical pcH Range: 7.6 – 7.9
Fe Concentrations: Generally <1 ppm with four analyses between 1 and 13 ppm.
Other Analytes: Ca ~800 ppm
K ~5,000 ppm
Mg ~2,000 ppm
Na ~90,000 ppm
Pb < 0.1 ppm until final 8 analyses showed 2-6 ppm.
TIC/TOC: 20/380 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Five of 14 filters showed just detectable Pu and all filters showed relatively high levels of precipitated or colloidal Fe in the 5 micron-sized filters.
H_2 Headspace Gas Content: 12.7 v/o H_2; 22.5 v/o N_2O; 25.0 v/o N_2; 0.02 v/o O_2; NO_3 was 32,000 ppm (this was the highest N_2 content of STTP)

D&D Observations (April 12, 2001):

Corrosion: Clear of corrosion except perceptible corrosion ring around the sampling port.
Brine: High turbidity with white chalky liquid that contained floating black specks. The color of the murky brine pool was yellow-olive drab.

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Bottom Solids: There was about 6 inches of a clay like mass that was loose on the top and hardened near the bottom. It was not cemented. There was a semi-gelatinous cohesive mass on the bottom of the screen.

Fe Mesh: The iron mesh plastic holder was full of a silt clay mass that could be washed off with water. After washing off the impacted solids, the Fe mesh was covered by a greenish-black deposit that was very heavy and the wire was somewhat corroded under the heavy coating.

Overall Assessment:

LS-24 was a Castile brine test at pcH 7.6 – 7.9 with a 2:1 brine to solid ratio in Envirostone. There was very limited solubilization of Pu (< 5ppb) and essentially no solubilization of Np, Th, Nd, and Am. U, as typical of Envirostone tests, had 1575 ppb in solution that slowly decreased to ~ 267 ppb at the end of the experiment. The soluble Fe concentration was < 1 ppm throughout the test. Although Pu was just barely detected in the brine as a soluble cation, 5 of 14 filters had low levels of Pu and all filters had low levels had Fe as colloids or microprecipitates.

The SS feedthroughs appeared not to be corroded but there was a perceptible corrosion ring around the sampling port. The screen was intact and not corroded. The Fe mesh holder was full of a silt-like material and after washing the Fe strands were covered with a greenish-black coating. There appeared to be corrosion of the Fe wire. This was a high nitrate (32,000 ppm) content in this test that yielded a high N_2O concentration in the headspace gas. H_2 was only 12.7 v/o but there must have been some radiolytic generation of N_2 at 25 v/o. There was about 6 inches of clay like mud that thickened as it approached the bottom.

Overall, there was essentially no solubilization of Pu and other actinides and any actinides and Fe that did solubilize were immediately precipitated. There was not much SS corrosion and the corrosion led to Fe precipitates that were identified in the filter paper samples.

Liter-Scale No. 25

Test Characteristics:

Waste:	Pyrochemical salts (Direct Oxide Reduction - DOR)
Total Waste Weight:	1320 g
Initial Actinide Content:	Pu 285 μg/g; Total Pu = 0.376 g Am 0.30 μg/g; Total Am 0.396 mg
Brine:	Brine A (2:1 Brine/Solid ratio)
Additives:	Fe Mesh: Nd, Th, U, Np

Soluble Actinide Histories: (5/8/95 – 12/6/99)

Pu - Started at 106 ppb and varied from 10 to 127 ppb for entire test period. Final result was 40 ppb but no trend was observed.

Am - Less than 1 ppb for entire test period.

U - Generally < 10 ppb for entire test period. No trend was observed.

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Np - Started low at 4.7 ppb and remained low for 7-8 months and increased steadily to 348 ppb and then began a slow decrease to 154 ppb at the end of the test period.
Th - Generally < 3 ppb; no trend observed.
Nd - Generally < 7 ppb; no trend observed.

Other Analyses (Nominal):

Typical pcH Range:	7.7 to 8.1
Fe Concentration:	Typically < 1 ppm with about 50% of results that varied from 1-20 ppm. The trend seemed to be towards < 1 ppm.
Other Analytes:	Ca ~80,000 ppm K 22,000 ppm Mg 22,000 ppm Na 8,000 ppm
TIC/TOC:	15/25 ppm
Particle Concentration:	10^{10} to 10^{11} particles/L
Filter Paper-WDXRF:	Pu was identified at a low level in 9 of 15 filters. No Fe was detected on any filter paper. There was high Sr and S identified on all filters. There was a correlation between Sr and Pu.
H_2 Headspace Gas Content:	H_2 = 13 v/o; O_2 = 0.08 v/o

D&D Observations (4/3/01):

Corrosion:	Green color of corrosion around SS feedthroughs.
Screen:	Corrosion around half of the o-ring; screen about 1/3 full of white crystals and sludge.
Brine:	Clear with much suspensions.
Bottom Solids:	Compacted solids ~ 5 inches in depth.
Fe Mesh:	Salt crystals all over plastic holder. Compacted salt in holder was a light blue.

Overall Assessment:

LS-25 was part of a set of Pyrochemical salt tests of LS-25, 26, and 27. Pyrochemical salt tests had much higher Pu loadings than other waste forms but LS-25 had the lowest Pu loading of the Pyrochemical salts. There was limited solubilization of Pu (10-127 ppb) in this Brine A test at a pcH range of 7.7 to 8.1. There was Fe solubilization at a low level during the test but no Fe was found in any filter paper. There was Pu at a low level in 9 of 15 filter papers so there was some colloidal species of Pu in the particle population. The lower Pu loading led to the lowest H_2 concentration in the Pyrochemical salt tests of 13 v/o. The H_2 generation rate can be related to the radiolytic effectiveness of the alpha activity.

There was evidence of corrosion on the SS feedthroughs and there was a green coloration that is a reduced form of Fe. The screen o-ring also had corrosion on half of the o-ring. The brine was rather clear but loaded with suspensions that settled. The Fe mesh showed some indication of dissolution based on the light blue color on the salts adjacent to the Fe mesh. This test seemed to have a reducing environment based on the color of the Fe compounds.

Liter-Scale No. 26

Test Characteristics:

Waste: Pyrochemical salts (Direct Oxide Reduction - DOR)
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 3075 µg/g; Total Pu = 4.06 g
Am 1.71 µg/g; Total Am 2.25 mg
Brine: Brine A (2:1 Brine/Solid ratio)
Additives: Fe Mesh: Nd, Th, U, Np
Other: None

Soluble Actinide Histories: (5/8/95 – 12/6/99)

Pu - Started at 42.9 ppb on 5/8/95 and increased to 70,000 ppb on 12/2/96 slowly decreasing to 3287 ppb at the end of the test (12/6/99). Pu (VI) was identified on 3/4/97 and was present until 8/24/98 (~ 1-1/2 years).

Am - Followed general trend of Pu up to 165 ppb on 12/2/96 and decreased to 9.9 ppb at end of test (12/6/99).
Other - Nd, Th, and Nd were less than 5 ppb and U was less than 15 ppb.

Other Analyses (Nominal):

Typical pcH Range: 7.6 to 8.2
Fe Concentration: Very low, 0.1 ppm generally with an occasional sample up to 3 ppm.
Other Analytes: Ca 100,000 ppm
K 21000 ppm
Mg 25,000 ppm
Na 11,000 ppm
TIC/TOC: 20/30 ppm
Particle Concentration: 10^{11} to 10^{12} particles/L
Filter Paper-WDXRF: Pu, Sr, and S correlate on the 5 micron filter paper data. Fe was not detected. Pu was identified in 5 micron filter papers but not in 1 micron or < 10µm filters. Ca was ~1000 to 5000 units.
H_2 Headspace Gas Content: ~73 v/o H_2.

D&D Observations (1/30/01):

Corrosion: Lid and SS fittings were corroded, the high H_2 gas content (73%) in the headspace might have had an influence on this.
Brine: Fairly clear, with a light yellow or straw color.
Bottom Solids: 3 to 3-1/2 inches uncemented solids.
Fe Mesh: Recovered; one spot with about a 4-cm diameter, was ~ 50% corroded with remainder of wire being essentially uncorroded. Black deposit on coating prevented corrosion of wire.

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Overall Assessment:

There appeared to be early corrosion of the Fe wire mesh in one spot. The Pyrochemical salt sludge and encrustations may have prevented free brine flow through Fe mesh plastic holder. The Fe mesh was impacted in the holder and developed a hard black coating that prevented further dissolution. Throughout the history of this test container all the Pyrochemical waste sludge was mostly available for exposure to the brine. Also, the soluble Fe concentrations were very low in this container. These two reasons could explain why Pu was so high in the container. Those two reasons could explain why Pu was so high in this container and the presence of Pu (VI) for such a long interval.

Nd, Th, Np, and U concentrations were generally less than 5 ppb and U was less than 15 ppb during the history of L26. Pu and Am were the only actinides that solubilized in this experiment. Because most of the 1320 grams of waste, including actinides, was available to the brine, radiolytic activity in the brine would be expected to be high for this experiment. The straw yellow color of the brine would indicate that Fe did not have a major influence in this test. This may also be the reason for the high Pu (VI) concentration in this test container. The particle concentration in L26 was relatively high.

The comminution of the Pyrochemical salt waste could have had a significant impact on the chemistry of this test because of the limited flow of brine to contact the Fe mesh. The percentage of Pu in the waste that solubilized in LS26 was as high as 0.5%, one of the highest in the STTP.

All the 5 micron sized filter papers (17 each) contained Pu as well as Sr and Sulfate, but no Fe was found in any filter papers regardless of size (5 micron, 1 micron, or <10μm). Apparently, there may be Pu colloids or microprecipitates associated with $SrSo_4$ or hydrated Pu, since Fe was not present as a filterable precipitate. The Pu was associated with microprecipitates larger than 5 micron but was not associated with precipitates in the 1 micron or <10μm range.

The H_2 gas content (~ 73 v/o) was very high for this experiment and there was no corrosion of the SS fittings; however, LS27 had much corrosion at a H_2 concentration of 65 v/o. Perhaps the major differences in the two containers is, the pcH for LS26 was 7.6 – 8.2 whereas the pcH for LS27 was 10.7 – 11.2.

Overall, this test had high concentrations of Pu and Am and very low concentrations of Nd, Th, Np, U, and Fe. The Fe mesh in the plastic container was essentially isolated from the brine by compaction of comminuted waste in the plastic holder. All the actinides were available to the brine because there was no cementation. This had to be an oxidizing environment.

Liter-Scale No. 27

Test Characteristics:

Waste:	Pyrochemical salts (DOR)
Total Waste Weight:	1320 g
Initial Actinide Content:	Pu 2585 µg/g; Total Pu = 3.41 g Am 1.18 µg/g; Total Am 1.56 mg
Brine:	Castile (2:1 Brine/Solid ratio)
Additives:	Fe Mesh: Nd, Th, U, Np
Other:	None

Soluble Actinide Histories:

Pu - Pu concentrations began at 47,673 ppb and peaked at 243,438 ppb on 10/30/95 and began a steady decrease to 13,390 ppb on 10/18/99. LS27 had the highest soluble concentration of any test container. Pu (VI) was not identified in LS27.

Am - Am concentration began at 147 ppb and peaked at 825 ppb on 10/30/95 (same as Pu) and then slowly decreased to 64 ppb on 10/18/99. Am concentrations followed the general trend of Pu concentrations.

U - U concentrations started at 33 ppb which was the lowest concentration of any of the other actinides or Nd. U concentrations increased to a high of 197 ppb on 5/6/96 and then started to decrease slowly to a final concentration of 50 ppb on 10/18/99.

Th - Th concentrations began relatively high for Th at 2842 ppb and increased to about 6000 ppb where it seemed to remain for about one year and then slowly decreased to a final concentration of 148 ppb on 10/18/99. LS27 had the highest long term concentrations of Th than any other STTP test container. LS25 and LS26 each had Th concentrations of < 5 ppb.

Np - Np concentrations started at 425 ppb and increased to about 1100 ppb on the next two sampling periods (6/12/95, 7/17/95) and then decreased to a final concentration of 68 ppb. Np concentrations seemed to increase in the presence of CO_2 in the pressurized tests but l27 did not have added CO_2.

Nd - Nd concentrations started at 122 ppb (5/8/95) and peaked at 5350 ppb on 10/30/95 which was the peak for Pu, U, Am, and Th (generally). Nd decreased similarly to Th, Pu, and Am to a final concentration of 167 ppb (10/18/99). LS27 had the highest concentrations of Nd than any other test container.

Other Analyses (Nominal):

Typical pcH Range:	10.7 to 11.2
Fe Concentration:	Fe concentrations ranged from 43 to 243 ppm and were generally in the 100 ppm level until 1/4/99 and the Fe decreased to a final concentration of 16 ppm (12/6/99).
Other Analytes:	Ca 80,000 ppm K 5000 ppm Mg < 10 ppm Na 44,000 ppm
Other:	Al, Ni, and Pb were generally less than concentrations
TIC/TOC:	10/50 ppm
Particle Concentration:	10^{11} to 10^{12} particles/L
Filter Paper-WDXRF:	There was relatively high Pu content on all filter papers analyzed (16 of 16). There was significantly high Sr and S content and no detectable Fe content on the filter papers. There were Pu colloids or microprecipitates but no Fe in this Castile brine experiment at pcH 10.7 to 11.2. This is surprising because there was soluble Fe in the brine most of the test.

H_2 Headspace Gas Content: 65 v/o H_2; O_2 = 4.8 v/o.

D&D Observations (1/30/01):

Corrosion:	There was severe corrosion on stainless steel fittings and feedthroughs.
Brine:	The main pool of brines was about 3 inches and was quite clear which is surprising because the sludge is green.
Bottom Solids:	There were no hardened or cemented solids. All the solids were loose and exposed to the brine. The solids in the screen were a pea soup consistency and green.
Fe Mesh:	The Fe mesh was totally recovered and did not appear to have dissolved. There was a blackish color around Fe mesh strands. The ends of the Fe mesh were shiny as if they had just been cut. The green color on the sludge above the screen shows that Fe dissolved from the top fittings and perhaps from the Fe mesh.

Overall Assessment:

LS27 was unique in that Pu, Am, Th, Np, and Nd were high on the initial sample.
All peak concentrations occurred about the same time and then decreased slowly until the end of the test. There was never any indication of Pu (VI) in LS27 which is not surprising because the green sludge shows that $FeCl_2 \cdot H_2O$ (reduced form of Fe) was present throughout the test. There was no solidified or cemented mass at the bottom of the test container and all the comminuted Pyrochemical salt waste was available to the brine, which may have been the reason for the very high actinide (except U) concentrations in this test container. The soluble Fe concentration was around 100 to 240 ppm early in the test and decreased to 20 to 100 ppm late in the test which indicated a depletion of soluble Fe with time.

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The green color on the sludge in the screen attests to the presence of Fe in the sludge but the clear color in the brine indicates that the Castile brine leached soluble Fe from the sludge at a slow rate at the very basic pcH (10.7 – 11.2). The effect of the high Fe on the nonsolidification of the Pyrochemical salt is not known but the low Mg content in this Castile brine may have been the reason for this. The high H_2 concentration in the headspace did not eliminate corrosion of the SS fittings. The Pu on the 5 micron filter papers and the centriprep filter papers (< 10 nm) showed that colloids or microprecipitates bearing Pu were present in the brine. The particle concentration was relatively high at 10^{11} to 10^{12} particles/liter. The absence of Fe at the 5 micron, 1 micron, and < 10 nm diameter filter papers was surprising because Fe was present as a soluble cation most of the test and perhaps the Fe was always in the Fe $^{2+}$ state rather than the more insoluble Fe^{3+} state. The high H_2 content (65%) attests to the high radiolysis rate of the brine but the reduced form of Fe in the sludge seemed to predominate in maintaining a relative low Eh. The peroxide or hypochlorite formed as a result of radiolysis could impact the Fe before the Pu. The Pu in the filter paper (5µ and < 10nm) was associated with Sr and sulfate in every case but not with Fe which was present as Fe^{2+}. This may be an important parameter to observe in other test containers.

The low magnesium content that could have led to the total availability of all the comminuted waste to the brine without cementation and the high radioactivity in the waste was probably the reason L27 had such high concentrations of all actinides. Radiolysis certainly had to have an impact on the chemistry but the oxidation of available soluble Fe^{2+} ion would use up the oxidation capacity of the radiolytically produced oxidants. The absence of Fe in the filter papers is evidence that Fe was being oxidized to Fe^{3+}, which is highly insoluble ferric hydroxide ($K_{sp} \sim 10^{-38}$) that could age and agglomerate into larger precipitates that would settle out and not be suspended as colloidal matter.

Liter-Scale No. 28 (Pressurized)

Test Characteristics:

Waste:	Pyrochemical Salts (DOR)
Total Waste Weight:	920 g
Initial Actinide Content:	Pu 11,530 µg/g; Total Pu = 10.607 g Am 1.35 µg/g; Total Am 1.242 mg
Brine:	Brine A (2:1 Brine/Solid ratio)
Additives:	Fe Mesh: Nd, Th, U, Np, 60 Bars (870 psig) of CO_2 pressure
Later Additives:	76.4 g of MgO added as slurry on 2/97.

Soluble Actinide Histories: (8/28/95)

Pu - Started at 5989 ppb and steadily increased to 90,942 ppb on 1/13/97. MgO was added on 2/97 which resulted in an increase in pcH to 7.70 from 4.48, and significant decrease of all actinides; Pu decreased to 18,097 ppb. After the addition of MgO and the initial reduction of Pu concentration, the Pu increased to a peak of 197,984 ppb on 9/21/98.

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Pu (VI) was identified in L28 on a sample taken 5/17/99. The total alpha activity increased from 1337 nCi/ml on 12/6/99 to 1683 nCi/ml on 5/15/01.

Am - Am started at 34.8 ppb and increased to 352 ppb prior to addition of MgO. After addition of MgO, the pcH increased from 4.48 to 7.70 and Am decreased to 40.1 ppb. Am increased to 392 ppb near the end of the test which was a level similar to that before the addition of MgO. Am followed the trend of Pu except at a much lower level. The total Am-241 activity increased from 19.3 nCi/ml on 12/6/99 to 152.5 nCi/ml on 5/15/01.

U - U started at 5,230 ppb and increased to 10,833 ppb on 1/13/97. After addition of MgO on 2/97 and the pcH increasing from 4.48 to 7.7, U decreased to 106 ppb and then increased to 4,520 ppb and the last analyses showed U at 668 ppb on 5/17/99.

Th - Th started 178 ppb and increased to 1359 ppb on 1/13/97. After the addition of MgO on 2/97 and an increase in pcH from 4.48 to 7.70, Th decreased to 36 ppb and then slowly increased to 531 ppb at the end of the test.

Np - Started at 3549 ppb and increased to 13,931 ppb on 1/13/97 and decreased to 166 ppb after addition of MgO on 2/97. Np increased to 2049 on 8/11/97 and had decreased to 744 ppb on 5/17/99.

Nd - Nd started at 15.4 ppb and increased to 31.5 ppb prior to addition of MgO. After addition of MgO and an increase of pcH from 4.48 to 7.70, Nd dropped to 5.3 ppb and then slowly increased to 57 ppb at end of the test.

Other Analyses (Nominal:)

Typical pcH Range: Prior to MgO: 4.48 – 5.35
After MgO: 5.03 – 7.70
Fe Concentration: Fe started at 19 ppm and increased to 165 ppm prior to MgO addition. After MgO addition, the pcH increased from 4.48 to 7.70 and the Fe decreased to 1.1 ppm and then increased to 50.8 ppb on 12/6/99.
NOTE: It is surprising that Pu (VI) was detected in LS-28 with all the Fe unless the Fe was in the form of Fe^{+3} or if soluble Fe was not available to the top portion of the brine.
Other Analytes: Ca 115,000 ppm
K 12,000 ppm
Mg 15,000 ppm
Na 4,000 ppm
Ni 300 ppm
TIC/TOC: 200/50 ppm
Particle Concentration: 1 x 10^{13} particles/L

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Filter Paper-WDXRF: Pu at rather high levels (29.6, 19.5, 57.1 μg/cm^2) was identified in 3 of 3 filters. Fe was identified in one filter. Sr was identified in all three filters.

H_2 Headspace Gas Content: Not analyzed.

D&D Observations (4/26/01):

Corrosion: There was no corrosion observed on feedthroughs.

Brine: The brine level was about ½ inch below the screen. The depth of the brine is about 2-1/2 inches. The brine is a cloudy and yellowish color liquid with suspensions.

Intermittent Level Solids: A very hard plug was found under the brine that essentially divided the test in two parts; one above the hard plug and one below the plug. The plug was very hard and was finally removed with a hammer and screwdriver point. The plug limited the communication between the top and bottom of the test container and could have been the reason that the chemistry of the upper brine was not long-termed. The plug probably formed when the MgO was added to the test container and consisted of sorel cement and other solidified masses that were very hard.

Bottom Solids: The bottom solids were very hard yellowish colored cement. A hammer and chisel were used to poke through the solids.

Fe Mesh: The Fe mesh was embedded in the bottom liquid, which had a oatmeal like consistency.

The Fe mesh holder was covered with a coarse layer of crucible shards that were discolored. The Fe mesh appeared to be nearly new and was mostly black covered with a thin dark coating.

Overall Assessment:

NOTE: An extended summary of the principal parameters of LS 28 is given in LA-UR-00-1606, "A Study of STTP Pyrochemical Salt Tests and Results Featuring Pu(VI)".

Liter-scale No. 28 was one of the most visible tests in the STTP because it contained such a high level of Pu, CO_2 pressure (870 psig), and added MgO and the fact that Pu (VI) was identified after the addition of MgO. The D&D showed that the MgO added to the test container immediately formed a hard solid, perhaps sorel cement, that isolated the top portion of brine from the bottom portion. This would have effectively allowed the top portion of soluble Pu and Am to form higher levels of radiolytic oxidants and oxidize soluble Pu to Pu(VI) at pcH 7.70.

The presence of high levels of soluble Pu in a test container pressurized with CO_2 gas at pcH 7.70 that dropped to pcH 5.03 (because of such a low volume of brine) after addition of MgO indicates that CO_2 was effective in solubilizing Pu and other actinides at pcH 4.48 and the addition of MgO only served to enhance the solubility and oxidative strength of the solution above the solid sorel cement mass. This finding strengthens the position that Pu(VI) will be found only in limited pockets in the WIPP.

Liter-Scale No. 29 (Pressurized)

Test Characteristics:

Waste: Pyrochemical salts (DOR)
Total Waste Weight: 920 g
Initial Actinide Content: Pu 4.715 µg/g; Total Pu = 4.338 g
Am 2.59 µg/g; Total Am = 2.38 mg
Brine: Brine A (2:1 brine/solid ratio)
Additives: Fe Mesh; Th, U, Np, and Nd
60 Bar (870 psig) of CO_2 pressure

Soluble Actinide Histories: (8/28/95 – 6/20/01)

Pu - Started at 161 ppb and increased to maximum of 8446 ppb on 8/11/97 and ended at 6865 ppm. The total alpha-activity of L29 increased from 360 nCi/ml on 9/20/98 to 1822 nCi/ml on 6/20/01.
Am - Started at 1.1 ppb and increased to ~ 37 ppb on 9/21/98. Am activity decreased from 9/21/98 (100 nCi/g) to ~ 50 nCi/g on 6/20/01.
U - Started at 1.1 ppb and increased to 4840 on 1/22/96 and then to 9513 on 9/21/98.
Th - Started at 2.8 ppb and increased to 377 on 9/21/98.
Np - Increased from 17.5 ppb(8/28/95) to 8179 ppb on 9/21/98.
Nd - Was less than 7 ppb for entire test.

Other Analyses (nominal):

Typical pcH Range: 4.73 – 5.68 (Acid side of neutral)
Fe Concentrations: Varied from 34 to 1468 ppm during test. This Fe concentration is very high.
Other Analytes: Ca 150,000 ppm
K 4,000 to 12,000 ppm
Mg 20,000 ppm
Na 2,000 ppm
TIC/TOC: 500/50 ppm
Particle Concentration: 3×10^{12} particles/Liter
Filter Paper-WDXRF: Pu in 3 of 4 filters; Fe on 2 of 4 filters. No Sr detected. Np and Th on one filter that had highest Pu (47.1).
H_2 Headspace Gas Content: No analyses.

D&D Observations (5/23/01):

Corrosion: No visible corrosion.
Brine: Fairly clear liquid with no suspensions.
Bottom solids: Dark muddy brown solids that had texture of sand. Part of material was hard and a portion was soft.
Fe mesh: Fe mesh was embedded in dark, muddy looking sludge. Fe mesh was coated with black thin coating. After washing, the coating was black to gray.

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Overall Assessment:

Liter-scale test container No. 29 was a Pyrochemical salt waste in Brine A and had ~870 psig CO_2 pressure placed on the headspace. The pcH started at 5.68 and decreased with time (8/28/95 – 9/21/98) to 4.73. Pu increased with time to a peak of 8446 ppb. There were 3 filters that had Pu but it did not appear to correlate with $SrSO_4$. The total alpha activity increased from 360 nCi/ml on 9/20/98 to 1822 on 6/20/01 during which no rotation was conducted on the drum. The Fe mesh did not appear to be corroded and had a black gray color. The particle concentration was relatively high at this pcH at ~ 3 x 10^{12} particles/liter. This test showed that even with 870 psig of CO_2 in a acid condition that actinides were not significantly solubilized.

Liter-Scale No. 30 (Pressurized)

Test Characteristics:

Waste:	Pyrochemical salts (DOR)
Total Waste Weight:	902 g
Initial Actinide Content:	Pu 2.185 μg/g; Total Pu = 2.010 g Am 2.59 μg/g; Total Am = 2.38 mg
Brine:	Castile brine (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd 60 Bar (870 psig) of CO_2 pressure

Soluble Actinide Histories: (8/28/95 – 6/20/01)

Pu -	Pu started at 2166 ppb and decreased to 1011 ppb. The total alpha-activity remained about the same from 9/20/98 (68 nCi/ml) to 6/20/01 (70 nCi/ml).
Am -	Am decreased from 20 ppb to 5.8 ppb during the test period.
U -	U decreased from 5663 ppb (8/28/95) to 2787 ppb (9/21/98).
Th -	Th started at 35 ppb and decreased to 32.9 ppb at end of test.
Np -	Np started at34.8 ppb and increased to 135 ppb during the test period.
Nd -	Nd started at 69 ppb and decreased to 6 ppb on 9/21/98.

Other Analyses (nominal):

Typical pcH Range:	5.9 – 6.6
Fe Concentrations:	Achieved a high of 1967 ppm on 1/22/96 which decreased to 9.2 ppm on 9/21/98.
Other Analytes:	Ca 30,000 ppm K 4,000 ppm Mg 20,000 ppm Na 22,000 ppm
TIC/TOC:	Coarse/Fine 700/80 ppm
Particle Concentration:	2 x 10^{11} particles/Liter
Filter Paper-WDXRF:	Pu in 3 of 3 filters; Fe in one filter. No Sr or Al detected. No other actinides.

H_2 Headspace Gas Content: No analyses.

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D&D Observations:

Corrosion:	No visible corrosion noted on lid or screen.
Brine:	Light gray to brown color with a consistency of oatmeal. Depth of brine pool was about 3 inches.
Bottom solids:	Very hard solid material with brown color.
Fe mesh:	Fe mesh in holder was embedded in a hard brown solid. The container had to be broken to retrieve the Fe mesh. The Fe mesh had a dark black color and did not appear to be corroded, however, the soluble Fe concentration was very high (1967 ppm) early in the test that rapidly decreased to 9.2 ppm near the end of the test. The color of the unwashed deposits on the mesh were red, yellow, and green.

Overall Assessment:

Liter-scale test container No. 30 was a Pyrochemical salt waste in Castile Brine with a pcH range of 9.5 – 6.6 under a CO_2 pressure of 60 Bars (870 psig).

Pu started at 2166 ppb and decreased to 1011 ppb. All other actinides decreased in concentration during the test except Np, which increased from 34.8 to 135 ppb. The total particle concentration was relatively low (~2 x 10^{11} particles/liter) which was surprising because the brine had an oatmeal like texture. Pu colloids or microprecipitates were found in all three of the filter papers analyzed but at relatively low levels. The Pu and other additives did not achieve high concentrations relative to other Pyrochemical salt tests.

Liter-Scale No. 31

Test Characteristics:

Waste:	Pyrochemical salt waste (O_2 Sparging)
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 612.5 μg/g; Total Pu = .809 g Am 0.49 μg/g; Total Am = 0.647 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd Bentonite – 120 g that was brine equilibrated

Soluble Actinide Histories:

Pu -	Began low <20 ppb for 2.5 years, then increased to 280 ppb for last sample (3/99).
U -	Began at 3,700 ppb and continued to decrease throughout the experiment, ending at a low of 500 ppb.
Np -	Began at 450 ppb then decreased to 120-200 ppb for the last 3 years of testing (9/96 – 3/99).

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Nd - Started at 71 ppb and slowly decreased to 6.4 ppb at end of test.
Other -Nd, Th, and Am were generally < 10 ppb during the test.

Other Analyses (nominal):

Typical pcH Range:	8.7 – 9.0
Fe Concentrations:	Very low at < 1 ppm
Other Analytes:	Ca 1,300 ppm K 50,000 ppm Mg 30,000 ppm Na 60,000 ppm
TIC/TOC:	35/25 ppm
Particle Concentration:	10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF:	There were 8 of 12 filters with Pu; 1 of 12 had Np; 4 of 12 had Th. This was one of the only tests that showed Th and Np on the filters.
Headspace Gas Content:	H_2 = ~ 33 v/o; O_2 ~ 0.80 v/o; N_2O ~ 0.5 v/o

D&D Observations (November 4, 1999): No data found.

Overall Assessment:

This Pyrochemical salt waste test with bentonite had a relatively low concentration of Pu and other actinides. The brine equilibrated bentonite may have had a role in maintaining low concentrations for Pu and all other actinides. Even though the Pu concentration was generally low but began a trend up to 275 ppb, the overall concentration was relatively low for Pyrochemical salt waste. There were 8 of 12 filters that had Pu colloids and 4 of 12 filters that had Th. The presence of Th in the test container was rather unique for the STTP. Fe was found on 3 filters but at very low levels. No Sr was found on the filter.

Liter-Scale No. 32

Test Characteristics:

Waste:	Pyrochemical salt waste (O_2 Sparging)
Total Waste Weight:	1,320 g
Initial Actinide Content:	Pu 3,105 μg/g; Total Pu = 4.10 g Am 2.21 μg/g; Total Am = 2.92 mg
Brine:	Brine A (2:1 brine/solid ratio)
Additives:	Fe Mesh; Th, U, Np, and Nd Bentonite – 120 g that was brine equilibrated

Soluble Actinide Histories: (5/15/95 – 3/8/99)

Pu - Started low <4 ppb, increased to 697 ppb after 16 months, then slowly decreased to a low of 158 ppb, reached at the end of sampling period.
Am - Started low (<0.1 ppb) and leveled off at 1-2 ppb after 16 months.
U - Began at a high of 3,173 ppb, and decreased to a low of 381 ppb at end of testing period.

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Np - Started at 161 ppb and slowly decreased to 65 ppb at end of testing period.
Nd - Started at 71 ppb and slowly decreased to 6.4 ppb at end of test.
Th - Started at 7.4 ppb and decreased to 1.3 ppb at end of testing period.

Other Analyses (nominal):

Typical pcH Range: 8.6 – 9.0
Fe Concentrations: Very low at < 1 ppm for most of test with 1 result of 1 ppm and another at 3 ppm.
Other Analytes: Ca 750 ppm
K 50,000 ppm
Mg 30,000 ppm
Na 60,000 ppm
Pb Up to 6.6 ppm and decreasing to 1.1 ppm
TIC/TOC: 30/30 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Pu at high level identified in 10 of 15 filter papers; Fe was identified in 5 of 15 filters; Sr was identified in the filters with highest Pu. S was in all filters.
Headspace Gas Content: H_2 = ~ 44.6 v/o; O_2 = 2.0 v/o

D&D Observations (December 15, 1999):

Corrosion: Lid had 3 areas of corrosion at SS feedthroughs. Screen was corroded with salt adhering to bottom.
Brine: Brine was fairly clear with some suspensions and had a pea soup consistency and color near bottom.
Bottom solids: Very hard cemented solid at bottom of test container.
Fe mesh: Was embedded under hardened solid and could not be located.

Overall Assessment:

LS-32 was a test with Brine A at a pcH of 8.6 – 9.0 (same as L 31) with added bentonite, a montmorillonite clay with colloidal silica. LS-32 had a relatively heavy loading of Pu (4.10 g) but none of the actinides achieved a high level of solubility (Pu max 697 ppb, Am max 2 ppb, U max 3173 ppb, Np 161 ppb, and <75 ppb for Th and Nd. The concentration of Fe was very low (<1 ppm) but the color of the brine suspensions may be from Fe. There was a significant cemented portion at the bottom of the test container that totally covered the Fe mesh. The particle concentration was low (10^9 to 10^{10} particles/liter) and the colloid-sized particles contained Pu and some Fe. There was evidence of corrosion in the SS feedthroughs on the lid of the container. The bentonite was effective in maintaining a relatively low actinide concentration. The headspace gas concentration of H_2 was ~45 v/o which is in agreement with the relatively high concentration of Pu.

Liter-Scale No. 33

Test Characteristics:
Waste: Pyrochemical salts (O_2 Sparging)
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 860 µg/g; Total Pu = 1.14 g
Am 0.83 µg/g; Total Am = 1.10 mg
Brine: Castile (2:1 brine/solid ratio)
Additives: Fe Mesh; Th, U, Np, and Nd
Bentonite – 120 g that was brine equilibrated

Soluble Actinide Histories:
Pu - Began low <20 ppb for one year, then increased to 130-190 ppb for remainder of test
Np - Began at 20-40 ppb for ~2 years, then decreased to 5 ppb for remainder of test
Other - Nd, Th, U, and Am were generally <5 ppb during the test

Other Analyses (nominal):
Typical pcH Range: 9.5-9.8
Fe Concentrations: < 0.1 ppm
Other Analytes: Ca 1,000 ppm
K 35,000 ppm
Mg 500 ppm
Na 100 ppm
TIC/TOC: 10/30 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Pu was detected as microprecipitates or colloids in 14 to 16 of the filter papers. Pu was associated with Sr on only three filter papers. Fe was associated with Pu on 6 filters. The Pu may be associated with bentonite on the other filter papers.
H_2 Headspace Gas Content: H_2 = 35 v/o; O_2 = 2.2 v/o

D&D Observations (1/30/01):
Corrosion: SS fittings and feedthroughs were corroded rather severely; upper ring on screen corroded and was weakened.
Brine: Milky white above screen with no evidence of floating suspensions; there was ~1/2 inch of gray sludge in screen; milky white brine below screen.
Bottom solids: No cemented or hardened solids at bottom of test container; mostly there was about 2 inches of uncemented suspension of Pyrochemical salts and bentonite and perhaps crucible shards.

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Fe mesh: None of the Fe mesh appeared to dissolve; the wire strands have a blackish color that is fairly thin. The cut ends of the Fe mesh were still shiny. There was apparently little contact of the Fe with the brine because the bentonite and salts packed the inside of the Fe mesh holder.

Overall Assessment:

There appeared to be no corrosion of the Fe wire in the Castile Brine at pcH 9.5-9.8. There was a black film or thin coating around the wire strands. The SS fittings and feedthroughs in the Ti metal lid were quite corroded in the headspace gas region. The Fe was precipitated and did not remain soluble as evidenced by <0.1 ppm concentration in the brine throughout the test. Overall, the bentonite appeared to be effective in maintaining a very low concentration of all soluble actinides throughout the life of the test.

Nd, Th, U, and Am were generally less than 5 ppb, and Np increased from 20 to 40 ppb initially, and then decreased to <5 ppb at the end of the test. Most of the waste including actinides was available to the brine, but the actinide concentrations remained very low and radiolysis was not effective in oxidizing Pu. The particle concentration was relatively low indicating that there was an agglomeration of colloids and fine particles. The comminution of the Pyrochemical salts and crucibles could have had a significant impact on the chemistry of this experiment. Bentonite, a Montmorillonite clay with colloidal silica, could have had a role in preventing the cementation of the Pyrochemical salts in Castile Brine, but the major role may have been the low Mg (500 ppm) because there was significant cementation in L32 with Brine A and a Mg content of ~ 30,000 ppm. The percentage of Pu solubilized in L33 was about $5x10^{-2}$%. The Pu filtered as microprecipitates or colloids were associated with Fe and Sr only at the larger concentrations. The Pu may have been associated with the bentonite. The rather high corrosion of the SS fittings and feedthroughs is interesting at a headspace gas concentration of ~35 v/o.

Liter-Scale No. 34

Test Characteristics:

Waste:	Pyrochemical salts (Direct oxide reduction)
Total Waste Weight:	880 g
Initial Actinide Content:	Pu 2325 μg/g; Total Pu = 2.05 g Am 3.06 μg/g; Total Am = 2.69 mg
Brine:	Brine A (3:1 Brine/Solid ratio)
Additives:	Fe Mesh; Nd, Th, U, Np, chelators, and 96.2 gm of $Ca(OH)_2$ Acetamide = 100 ppm Sodium Acetate = 139 ppm Ascorbic Acid = 101 ppm Trisodium Citrate Dihydrate = 154 ppm Oxalic Acid Dihydrate = 143 ppm; Ammonium Thiocyanate = 148 ppm

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Soluble Actinide Histories: (5/15/95 – 3/8/99)

Pu -	Started at 5.9 ppb and increased to 33 ppb after one year and varied from 10 to 50 ppb for the remainder of the test.
U -	Started at a peak of 776 ppb and has slowly decreased to a final concentration of 74 ppb.
Th -	Varied between 4.2 and 38.9 ppb during the test period until a final concentration of 11.1 ppb.
Np -	Started at 187 ppb and varied between 150 to 254 for the entire test period to a final concentration of 152 ppb. The trend seemed to decrease in concentration very slowly.
Nd -	Generally < 2 ppb throughout the test.

Other Analyses (nominal):

Typical pcH Range:	8.6 – 9.0
Fe Concentrations:	Generally < 2 ppm for the entire test.
Other Analytes:	Ca 9,000 ppm K 45,000 ppm Mg 24,000 Na 65,000 ppm Pb 0.1 to 6 ppm
TIC/TOC:	10/80 ppm
Particle Concentration:	10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF:	Essentially all filters contained Pu. No filters had Fe. No filter had Sr.
H_2 Headspace Gas Content:	H_2 = 28.6 v/o; O_2 = 0.66 v/o; N_2 = 2.2 v/o; N_2O = 1.1 v/o

D&D Observations (03/26/01):

Corrosion:	Sample port – Blue and brown colored corrosion spots at SS feedthroughs.
Screen:	Corrosion observed on o-ring around the top of the screen. Full of white solids. Salts in screen about 1/8-inch thick crystals. Very difficult to remove.
Brine:	Colorless with suspensions; 1 liter removed.
Bottom solids:	About 8 inches of solids of oatmeal consistency on top and very hard on the bottom. The solids totally encompassed the Fe mesh.
Fe mesh:	Could not remove the Fe mesh from the bottom solids, which were very hard.

Overall Assessment:

LS-34 was part of the test set of LS-34 (OS), LS-35 (DOR) and LS-36 (DOR). Chelators and $Ca(OH)_2$ were added to each test. LS-34 was a Brine A experiment with a Pu loading of 2.05 g in a 3:1 brine to solid ratio test. Chelators and 96.2 gm of $Ca(OH)_2$ were added to this test but not much solubilization of actinides took place as Pu was generally <30 ppb at the pcH range of 8.6-9.0. There was <2 ppm of Fe solubilization at any time during this test. LS-34 had historically been difficult to sample because the screen was loaded with crystals and particulate. Essentially all (11 of 13) filters contained Pu but no Fe or Sr was identified on any filter paper.

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There was corrosion on the SS penetrations on the Ti lid and the SS o-ring. The screen showed evidence of corrosion. The corrosion found on the lid and screen o-ring did not result in much soluble Fe or precipitated Fe. Overall, the actinides added to this Brine A test in the presence of chelators did not result in much solubilization. This is in sharp contrast to the drum-scale tests and LS-36 with added chelators, which showed much solubilization. Of course, LS-34 is an Oxygen Sparging waste (rich in Na and K chloride) rather than a DOR (rich in $CaCl_2$) experiment.

Liter-Scale No. 35

Test Characteristics:

Waste:	Pyrochemical salts (Direct oxide reduction)
Total Waste Weight:	880 g
Initial Actinide Content:	Pu 510 μg/g; Total Pu = 0.449 g Am 0.79 μg/g; Total Am = 0.07 mg
Brine:	Brine A (3:1 Brine/Solid ratio)
Additives:	Fe Mesh; Nd, Th, U, Np, chelators, $Ca(OH)_2$ Acetamide = 100 ppm Sodium Acetate = 139 ppm Asorbic Acid = 101 ppm Trisodium Citrate Dihydrate = 154 ppm Oxalic Acid Dihydrate = 143 ppm; Ammonium Thiocyanate = 148 ppm Calcium Hydroxide = 96.2 g

Soluble Actinide Histories: (5/15/95 – 3/8/99)

Pu - Began at 930 ppb and increased to a high of 1458 ppb after six months and very slowly tailed off to a final 86 ppb at the end of the test. Chelators in Brine A and Pyrochemical salts had a small influence in solubilizing Pu.

U - Followed the same trend as Pu. Started at 233 ppb and increased to 423 ppb and then slowly decreased to 53 ppb at the end of the test period.

Th - Started at 271 ppb and increased to 575 ppb after six months and then slowly decreased to 62 ppb at the end of the test period. Th was minimally solubilized by chelators in Brine A at pcH 8.2 – 8.3.

Np - Started at 436 ppb and peaked at 2308 ppb after about six months and very slowly decreased to 1260 ppb at the end of the test period.

Am - Followed the same trend as Pu but at a much lower level. Started at 9.7 ppb and peaked at 18.6 ppb and slowly decreased to < 1 ppb at the end of the test period.

Nd - Generally < 5 ppb throughout the test. No trend was observed.

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Other Analyses (nominal):

Typical pcH Range:	8.2 – 8.3
Fe Concentrations:	Generally < 1 ppm with nine results between 1 and 3 ppm.
Other Analytes:	Ca 86,000 ppm K 28,000 ppm Mg 23,000 Na 20,000 ppm
TIC/TOC:	15/60 ppm
Particle Concentration:	10^{10} to 10^{11} particles/Liter
Filter Paper-WDXRF:	Only 2 filters (5 micron sized) had just detectable Pu. There was no Fe on any of the filters. There was essentially no Sr (3 each) on the filters. Apparently, the chelators complexed the Pu and Fe in this test whereas LS-34 and LS-36 had significant Pu on most filter papers. Essentially none of the filters from LS-34, 35, and 36 had Fe.

H_2 Headspace Gas Content: H_2 = 20.9 v/o; O_2 = 0.07 v/o; N_2 = 1.7 v/o

D&D Observations (03/13/01):

Corrosion:	Sample port - Blue-black coloration/corrosion Level Probe - Blue-black coloration/corrosion with large white crystals Gauge port - No coloration/corrosion Screen - Blue around outer o-ring
Brine:	Color is murky beige with the consistency of oatmeal. We were only able to retrieve about 200 ml of thick solution.
Bottom solids:	There was a lot of solids and sludge to within 3 inches of the top of the screen. The solids were voluminous and totally covered the Fe mesh but were not cemented.
Fe mesh:	The inside of the plastic holder was full of solids and salts and comminuted Pyrochemical salts. The material around the Fe mesh was a greenish-blue paste. There were blue colored salts in the holder. The Fe mesh did not seem corroded and was coated with a blue-black colored coating.

Overall Assessment:

LS-35 was a Castile brine test as part of a set of LS-34 (OS), LS-35 (DOR) and LS-36 (DOR) with added chelators and $Ca(OH)_2$. The pcH range of 8.2 to 8.3 was the least basic of this set (LS-34 8.7-8.9 and LS-36 11.0-11.4). Although, LS-34 had a cemented portion that covered the Fe mesh and LS-36 had ~ ½-inch of a cemented solid block, LS-35 had voluminous solids that was not cemented. LS-35 was unique in the greenish-blue coloration/corrosion on the three SS feedthroughs and the metal o-ring around the screen. There was little solution (~200 ml) retrievable from the main brine pool. There was a greenish-black color around the Fe mesh. The Fe mesh did not appear to be corroded but the vivid green-black color around the mesh attested to the solubilization of the Fe strands.

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There was minimal Pu solubility in LS-35 and the added chelators did not solubilize much Fe or other actinides. This is in stark contrast to the drum-scale tests, which showed much solubilization of all actinides. There was minimal solubilization of Fe (1-3 ppm) and only 2 filters showed a low level of Pu. The H_2 in the headspace was ~ 21 % and CO_2 was not detectable from the added chelators that resulted in a rather low TOC of 60 ppm.

Liter-Scale No. 36

Test Characteristics:

Waste: Pyrochemical salts (Direct oxide reduction)
Total Waste Weight: 880 g
Initial Actinide Content: Pu 12,575 μg/g; Total Pu = 11.07 g
Am 5.61 μg/g; Total Am = 4.94.mg
Brine: Castile (3:1 Brine/Solid ratio)
Additives: Fe Mesh; Nd, Th, U, Np
Chelators: Acetamide = 100 ppm; sodium acetate = 139 ppm; ascorbic acid = 101 ppm; trisodium citrate dihydrate = 154 ppm; oxalic acid dihydrate = 143 ppm;
ammonium thiocyanate = 148 ppm
Calcium hydroxide (96.2 gm)

Soluble Actinide Histories: (5/15/95 – 3/8/99)

Pu - Began very high 20,000 ppb and continued decreasing until a low of 700 ppb was reached in January 1999. Final Pu concentration was 1439 ppb.
U - Began at a high of 300 ppb, decreased to < 5 ppb by 3/8/99.
Th - Began at a high of 6,000 ppb, decreasing to final concentration of 53 ppb on 3/8/99.
Np - Began at 670 ppb and continued decreasing to a final concentration of 17 ppb on 3/8/99.
Am - Started at a high of 75-90 ppb, and decreased to a final concentration of 6.7 ppb on 3/8/99.
Nd - Started at a high around 15-20 ppb, decreasing to a low of 1-3 ppb on 3/8/99.

Other Analyses (nominal):

Typical pcH Range: 11.0-11.4
Fe Concentrations: Ranged from 50 ppm to 100 ppm during most of the test and ended up at 17 ppm.
Other Analytes: Ca 66,000 ppm
K 5,500 ppm
Mg less than undetectable
Na 57,000 ppm

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TIC/TOC: 10/85 ppm
Particle Concentration: 10^{10} to 10^{11} particles/Liter
Filter Paper-WDXRF: All 16 filters had relatively high Pu; one filter which had the highest Pu (315) also had Np and Th; Fe was not found on most filter papers and only two had Fe. Fourteen filters had Sr and S and correlated to high Pu. Fe did not correlate to Pu at this pcH.
H_2 Headspace Gas Content: H_2 = 70 v/o; O_2 = 15 v/o (the highest in the STTP); N_2 = 0.2
The high O_2 was due to radiolysis rather than air in-leakage.

D&D Observations (11/29/00):

Corrosion: Sample port was nearly plugged with corrosion products. There was considerable corrosion on and around all SS feedthroughs.
Brine: Brine was a greenish-gray liquid that was thickened near the bottom of the test container with suspended material.
Bottom solids: There was 3 or 4 inches of loose solids that were gray in color and appeared as gravel. Below this muck was about ½" of cemented solids that nearly encompassed the wire mesh.
Fe mesh: The plastic holder that contained the mesh was embedded in about ½" of cemented solid. Only one half of the mesh could be removed from the plastic holder. The Fe mesh appeared to not be corroded and covered with white deposits that upon washing revealed a hard black coating.

Overall Assessment:

LS 36 was a Castile Brine test with a relatively basic pcH (11.0 – 11.4) that had added chelators. The effect of the chelators was much more pronounced in LS 36 for all actinides and especially Pu and Am at the basic pcH. This pcH was effective at precipitating Mg and perhaps some Ca. This test had the greatest mass of Pu in the STTP. The colloidal particle concentration for this test was rather high (10^{10} to a maximum of 10^{12} particles per liter) and was identified in both the 5 micron filters and the centriprep or < 10 nm filters. The concentration of Pu and Am was high for most of the test period but decreased with time. The chelators were effective in maintaining a high Fe concentration most of the test period. It was surprising that there was so few (two each) filters that had Fe. All filters contained Pu to high levels and the Pu correlated with Sr and S. The Pu could have been entrained with $SrSO_4$ at this pcH and not with Fe. The Fe concentration throughout the test should have maintained a reducing environment unless the Fe was oxidized and precipitated as $Fe(OH)_3$ which has a much lower K_{sp} than $Fe(OH)_2$. The SS feedthroughs were severely corroded in the headspace which had an O_2 content of ~ 15 v/o, highest in the STTP. However, the Fe mesh did not appear to be corroded with a black coating on the surface of the Fe wire strands.

There was a cemented solid block about ½ - inch thick at the bottom of the test container that embedded about half the plastic Fe mesh holder. This was rather surprising because the soluble Mg content was less than detectable for the entire test period.

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The cemented solid could have been immediately formed by the available but limited Mg content at the beginning of the test to form a sorel cement solid. Overall, this was an experiment with many variables that only begins to make sense in the context of all the other experiments. Pu and Am are certainly solubilized by the chelators but other factors tend to reduce the soluble concentration over a long time period. The pcH of 11.0 – 11.4 certainly had a strong influence on the chemistry of this test. The Ca should have been higher because of the addition of 96 g $Ca(OH)_2$ to this test.

Liter-Scale No. 37

Test Characteristics:

Waste: Pyrochemical salts (Direct oxide reduction)
Total Waste Weight: 1320 g
Initial Actinide Content: Pu 3,295µg/g; Total Pu = 4.35 g
Am 0.83 µg/g; Total Am = 1.1 mg
Brine: Brine A (2:1 Brine/Solid ratio)
Additives: No Fe mesh added; no Nd added; 75 mg of Am-241 added as soluble salt, equivalent to ~ 37,000 ppb

Soluble Actinide Histories: (5/15/95 – 3/15/99)

Pu - Began low, 45 ppb, decreasing to a low of 20 ppb by September 1996 through February 1997, then increased to a high of 380 ppb by January 1999.
Other - Nd, Th, Np, U, and Am were <5 ppb during the experiment and showed no signs of a trend.

Other Analyses (nominal):

Typical pcH Range: 7.6 – 8.3
Fe Concentrations: < 10 ppm for part of the test and < 2 ppm for most of the test period.
Other Analytes: Ca 150,000 ppm
K 30,000 ppm
Mg 27,000 ppm
Na 7,000 ppm
TIC/TOC: 15/25 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Low levels of Pu found in last 8 filters; low levels of Fe identified in 6 of 8 filters; Sr and S identified on all high Pu filters.
H_2 Headspace Gas Content: H_2 = ~ 50 v/o; O_2 = ~ 4.7 v/o

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D&D Observations (12/06/00):

Corrosion: SS fittings and feedthroughs were corroded; level probe fell off but was shiny. Black scale could have prevented sampling through sample port. There was much salt on the lid. Greenish colored gel around o-ring.

Brine: Clear with tan-colored fines; many crystals throughout.

Bottom solids: Compacted silt/clay at bottom that yielded to a screwdriver. Compacted solids were at an angle from ~ 1 to 4 inches at a slant.

Fe mesh: No Fe mesh.

Overall Assessment:

LS-37 was a DOR Pyrochemical salt test in Brine A at pcH 7.6 – 8.3 and had 75 mg (37,000 ppb) of Am-241 added as a soluble salt. There was no Fe mesh added to this test but there was a persistent low level of Fe (< 2 ppm) throughout the test period. Pu was stable in the range of 20-40 ppb until 3/9/98 and increased to 200-400 ppb the last 5 or 6 samples. All other actinides including Am-241 were generally < 2 ppb. The Am-241 added as a soluble salt precipitated immediately and settled out at the bottom of the test container. There was a relatively low concentration of colloids or microprecipitates (10^9 to 10^{10}) and on the last 8 filters showed Pu. The Pu appeared to be associated with Sr rather than Fe. The greenish gel near the upper o-ring of the screen attests to the presence of $Fe(Cl)_2$ and may have been the source of Fe during the test. The stainless steel feedthroughs in the headspace showed signs of corrosion. The headspace gas was ~ 50 v/o with O_2 at about 4.7 v/o.

Liter-Scale No. 38

Test Characteristics:

Waste:	Pyrochemical salts (O_2 Sparging)
Total Waste Weight:	1320 g
Initial Actinide Content:	Pu 2045 μg/g; Total Pu = 2.736 g Am 5.55 μg/g; Total Am 7.43 mg
Brine:	Brine A (2:1 Brine/Solid ratio)
Additives:	75 mg of Am-241 added as a soluble salt is equivalent to 37,000 ppb assuming 2000 ml; no Fe mesh added; no Nd added.

Soluble Actinide Histories: (5/95 – 3/99)

Pu - Was low, vacillating during the time of testing from 3-20 ppb with an average of about 10 ppb.

Am - Was < 1 ppb for the entire test which is surprising because 75 mg of soluble ^{241}Am was added to this test container.

Other – Th, Np, U, and Am remained ≤ 4 ppb during the test; Nd was not added.

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Other Analyses (Nominal):

Typical pcH Range: 7.5 – 8.1
Fe Concentration: < 1.0 ppm
Other Analytes: Ca 76,000 ppm
K 40,000 ppm
Mg 30,000 ppm
Na 24,000 ppm
TIC/TOC: 15/35 ppm
Particle Concentration: 10^9 to 10^{10} particles/L
Filter Paper-WDXRF: There was no Pu, Fe, or Sr found on filter papers.
H_2 Headspace Gas Content: 51.3 v/o H_2; O_2 = 8.7 v/o

D&D Observations (2/6/01):

Corrosion: SS fittings and feedthroughs had light colored crystals on surfaces. Crystals also on level probe.
Brine: Brine is color of tea or light coffee.
Bottom Solids: Approximately ¼ inch of yellowish-brown fines on top of very hard or cemented mass.
Fe Mesh: No Fe mesh was added to this test container.

Overall Assessment:

LS38 was a Pyrochemical salt test in Brine A. There was added ^{241}Am (75 mg) which precipitated immediately in the brine pcH 7.5 – 8.1. There was no soluble Fe over 1 ppm in the entire period of the test (5/95 – 3/99). Neodymium and Fe mesh were not added to the test. Thorium, uranium, and Np were all essentially < 1 ppb for the entire test. There was no Pu detected on the filter papers (5 μ, 1 μ, and < 10 nm), nor Fe or Sr. The precipitated Pu and Am were present as precipitates on top of a cemented solid at the bottom or was incorporated into the solid mass. It may be that the Pu and Am once precipitated was incorporated into the cemented mass which would have depleted the available inventory of 2.74 g of Pu and 7.43 mg of ^{241}Am. The 75 mg of ^{241}Am added to the 7.43 mg already present in the waste gave a total available mass of 82.43 mg of ^{241}Am . The 75 mg of Am was added as soluble chloride salt. The theoretical concentration of ^{241}Am assuming 2 liters of brine and 100% solubility would have been 41,215 ppb. The average Am concentration was less than 1 ppb or 2.4 x 10^{-3} %. The percentage of Pu that dissolved relative to what was available in the 1320 g of waste was 7.0 x 10^{-4} %. The precipitated Pu and Am resulted in a radiolytically generated hydrogen content of ~ 51.3 v/o and O_2 at 8.7 v/o.

LS-38 in Brine A showed no Pu in the filters while LS-39 in Castile Brine showed Pu in essentially all filters. There appeared to be greater colloids containing Pu in LS-39 than LS-38 but the particles per liter were about the same.

Liter-Scale No. 39

Test Characteristics:

Waste: Pyrochemical Salts (O_2 Sparging)
Total Waste Weight: 1,320 g
Initial Actinide Content: Pu 3350 μg/g; Total Pu = 4.42 g
Am 8.7 μg/g; Total Am = 11.5 mg
Brine: Castile (2:1 Brine/Solid ratio)
Additives: Th, U, Np (No Nd and no Fe mesh) Am-241 added as 75 mg soluble salt; equivalent to 37,000 ppb at 2000 ml.

Soluble Actinide Histories: (5/95- 3/99)

Pu - Began low, 14 ppb, and then increased to 2,600 ppb after 2.5 years, and ended at ~2,000 ppb
Am - Started at <0.4 ppb and slowly increased to 18 ppb during the test; this is a significant increase for Am-241.
U - Started at 470 and decreased to 30 ppb
Np - Started at 50 ppb and decreased to 6 ppb
Th - Was <1 ppb during the test
Nd - Not added

Other Analyses (nominal):

Typical pcH Range: 9.4-9.9
Fe Concentrations: <1 ppm for entire test, no Fe mesh added
Other Analytes: Ca 6,700 ppm
K 7,000 ppm
Mg 2,000 ppm
Na 70,000 ppm
TIC/TOC: 10/30 ppm
Particle Concentration: 10^9 to 10^{10} particles/Liter
Filter Paper-WDXRF: Pu filtered in filter papers was rather high in mass and in 13 out of 14 filter papers. No Fe was associated with the Pu. Sr was associated with the high level precipitates.
H_2 Headspace Gas Content: ~46 v/o; O_2 at 11.9 v/o (this is high for O_2).

D&D Observations (11-15-00):

Corrosion: SS fittings were corroded, but level probe was clean; rust colored deposits (~1 mm thick) surrounded the fittings. Screen impacted with brown scale.
Brine: A pale brownish-gray colored liquid that was not viscous. The liquid was opaque.
Bottom Solids: There was a cemented solid at the bottom of the test container that was at a slant (~2" to 1" from the bottom). There was a pasty sludge ~1-1/2 inch depth above a hard or cemented solid.
Fe mesh: None added.

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Overall Assessment:

No Fe mesh added to this test container, and the soluble Fe concentration was less than 1 ppm for the entire test. The addition of 75 mg of ^{241}Am in soluble form did not seem to increase the concentration of Am until after 2-3 years into the test and Am increased from less than 1 ppb to ~18 ppb. The inventory of Am was about 86.6 mg or a concentration of ~ 43,300 ppb assuming 100% dissolution. However, the overall solubility of actinides in L-39 was very low compared to the inventory available to the brine. The percentage of Pu that solubilized relative to what was available in the 1,320 g of waste (4.42 g) was about $8x10^{-2}$ %. The presence of Pu in all > 5 micron filters after 11/13/95 verifies that Pu colloids or microprecipitates were present most of the test period. The pcH range 9.4 – 9.9 apparently precipitated the Pu in a form not associated with Fe since Fe was not in the filters. Sr was associated with the filters with the highest Pu content.

The Am was added as a soluble salt and immediately precipitated and was less than 1 ppb for about 6 months. The precipitated Pu and Am resulted in a radiolytically generated hydrogen concentration of ~ 46 v/o and an O_2 of 11.9 v/o, the second highest in the STTP. LS 36 was the highest.

There was a cemented solid at the bottom of the test container that was slanted from a high of ~ 2 inches to about 1 inch. There was a pasty sludge of ~ 1 ½ inches above the cemented solid.

The Pu and Am had leveled off at around 2,000 ppb for Pu and 18 ppb for Am. This was an increase for both actinides from the initiation of the experiment. The color of the brine (pale brownish-gray) has been an indication that this was not a reduced environment experiment in contrast to LS 37.

The identification of Pu in most of the filters was interesting relative to LS-38 which showed no Pu.

IV. (b) Deactivation and Decommission (D&D) of Test Containers

Plan for Deactivating and Decommissioning the Actinide Source-Term Waste Test Program

Goal:
To deactivate and decommission (D&D) the Actinide Source-Term Waste Test Program (STTP) experiments within one year, according to facility, NMT-Division, LANL (Los Alamos National Laboratory), and DOE (Department of Energy) regulations. The STTP experiment is located in Wing 9, of the CMR (Chemistry & Metallurgy Research) Building, housed in two environmental enclosures within rooms 9010A and 9010B. The CMR is a Nuclear Facility under NMT (Nuclear Materials & Technology) Division management. All safety protocols must be incorporated into the D&D process.

Description of STTP:
The STTP is an experimental program conducted by Los Alamos National Laboratory for the Department of Energy, Carlsbad Area Office (CAO). The STTP was implemented in 1995 and has been maintained for five and one-half years. The STTP is a dynamic test program, designed to:

1. Provide time sequential quantitative measurements of mobile actinide concentrations in synthetic WIPP (Waste Isolation Pilot Plant) brines that have been in continual contact with actual TRU (Transuranic) wastes for over five years;
2. Establish the influence of Salado type brine (Brine A) and Castile brine on the chemistry and concentration of mobile actinides; and
3. Allow for comparison with the hypotheses of actinide solubility models developed from laboratory tests and actinide literature.

The STTP consists of 39 liter-scale test containers and 15 drum-scale test containers. The 39 liter-scale test containers are configured as follows:

12 Portland cement containers
12 Envirostone containers; and
15 Pyrochemical salt containers.

The drum containers were divided as follows:

12 heterogeneous TRU wastes; and
3 massive metal TRU wastes.

Included in the liter-scale tests are 6 test containers that are much heavier duty and are pressurized to 60 bars (870 psig) with CO_2. Three of these contain Portland cement waste and three are Pyrochemical salt waste.

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All STTP test containers have added soluble ^{232}Th, ^{238}U, and ^{237}Np. Six liter-scale containers have added ^{241}Am. All test containers have added Fe mesh, which should be observed and examined as part of the D&D process. Most STTP containers were fabricated from titanium metal and have stainless steel hardware affixed to the lids.

D&D Preparatory Activities:

- Establish D&D process and extent of D&D including/not including enclosures.
- Assure completion of CMR Nuclear Facility Authorization Basis Document, which includes Basis for Interim Operations (BIO).
- Initiate notification to the New Mexico Environmental Department through DOE-LAAO (Los Alamos Area Office) that D&D process will be implemented.
- Assure continuation of required EPA and RCRA documentation from daily inspections in RCRA interim storage area.
- Initiate documentation to close-out STTP as a Permitted Interim Status Storage Area
- Assure compliance with STTP Environmental Assessment Document for close out of STTP.
- Develop a Closure Plan
- Complete Hazards Analysis for D&D Operations in CMR
- Develop SOP or Work Instruction According to NMT Division Guidelines.
- Complete Hazard Control Plan (HCP) for the STTP D&D process for both liter-scale and drum-scale operations.
- Obtain approval for fabrication of any new equipment and installation into facility for the D&D process
- Assure any new equipment has passed Swagelok Testing according to NMT procedures.
- Develop path forward plan for disposal of STTP wastes generated by the D&D process.
- Develop a Transuranic Waste Interface Document (TWID)

D&D Process:
STTP Liter-scale Experiment:

- Brine from liter-scale test containers (35-50 liters)
- TRU waste brine
- Mixed TRU waste brine
- Low level brine waste
- Low level mixed waste brine
- Hardware from lid on liter-scale test containers
- Pressure relief tubing and hardware connected to facility ventilation system (Facility interface contractor maybe required)
- Rotators for liter-scale test containers
- Rotators for pressurized liter-scale test containers
- Brine sampling hardware for liter-scale containers
- Headspace gas sampling hardware and apparatus
- Disassembly and disposal of 40 temperature probes from liter-scale test containers

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- Continuous Air Monitors (CAM) disposal and/or reuse
- Disassembly of hard-piped Fixed Air Sample System (Facility interface to vacuum system, contractor maybe required)
- Eye-wash station deactivation and /or disassembly
- D&D of equipment and instrumentation to be re-used rather than going through disposal
- Packaging of STTP wastes according to LANL and NMT-Division waste packaging protocols and approved by waste packaging specialists
- Documentation of all waste packaging activities
- Assuring accountability of nuclear material in STTP test containers is transferred from STTP to waste account
- Decontaminate enclosure for transfer to facility or D&D and dispose of enclosure. For D&D and disposal operation obtain contractor to conduct D&D, which will include:
- Enclosure ventilation system
- Pumps and filtration system
- Pressure relief filtration system
- Electrical system
- Lighting system
- Enclosure walls
- Disconnecting utility system from facility
- Disconnecting telephone and emergency response system

STTP Drum-Scale Experiment:

- Brine from Drum-scale tests (750-850 gallons or 2,800-3,200 liters)
- TRU waste brine
- Mixed TRU waste brine (includes F-listed and D-listed substances)
- Low level waste brine
- Low level mixed waste brine (includes F-listed and D-listed materials)
- Fabrication of equipment to D&D 65-gallon all-titanium drums weighing about 800 lbs (360 kg)
- Obtain approval for fabricating and installing equipment in enclosure for D&D process on drums
- Determine need for contractor to install heavy-duty equipment for D&D operation
- Assure any new equipment has passed Swagelok Testing according to NMT procedures
- Hardware from STTP drums
- Rotators for drums
- Disassemble drum connections to facility utilities and dispose
- Disassemble drum-scale pressure relief tubing and hardware connected to Facility ventilation system (Facility interface contractor maybe required)

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- Brine sampling hardware for drum-scale containers, disposal
- Headspace gas sampling hardware and apparatus , disposal
- Disassembly and disposal of 15 temperature probes from drum-scale test containers
- Disconnect Continuous Air Monitors (CAMs) and dispose or decontaminate for reuse
- Disassembly of hard-piped Fixed Air Sample System (Facility interface to vacuum system, contractor maybe required)
- Eye-wash station deactivation and /or disassembly
- D&D of equipment and instrumentation to be re-used rather than going through disposal
- Packaging of STTP wastes according to LANL and NMT-Division waste packaging protocols and approved by waste packaging specialists
- Documentation of all waste packaging activities
- Assuring accountability of nuclear material in STTP test containers is transferred from STTP to waste account
- Decontaminate enclosure for transfer to facility or D&D and dispose of enclosure. For D&D and disposal operation obtain contractor to conduct D&D, which will include:
- Enclosure ventilation system
- Pumps and filtration system
- Pressure relief filtration system
- Electrical system
- Lighting system
- Enclosure walls
- Disconnecting utility system from facility
- Disconnecting telephone and emergency response system

Process for D&D of Drums from STTP Drum-Scale Experiment:

Several different plans were developed to D&D the drum-scale tests. To complete the D&D of the drum-scale test containers within the budget projected for this work effort, a plan was required that did not necessitate opening the lid of the drum in a glovebox environment. Of the several work plans that were developed the most straightforward and economical was not to open the drum lid but to solidify the ~50 gallons of brine by adding AQUASORBE 22-12 to the drum. Brine was sampled from several drums to establish the ratio of AQUASORBE to brine that was needed to completely solidify the brine within a 65-gal test container. The ration established for Brine A and Castile Brine was tested on two cold drums with added non-radioactive surrogate wastes. A large funnel with a wide opening ball valve was used to add the AQUASORBE. It was soon learned that the waste floating in the brine impeded the flow of adsorbent and so some of the brine from each drum was pumped out of the drum into a plastic bag contained in a second drum. After pumping out a portion of brine, AQUASORBE 22-12 was added to the drum, which was now about half full.

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The AQUASORBE then flowed unimpeded into the partially emptied drum and the brine that was initially pumped out was pumped back into the drum. Any excess brine was adsorbed in the bag and was disposed with the 65-gal drum containing the adsorbed brine in a standard waste box. This process was very successful in allowing disposal of the 65-gal drum and any excess brine that was adsorbed. We estimated that this process saved the project about $1-2 million. However, visual observation of the waste, additives, or the Fe mesh-contained vessels was not made. All 15 drum-scale test containers were processed through this D&D procedure without spread of contamination. Indeed there was not a single contamination incident in the entire STTP D&D process.

CMR Analytical Laboratories:

- D&D of laboratories dedicated to STTP D&D liter-scale operation
- D&D of hoods dedicated to STTP D&D activities
- D&D of analytical instrumentation dedicated to STTP analyses

Analytical Support Required for D&D of STTP:

- Radiochemistry of brine required for disposal
- pcH of brine required for disposal
- Analyses of RCRA elements required for disposal
- Analyses of actinide elements required for final disposal
- X-ray analyses of select materials may be required for disposal
- Radiochemistry required for safety examination of Fe mesh required for programmatic reasons
- Examination of unexpected crystals, residues, and salts required for programmatic reasons
- Visual observation of all liter-scale D&D efforts will be conducted (Management Safety Walk-Around required by Division Management)

Current Waste Recharge Rates at LANL TA-54

Waste Type	Dollars/Volume
Hazardous Waste (Non-DP)	11.00 per kg
Solid LLW Non-Compactible (non-DP)	2,486 per m^3
Solid LLW Compactible (non-DP)	1,250 per m^3
Mixed LLW (non-DP)	88,305 per m^3
TRU Waste (non-DP)	58,000 per m^3

Estimated Volumes for Liter-Scales:

39 liter-scale test containers	1 m^3
Solidified brine @ 10% efficiency	0.3 m^3
Other hardware	0.7 m^3

Estimated Volumes for Drum-Scales:

15 drum-scale test containers @ 0.25 m3 each	3.75 m^3
Brine to be shipped to outside contractor	
Other hardware	1.25 m^3

Estimated Waste Volume Cost*:

Liter Scale	$2\ m^3 \times \$58{,}000 =$	$116,000
Drum Scale	$5\ m^3 \times \$88{,}305 =$	$441,500
TOTAL COST		$557,500

* Does not include enclosures and hardware.

Personnel and Capabilities Required for D&D Operations:

- STTP Management Team
- Project Leader (1)
- Principle Investigator (1)
- Administrative Assistant / Budget Analyst (1)
- QA Specialist (1)
- Training Specialist (1)
- Document Control Specialist (1)

Continued on next page

- Data Management / Report Writing (2)
- D&D Technicians & Staff
    - Brine and hardware (2)
    - Gas Analyses (2 @ 30%)
    - Engineer (0.6)

- NMT-1 Analytical Group
    - D&D Technicians (3)
    - D&D Staff (1)
    - Radiochemistry (1)
    - PcH (0.5)
    - RCRA (1)
    - Anions (0.5)
    - Gas (See STTP Mngt. Team)
    - LIMS (0.5)

- CST-9 Analytical Group
    - Actinides (1)

- NMT-11 Surface Science Team
    - Fe Analyses (0.3)
    - Other Analyses (0.3)

- ESA-EPE Engineering
    - Design & Implementation (0.3)
    - Fabrication & Operation (0.3)

- Waste Management
    - Waste Coordinator (0.2)
    - Waste Packaging Specialist (0.2)
    - RCRA Waste Specialist (0.2)

- Nuclear Materials Representative
    - NM Specialist (0.1)
- Transportation
    - Transportation Specialist

- Outside Contractor
    - STTP Enclosure – CMR Interface ($200.0k)
- Facility Personnel
    - Engineers

Continued on next page

  - Radiation Control Technicians (RCT)
  - Property Management
- TA-54
  - DVRS Costs for Storage and Volume Reduction
- Closure Plan
  - Costs driven by NMED

Concurrent Safety Maintenance Activities:
(During the D&D process, STTP safety maintenance must continue as part of the overall safety program and regulatory compliance work)

- STTP Management Team
- RCRA Inspections and Documentation
- EPA Inspections and Documentation
- Pressure Relief Operations for test containers that exceed 8-10 psig (pressure developed from radiolysis of brine and brine constituents)
- Preparation of test containers for D&D operations
- Decontamination of test containers that exclude brine contaminated salts
- Maintenance of test containers that exhibit plugging of pressure gages
- Maintenance of sampling port to allow depressurization of test containers
- Maintenance of all life-safety systems in enclosures
- Assuring ventilation system in enclosures maintain 5-7 turnover volumes per hour
- Assuring operation of all emergency response systems
- Replacement of pressure gages that become plugged; testing to assure proper operation
- Maintain documentation of historical maintenance of test containers
- Apply QA to all operations
- Maintain training of all workers as RCRA TSD workers

Disposal of STTP Legacy Wastes at WCRRF:
(Waste developed as part of the opening of waste drums and loading of STTP test containers still resides at the Waste Characterization, Reduction, and Repackaging Facility. STTP is responsible for characterization and repackaging of this waste for disposal.)

Activities at the WCRRF

- Identify STTP Legacy Waste
- Characterize Waste Forms
- TRU Waste

- Mixed TRU Waste
- Mixed Low Level Waste
- Low Level Waste
- Package Waste
- Dispose of Waste

STTP Budget Options & Considerations*

Cost Estimates ($M):

Option 1: Maintain STTP in Standby Condition

FY 2001	2.2
Standby Total:	**$2.2M**

Option 2: D&D Process will require 2 years

Majority of work will be in FY 20001

Basic STTP Operational/Management Team	2.2
D&D Liter-Scale (LS) Test Containers	2.0
D&D Drum-Scale (DS) Test Containers	2.0
D&D STTP Residual Wastes	0.5
Total:	**$6.7M**

Complete D&D Work in FY 2002

Basic STTP Team	1.4	
Complete Unfinished D&D (if needed)	(1.0)	
D&D of Enclosures (if needed)	(1.0)	
D&D of Administrative Functions/Records		0.3
Total:	**$1.7 -**	**3.7M**
2 yr. D&D Total:	**$8.4 -10.4M**	

Option 3: Conduct D&D in 3 Years (equally divided)

Basic STTP Team	3 x 2.2	=	6.6
D&D LS and DS Tests	4.0		
D&D Enclosures (if needed)	(1.0)		
D&D Administrative Functions	0.3		
3 yr. D&D Total:	**$12.4M**		

**Estimate does not include 38% space tax*

Proposal for the Deactivating and Decommissioning Plan for the Actinide Source-Term Waste Test Program

Subject: D&D Plan for STTP with Budget and Safety Considerations

The D&D of the STTP in the Chemistry & Metallurgy Research (CMR) Building must be completed according to **all** the requirements for conducting work in a DOE operated Nuclear Facility. There can be no shortcuts to Safety, Quality Assurance, Training, and Formality of Operations! The retention of the existing management and operation team is essential for the D&D operation to be completed in an effective and efficient manner.

The STTP experiment has not had a safety incident in over four years of operation. The required D&D process is a very complicated set of activities with highly radioactive test containers, brine, brine wetted components, sludge, and hardware. The potential for a contamination incident is always present, but was easier to mitigate with the sampling type work previously done. The D&D process is much more complicated, and needs to be monitored carefully at all times. A single contamination incident can set the D&D plan back for an indeterminate period, thus delaying the anticipated schedule for completion of the D&D process. Safety or security infractions by any non-STTP activity in the CMR or TA-55 can result in DOE, LANL, or the Nuclear Materials and Technology (NMT) Division placing a “Stop Work” or “Stand Down” order on all activities. These orders require lengthy and expensive resumption activities for all projects and teams within the facilities. These prevalent risks must be acknowledged by the sponsor of projects in DOE-operated Nuclear Facilities.

The D&D plan for the STTP takes into consideration this complex set of activities to be conducted in an effective and sequentially-organized manner according to rules and regulations applicable to DOE operations in a Nuclear Facility. These include:

1. Code of Federal Regulations
    - EPA mandates
    - RCRA mandates
2. DOE-Orders for Formality of Operations
3. DOE required Quality Assurance for all operations
4. Price-Anderson Act Compliance
5. LANL Safety Requirements
6. NMT Division Safety Requirements
7. DOE Authorization Basis Documentation
    - Basis of Interim Operation (BIO)
8. Hazards Analyses Documentation
9. Standard Operating Procedures
10. Hazard Control Plans
11. Work Instructions

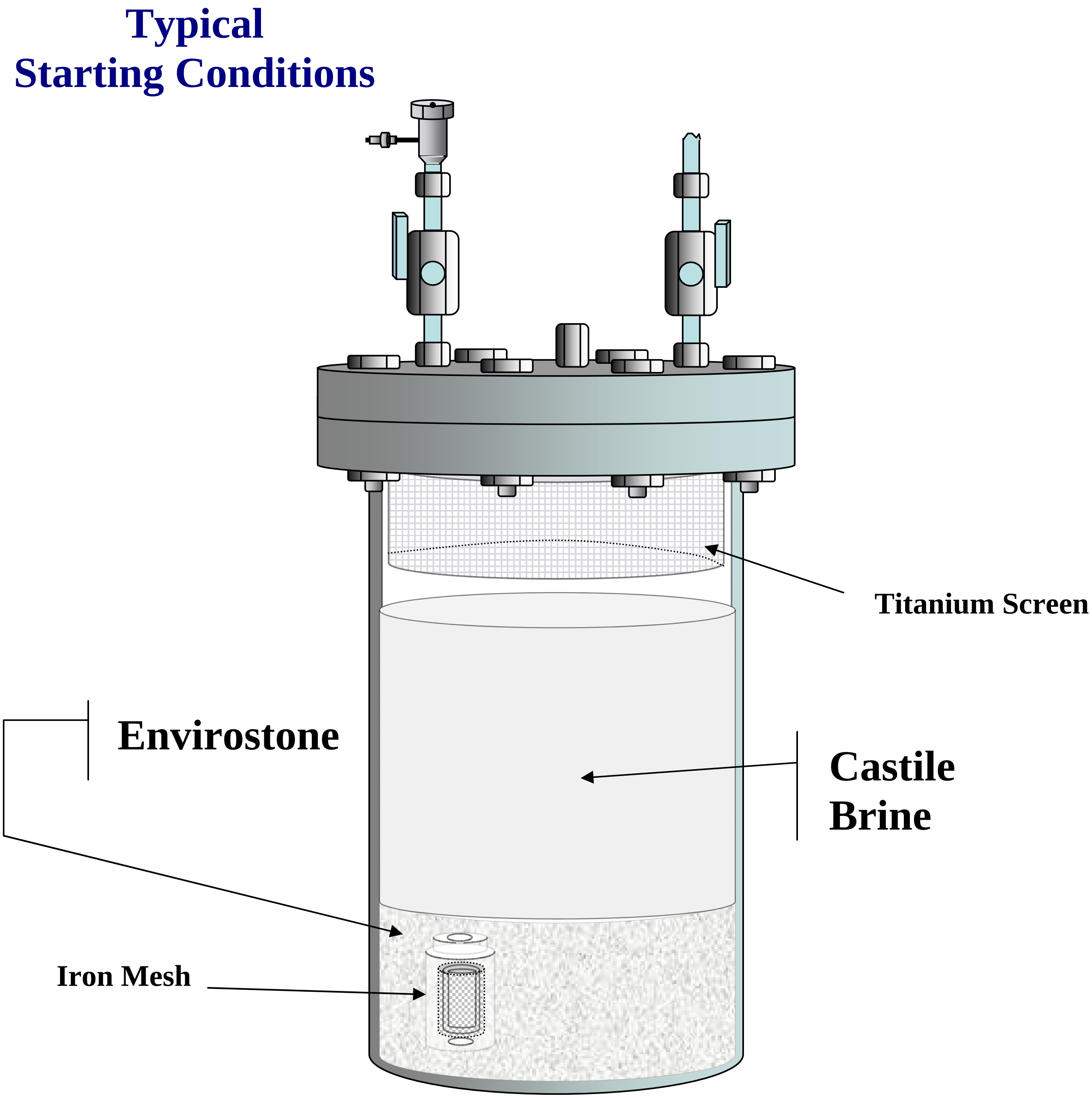
Continued on next page

12. Radioactive Work Procedures
13. Special Work Permits
14. Compliance Training
15. Technical Training
16. On-the-Job Training (OJT)

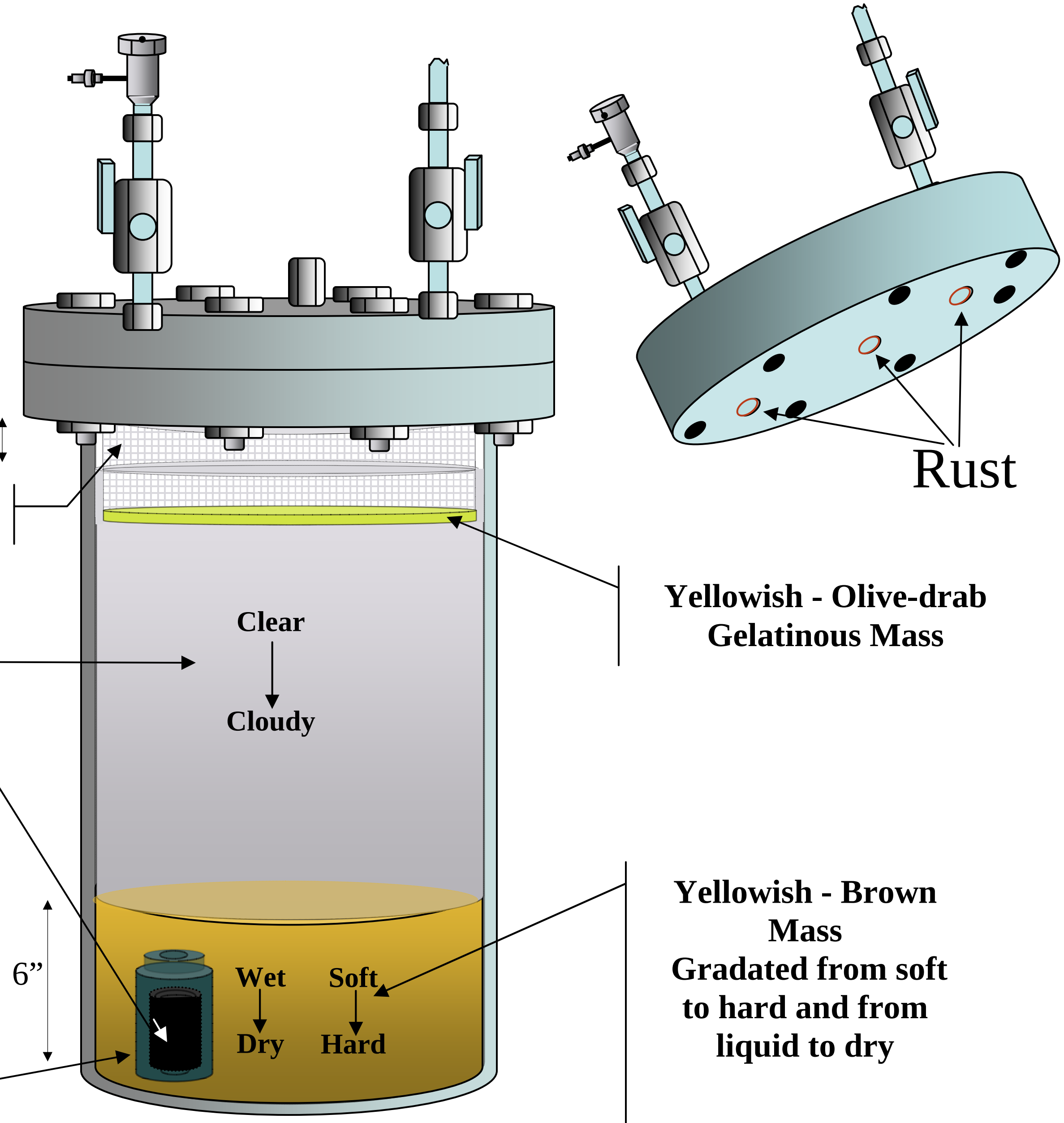
Furthermore, NMT Division will assess a 38 to 46% space tax on all non-DP (Defense Programs) projects, of which STTP is one, located within CMR, because it is a DP Nuclear Facility.

IV. (b) Deactivation and Decommission (D&D) of Test Containers

Diagrams



#24 Envirostone with Castile



Brine is Gradated from Clear to Cloudy

Headspace

Yellowish - Olive-drab Gelatinous Mass

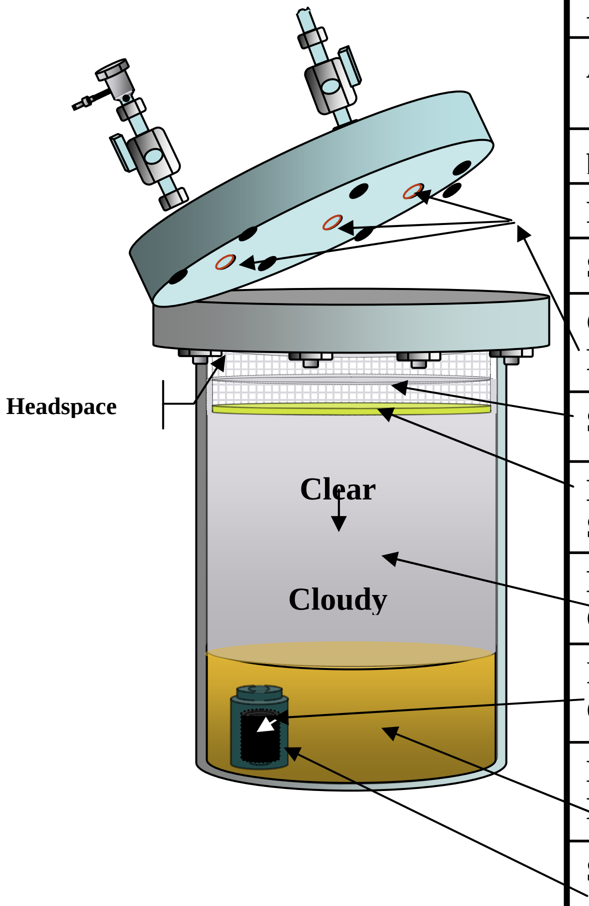
Iron Mesh is Intact, Heavily Coated with Black Powder that is Greenish - Black Underneath

Yellowish - Brown Mass Gradated from soft to hard and from liquid to dry

Powder surrounding the mesh is Greenish - Black

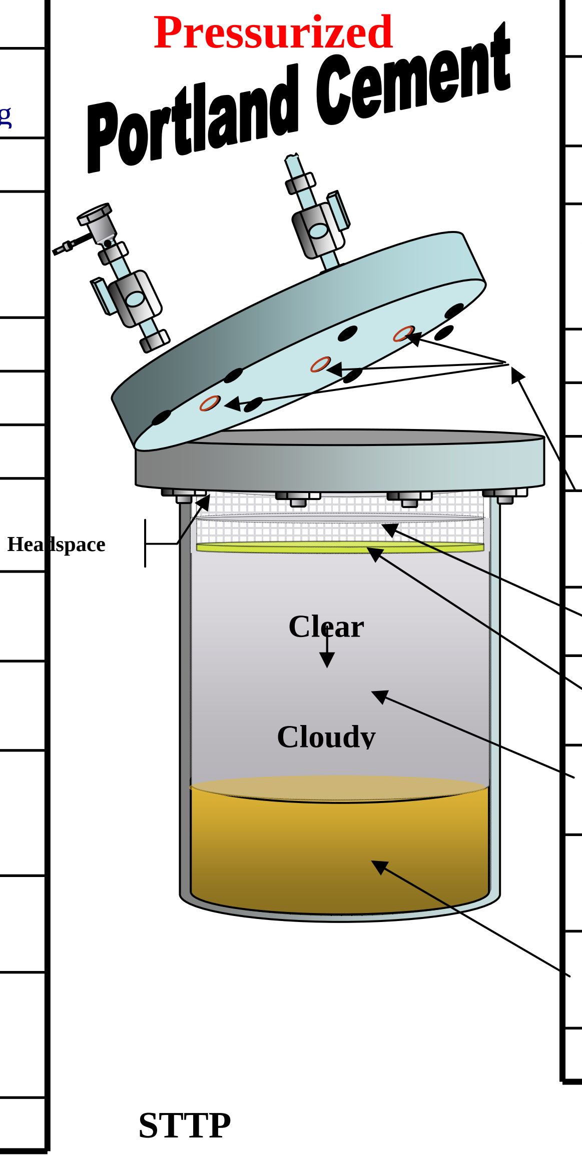
Portland Cement

	L-1	L-2
Waste Type	Portland Cement	Portland Cement
Pu Content	0.018g	0.165g
Brine	A	A
Additives	Fe Mesh Actinides	Fe Mesh, Actinides
pcH Range	8.7-9.0	10.3-10.6
Fe, ppm	< 1	< 1
Special (ratio)	10:1	2:1
Corrosion of s.s. Feed Throughs	None	None
Screen Condition	Black, No Corrosion	No Corrosion
Material in Screen	Some Solids	Filled with Solids
Brine Color/viscosity	Clear	Clear, Gray
Iron Mesh Color/Corrosion	Gray, Black No Corrosion	Gray, Black No Corrosion
Bottom Solids Loose/Cemented	3” Loose	7” Loose
Sludge	Gray, Compacted	Gray, Compacted



	L-3
Waste Type	Portland Cement
Pu Content	0.123g
Brine	Castile
Additives	Fe Mesh, Actinides
pcH Range	12.8-13.1
Fe, ppm	< 1
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	None
Screen Condition	No Corrosion
Material in Screen	1/2 Filled
Brine Color/viscosity	Clear, Gray
Iron Mesh Color/Corrosion	Gray, Black No Corrosion
Bottom Solids Loose/Cemented	8” Loose
Sludge	Gray, Compacted

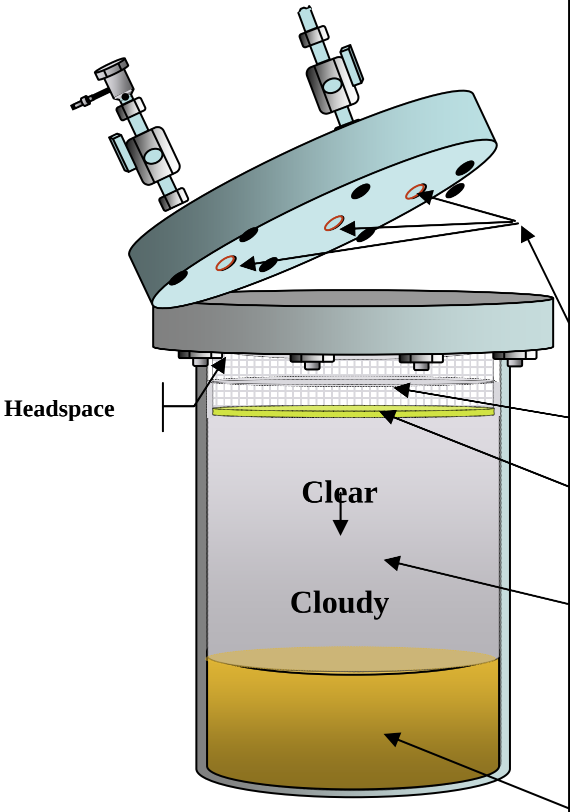
	L-4	L-5
Waste Type	Portland Cement	Portland Cement
Pu Content	Pu, 18.95 mg; Am, 0.233 mg	Pu, 51.2 mg; Am, 0.595 mg
Brine	A	A
Additives	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar
pcH Range	7.21-7.43	7 - 7.44
Fe, ppm	3.1 - 162.4	7 - 57.1
Special (ratio)	10:1	3:1
Corrosion of s.s. Feed Throughs	None	None
Screen Condition	None	None
Material in Screen	None	None
Brine Color/viscosity	Clear, non-viscous light gray	Clear, non-viscous light brown
Iron Mesh Color/Corrosion	Green-gray	Black with blue tint
Bottom Solids Loose/Cemented	Compacted, light gray	5.5” yellow-brown Compacted
Sludge	gray	Peanut butter



	L-6
Waste Type	Portland Cement
Pu Content	Pu, 97.4 mg; Am, 0.994 mg
Brine	Castile
Additives	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar
pcH Range	7.49 - 7.87
Fe, ppm	2 - 41.4
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	None
Screen Condition	None
Material in Screen	None
Brine Color/viscosity	Milky, ~2” deep
Iron Mesh Color/Corrosion	Dark colored
Bottom Solids Loose/Cemented	~8” Brownish-gray soft solid
Sludge	Clay-like

	L-7	L-8
Waste Type	Portland Cement	Portland Cement
Pu Content	0.025g	0.117g
Brine	A	A
Additives	No Fe Mesh Actinides	No Fe Mesh, Actinides
pcH Range	8.7-8.9	9.1-9.56
Fe, ppm	< 2	< 1
Special (ratio)	10:1	2:1
Corrosion of s.s. Feed Throughs	Yes	None
Screen Condition	No Corrosion	No Corrosion
Material in Screen	Thin Coating	1/8” Solids
Brine Color/viscosity	Colorless Liquid	Gray Liquid
Iron Mesh Color/Corrosion	Not Added	Not Added
Bottom Solids Loose/Cemented	8” Loose Muddy Solids	8” Loose 4” Cemented
Sludge	N/A	N/A

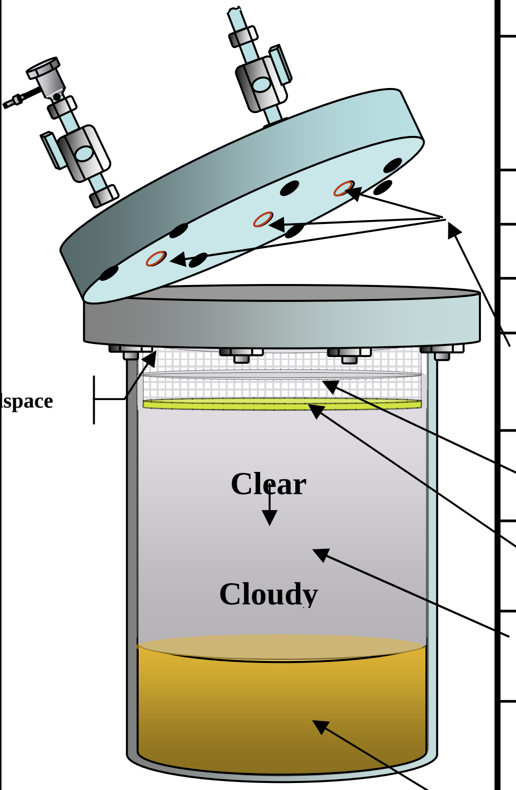
Portland Cement



	L-9
Waste Type	Portland Cement
Pu Content	0.107g
Brine	Castile
Additives	No Fe Mesh, Actinides
pcH Range	12.9-13.1
Fe, ppm	< 1
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	None
Screen Condition	No Corrosion
Material in Screen	1/2 “ of Gray Paste
Brine Color/viscosity	Clear Liquid with Suspensions
Iron Mesh Color/Corrosion	Not Added
Bottom Solids Loose/Cemented	6-8” Loose Not Cemented
Sludge	N/A

Portland Cement

	L-10	L-11
Waste Type	Portland Cement	Portland Cement
Pu Content	0.021g	0.12g
Brine	A	A
Additives	No Fe Mesh Actinides ^{241}Am	No Fe Mesh, Actinides ^{241}Am
pcH Range	8.2-8.9	9.0-10.8
Fe, ppm	< 1	< 1
Special (ratio)	10:1	2:1
Corrosion of s.s. Feed Throughs	Yes	Yes
Screen Condition	Some Corrosion	Corrosion Products
Material in Screen	1/8" Sludge and Rust	1-2" Gray Sediment with Rust
Brine Color/viscosity	Clear	Gray
Iron Mesh Color/Corrosion	Not Added	Not Added
Bottom Solids Loose/Cemented	3-4" Compacted	8" Loose, 1" Compacted
Sludge	N/A	N/A

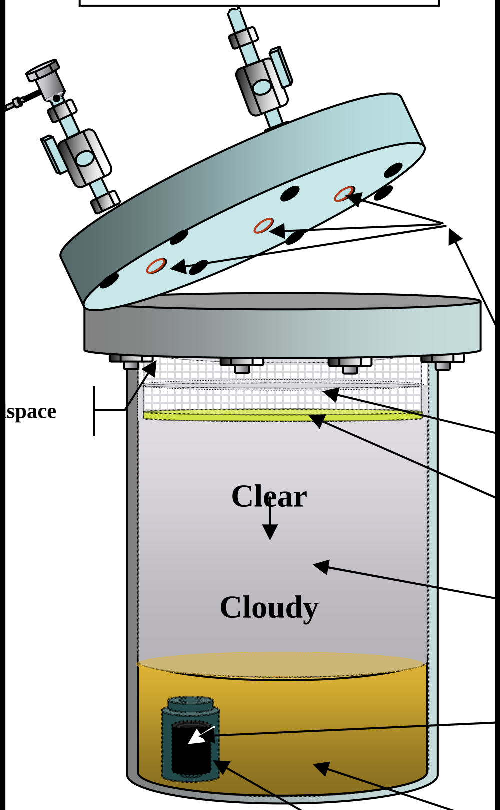


	L-12
Waste Type	Portland Cement
Pu Content	0.108g
Brine	Castile
Additives	No Fe Mesh, Actinides ^{241}Am
pcH Range	12.7-13.0
Fe, ppm	< 1
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	Yes
Screen Condition	Black and Coated
Material in Screen	~1/4" Solids, Gray
Brine Color/viscosity	Pale Gray-Green
Iron Mesh Color/Corrosion	Not Added
Bottom Solids Loose/Cemented	8" Loose gray Sludge
Sludge	N/A

	L-13	L-14
Waste Type	Envirostone	Envirostone
Pu Content	3.4g	3.42g
Brine	A	A
Additives	Fe Mesh Actinides Organics	Fe Mesh, Actinides Organics
pcH Range	7.0-7.29	6.9-7.3
Fe, ppm	14 - 326	100 - 466
Special (ratio) H_2 in vol. %	2:1, H_2 =57 %	2:1 , H_2 =37 %
Corrosion of s.s. Feed Throughs	None TOC = 3300ppm	None TOC = 4000ppm
Screen Condition	No Corrosion	No Corrosion Looked new
Material in Screen	Coating of Yellow Paste	Thin coating of white Material
Brine Color/viscosity	Clear with Suspensions	Clear with Suspensions
Iron Mesh Color/Corrosion	No Corrosion, Greenish-yellow Sludge	No Corrosion, Dark Color
Bottom Solids Loose/Cemented	~4" of peanut butter Consistency	4.5" of yellowish paste
Sludge	Impacted	Impacted

Envirostone

80-90% $CaSO_4$ with 10-20% Melamine-Formaldehyde & 0.1% NH_4Cl

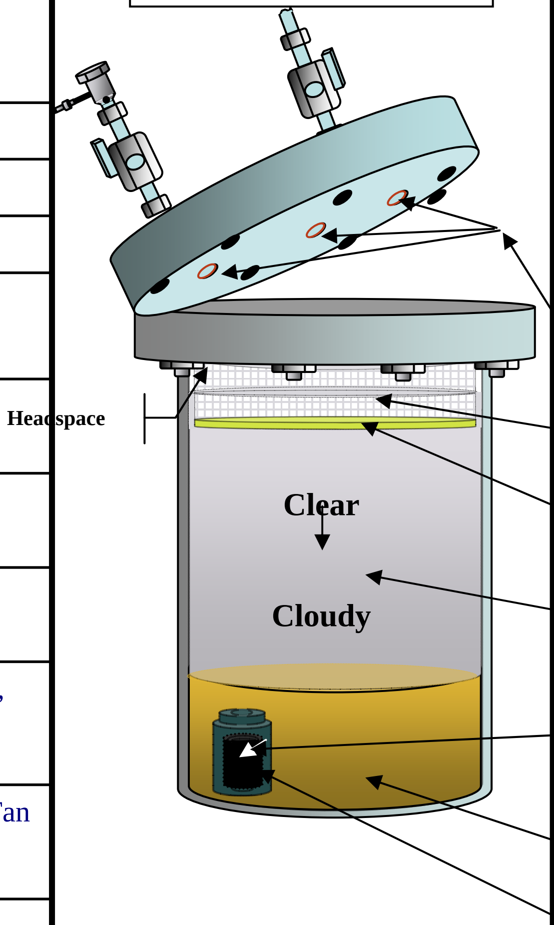


	L-15
Waste Type	Envirostone
Pu Content	0.042g
Brine	Castile
Additives	Fe Mesh, Actinides Organics
pcH Range	6.8-7.1
Fe, ppm	1 - 36
Special (ratio)	2:1 , H_2 =3 %
Corrosion of s.s. Feed Throughs	None TOC = 1400 ppm
Screen condition	No Corrosion
Material in Screen	~2" Oatmeal-like Material
Brine Color/viscosity	Cream Colored with Oatmeal Consistency
Iron Mesh Color/Corrosion	No Corrosion, Gray-Black material
Bottom Solids Loose/Cemented	5-7" of loose solids
Sludge	Impacted

	L-16	L-17
Waste Type	Envirostone	Envirostone
Pu Content	0.62g	1.5g
Brine	A	A
Additives	Fe Mesh Actinides	Fe Mesh, Actinides
pcH Range	7.3-8.0	7.7-8.0
Fe, ppm	1 - 33	< 1
Special (ratio)	2:1	2:1
Corrosion of s.s. Feed Throughs	None Like New	None Like New
Screen Condition	Like New	Like New
Material in Screen	Tan Fines in Screen	No Sediment
Brine Color/viscosity	Tan, Cloudy	Tan, Clear
Iron Mesh Color/Corrosion	No Corrosion, Greenish-Black	No Corrosion, Immersed in Tan Sludge
Bottom Solids Loose/Cemented	8” of Tan loose Sludge	8” of Black-Tan Sludge
Sludge	Tan	Black-Tan

Envirostone

80-90% $CaSO_4$ with 10-20% Melamine-Formaldehyde & 0.1% NH_4Cl

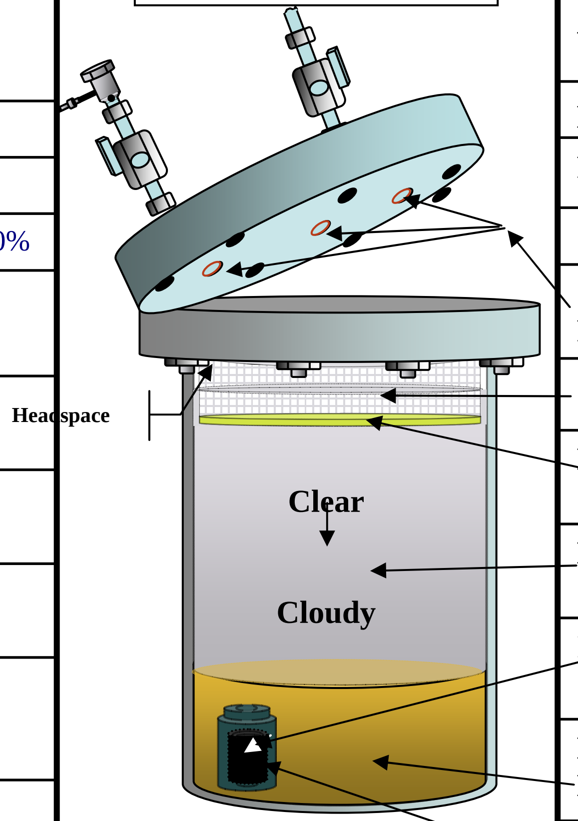


	L-18
Waste Type	Envirostone
Pu Content	2.6g
Brine	Castile
Additives	Fe Mesh, Actinides
pcH Range	7.0-7.8
Fe, ppm	2 - 50
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	No Corrosion Orange-brown Solids
Screen Condition	Thin-brown Sludge on Screen
Material in Screen	Thin Coat of Muddy Clay
Brine Color/viscosity	Yellow Tan with Suspensions
Iron Mesh Color/Corrosion	Black Clay, Black Wire, No Corrosion
Bottom Solids Loose/Cemented	Muddy Suspension
Sludge	Yellow-Tan

	L-19	L-20
Waste Type	Envirostone	Envirostone
Pu Content	0.502g	0.080g
Brine	A	A
Additives	Fe Mesh Actinides	Fe Mesh, Actinides
pcH Range	7.9-8.2	7.2-7.8
Fe, ppm	< 1	20 - 95
Special (ratio)	2:1, N_2O = 16%	2:1, N_2O = 20%
Corrosion of s.s. Feed Throughs	None	
Screen Condition	Like New	
Material in Screen	1/8" Sludge - Orange	
Brine Color/viscosity	Clear-light yellow	
Iron Mesh Color/Corrosion	Black Sludge, Black coating, Some Corrosion	
Bottom Solids Loose/Cemented	Soft Sludge	
Sludge	Black	

Envirostone

80-90% $CaSO_4$ with 10-20% Melamine-Formaldehyde & 0.1% NH_4Cl

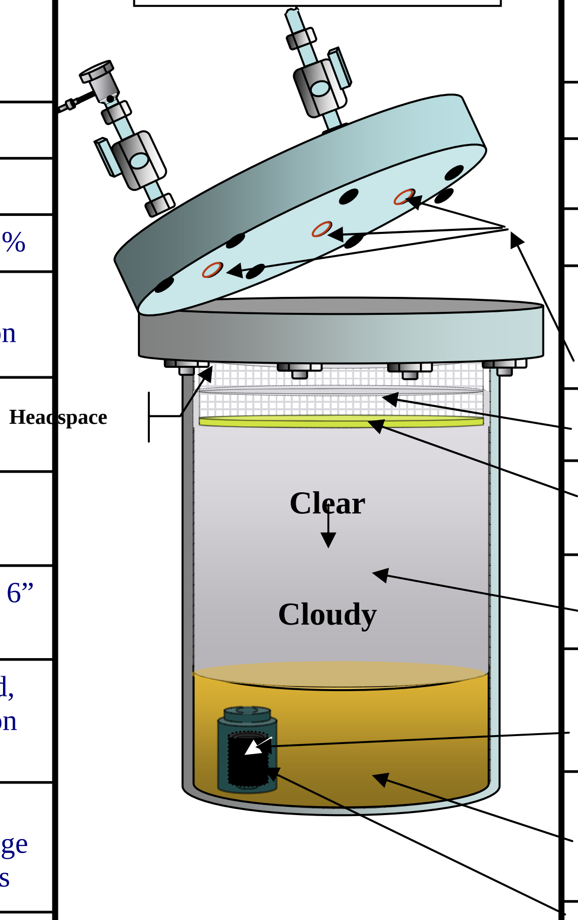


	L-21
Waste Type	Envirostone
Pu Content	0.251g
Brine	Castile
Additives	Fe Mesh, Actinides
pcH Range	7.5-8.1
Fe, ppm	< 0.1
Special (ratio)	2:1, N_2O = 19%
Corrosion of s.s. Feed Throughs	None
Screen condition	Like New
Material in Screen	Clear- Orange Tinge
Brine Color/viscosity	Clear- Orange Tinge
Iron Mesh Color/Corrosion	Black Coating, No Corrosion
Bottom Solids Loose/Cemented	Loose Solids
Sludge	White and Orange Tinge

	L-22	L-23
Waste Type	Envirostone	Envirostone
Pu Content	0.238g	0.502g
Brine	A	A
Additives	Fe Mesh Actinides	Fe Mesh, Actinides
pcH Range	6.8-7.2	7.0-7.4
Fe, ppm	50-120	10-102
Special (ratio)	2:1, N_2O = 39%	2:1, N_2O = 31%
Corrosion of s.s. Feed Throughs	None	None Discoloration
Screen Condition	No Corrosion	No Corrosion
Material in Screen	3/4” Sediment	Gold Colored Sludge, thin
Brine Color/viscosity	Light Brown to gold, Murky	Gold Colored 6” deep
Iron Mesh Color/Corrosion	3 Pieces, Greenish Corrosion	Black Colored, some corrosion
Bottom Solids Loose/Cemented	7” of Gold Colored Sludge	6” of Gold Colored Sludge Loose solids
Sludge	Black	

Envirostone

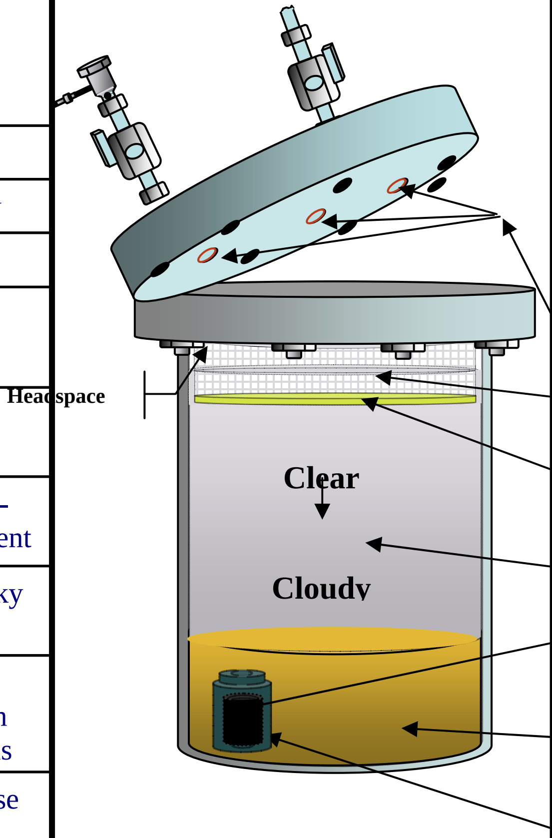
80-90% $CaSO_4$ with 10-20% Melamine-Formaldehyde & 0.1% NH_4Cl



	L-24
Waste Type	Envirostone
Pu Content	0.305g
Brine	Castile
Additives	Fe Mesh, Actinides
pcH Range	7.6-7.9
Fe, ppm	< 1
Special (ratio)	2:1, N_2O = 25%
Corrosion of s.s. Feed Throughs	None Discoloration of Sampling Port
Screen condition	Trace Corrosion
Material in Screen	Thin Coating, Semi-Gelatinous
Brine Color/viscosity	Yellow-olive-drab, murky
Iron Mesh Color/Corrosion	Greenish-black deposit on wire, some corrosion
Bottom Solids Loose/Cemented	6” of Clay-like mass of loose solids
Sludge	

	L-25	L-26
Waste Type	Pyrochemical Salts (DOR)	Pyrochemical Salts (DOR)
Pu Content	0.38g	4.1g
Brine	A	A
Additives	Fe Mesh Actinides	Fe Mesh Actinides
pcH Range	7.7-8.1	7.6-8.2
Fe, ppm	< 1; 1-20 50%	< 1 -generally
Special (ratio)	2:1	2:1
Corrosion of s.s. Feed Throughs	Yes, Green Color	Yes
Screen Condition	O-ring Corrosion	No Corrosion
Material in Screen	1/3 full of crystals and Sludge	1/2" yellow-brown Sediment
Brine Color/viscosity	Whitish murky color	Whitish murky color
Iron Mesh Color/Corrosion	Embedded in light blue solids	Corrosion noted, much encrustations
Bottom Solids Loose/Cemented	5" depth, not cemented	3-31/2" Loose Solids
Sludge	Light Blue	Black-White Precipitate

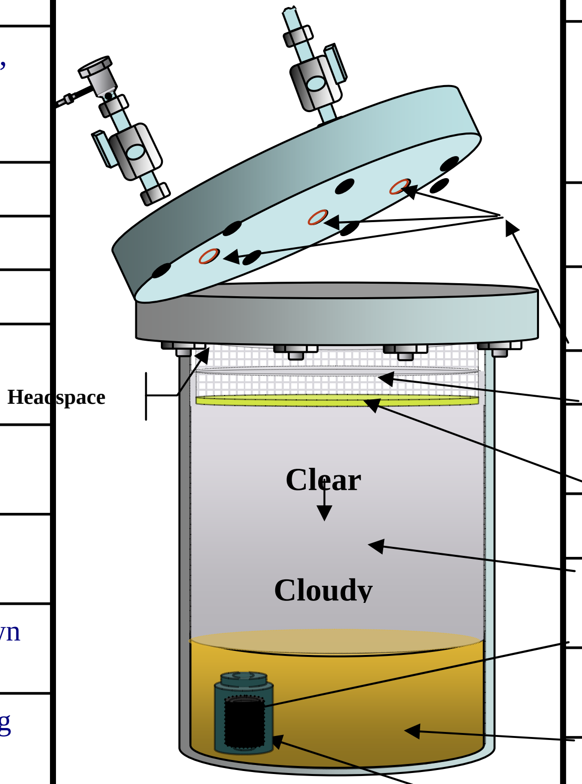
Pyrochemical Salts



	L-27
Waste Type	Pyrochemical Salts (DOR)
Pu Content	3.41g
Brine	Castile
Additives	Fe Mesh Actinides
pcH Range	10.7-11.2
Fe, ppm	43-243
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	Yes, Severe Corrosion
Screen Condition	Rust Particles
Material in Screen	Full of Green Colored Deposits
Brine Color/viscosity	Clear Whitish color
Iron Mesh Color/Corrosion	Black Color around Fe Mesh
Bottom Solids Loose/Cemented	7" Loose Solids
Sludge	Loose Solids

	L-29	L-30
Waste Type	Pyrochemical Salts (DOR)	Pyrochemical Salts (DOR)
Pu Content	Pu, 4.338 mg; Am, 2.38 mg	Pu, 2.010 mg; Am, 2.38 mg
Brine	A	Castile
Additives	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar
pcH Range	4.73 - 5.68	5.9 - 6.6
Fe, ppm	34 - 1468	1967 - 9.2
Special (ratio)	2:1	2:1
Corrosion of s.s. Feed Throughs	None	None
Screen Condition	None	None
Material in Screen	None	None
Brine Color/viscosity	clear	Gray to brown oatmeal
Iron Mesh Color/Corrosion	Black thin coating	Dark coating
Bottom Solids Loose/Cemented	Muddy brown - sand texture	Brown hard solid
Sludge	Dark	Hard brown solid

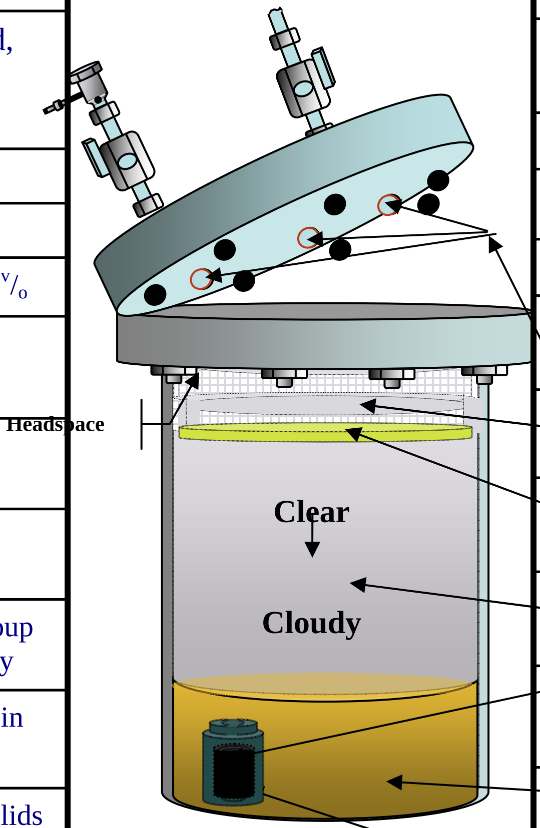
Pressurized Pyrochemical Salts



	L-28
Waste Type	Pyrochemical Salts (DOR)
Pu Content	Pu, 10.6 mg; Am, 1.24 mg
Brine	A
Additives	Fe mesh, Nd, Th, U, Np, CO_2 60 Bar; 76.4 g MgO (2/97)
pcH Range	4.48 - 5.35; 5.03 - 7.7 after MgO
Fe, ppm	19 - 165 ; 4.48 - 7.7 after MgO
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	None
Screen Condition	None
Material in Screen	None
Brine Color/viscosity	Cloudy to yellow
Iron Mesh Color/Corrosion	Thin dark coating, new like
Bottom Solids Loose/Cemented	Very hard yellow cement
Sludge	Oatmeal like

	L-31	L-32
Waste Type	Pyrochemical Salts (DOR)	Pyrochemical Salts (OS)
Pu Content	Pu, 0.809 g; Am, 0.647 mg	Pu, 4.10 g; Am, 2.92 mg
Brine	A	A
Additives	Fe mesh, Nd, Th, U, Np,	Fe mesh, Nd, Th, U, Np,
pcH Range	8.7 - 9.0	8.6 - 9.0
Fe, ppm	< 1	< 1
Special (ratio)	2:1, $H_2 = 33\ ^{v}/_{o}$	2:1, $H_2 = 44.\ ^{v}/_{o}$
Corrosion of s.s. Feed Throughs	No Data	Yes
Screen Condition	No Data	Yes
Material in Screen	No Data	Salts
Brine Color/viscosity	No Data	Clear Pea soup consistency
Iron Mesh Color/Corrosion	No Data	Embedded in cement
Bottom Solids Loose/Cemented	No Data	Cemented solids
Sludge	No Data	Cemented solids

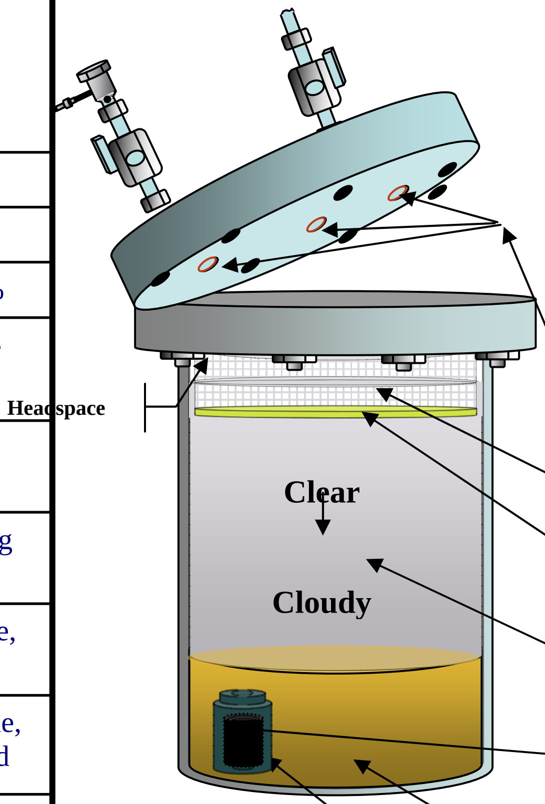
Pyrochemical Salts



	L-33
Waste Type	Pyrochemical Salts (OS)
Pu Content	Pu, 1.14 g; Am, 1.10 mg
Brine	Castile
Additives	Fe mesh, Nd, Th, U, Np,
pcH Range	9.5 - 9.8
Fe, ppm	< 0.1
Special (ratio)	2:1, $H_2 = 35\ ^{v}/_{o}$
Corrosion of s.s. Feed Throughs	Severely corroded
Screen Condition	Upper ring Corroded
Material in Screen	1/2" grey sludge
Brine Color/viscosity	Milky White
Iron Mesh Color/Corrosion	Black coating, no visible corrosion
Bottom Solids Loose/Cemented	No cemented solids,~2" waste
Sludge	~ 2"

	L-34	L-35
Waste Type	Pyrochemical Salts (DOR)	Pyrochemical Salts (DOR)
Pu Content	2.1g	0.45g
Brine	A	A
Additives	Fe Mesh Actinides, Chelators $Ca(OH)_2$	Fe Mesh Actinides, Chelators $Ca(OH)_2$
pcH Range	8.6-9.0	8.2-8.3
Fe, ppm	< 2	< 1
Special (ratio)	3:1, H_2 = 29%	3:1, H_2 = 21%
Corrosion of s.s. Feed Throughs	Yes, Blue & Brown	Yes, Blue - Black
Screen Condition	O-ring Corroded	O-ring Blue
Material in Screen	Full of White Solids	Thin Coating
Brine Color/viscosity	Colorless with Suspensions	Murky Beige, very thick
Iron Mesh Color/Corrosion	Embedded in cemented solids	Greenish-blue, not corroded
Bottom Solids Loose/Cemented	5" with 3-4" cemented	8" Loose Solids
Sludge	Oatmeal Consistency	Blue colored layer

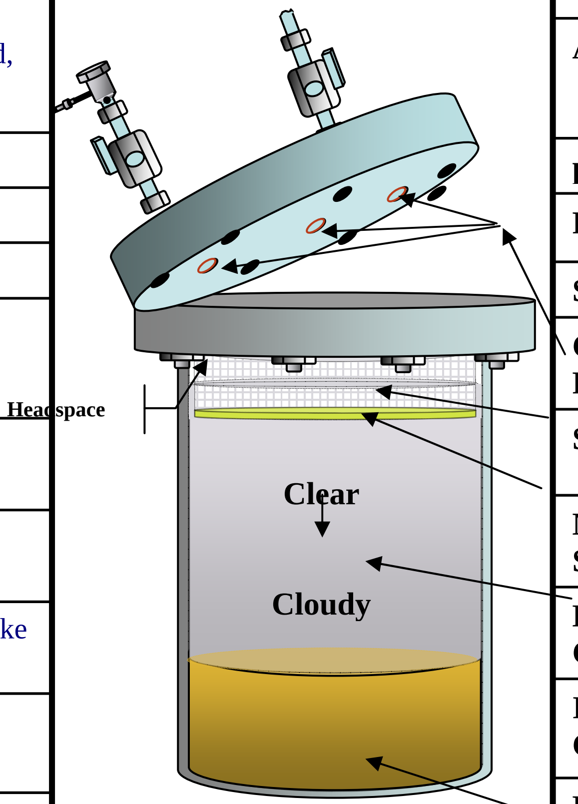
Pyrochemical Salts



	L-36
Waste Type	Pyrochemical Salts (DOR)
Pu Content	11.1g
Brine	Castile
Additives	Fe Mesh Actinides, Chelators $Ca(OH)_2$
pcH Range	11.0-11.4
Fe, ppm	50-100
Special (ratio)	3:1, H_2 = 70%
Corrosion of s.s. Feed Throughs	Yes, Rust Colored
Screen condition	Rust Particles
Material in Screen	Full of gray Muck
Brine Color/viscosity	Greenish-gray, thickened near the bottom
Iron Mesh Color/Corrosion	Embedded in cemented solids, 1/2 retrieved
Bottom Solids Loose/Cemented	3-4" Loose Solids, 1/2 cemented
Sludge	Gray Sludge

	L-37	L-38
Waste Type	Pyrochemical Salts	Pyrochemical Salts
Pu Content	4.42g	2.74g
Brine	A	A
Additives	No Fe Mesh, Th, U, Np, Nd, ^{241}Am	No Fe Mesh, Th, U, Np, Nd, ^{241}Am
pcH Range	9.4-9.9	7.5-8.1
Fe, ppm	< 1	< 1
Special (ratio)	2:1	2:1
Corrosion of s.s. Feed Throughs	Yes, rust surrounded fittings	Some
Screen Condition	Green-gel on screen	Rust particles
Material in Screen	Brown Scale in Screen	1/8” thick Rusticles
Brine Color/viscosity	Tan, Clear	Tan, Clear (like Tea)
Iron Mesh Color/Corrosion	Not Added	Not Added
Bottom Solids Loose/Cemented	Compacted Solids at Angle	1-2” Cemented Solid
Sludge	N/A	N/A

Pyrochemical Salts



	L-39
Waste Type	Pyrochemical Salts
Pu Content	4.35g
Brine	Castile
Additives	.No Fe Mesh, Th, U, Np, Nd, ^{241}Am
pcH Range	7.6-8.3
Fe, ppm	< 2
Special (ratio)	2:1
Corrosion of s.s. Feed Throughs	Yes
Screen Condition	O-ring has green gel
Material in Screen	Black Scale
Brine Color/viscosity	Taupe Opaque Liquid
Iron Mesh Color/Corrosion	Not Added
Bottom Solids Loose/Cemented	Cemented Solids at Angle
Sludge	N/A

Recommended Experimentation (partial list)

- Conduct proposed Fe experiment in the WIPP; this is critical; Fe in heterogeneous waste forms.
- Determine composition of brine in the disposal rooms; Sr and Ba.
- Conduct experiments in recommended glass test container.
- Investigate precipitation of Mg and Ca and impact on chelators; MgO should mitigate effect of chelators.
- Cementation occurred in both Castile and Brine A in Pyrochemical Salt; determine limits of Mg involvement in cementation.
- Non-comminution of waste should be tested.
- Slow addition of brine to MgO experiments, rather than MgO to brine.
- Conduct Pu(IV), (V), (VI) tests in wastes that include MgO.

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THE ACTINIDE SOURCE-TERM WASTE TEST PROGRAM (STTP)

Final Report

Prepared for the DOE-Carlsbad Field Office

Fall 2001

VOLUME III

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I. Summary of Volume III; STTP Results and Discussions

- All waste drums selected for the STTP tests contained > 5 gm of Pu per 55-gal drum.

- All homogeneous wastes were comminuted to allow greater mixing and contact of the brine with the waste to shorten the time of determining the influence of the waste on the behavior of actinides in the brine.

- Soluble salts of Th, U, and Np were added to all test containers. Nd was added to all test containers except the six test containers (LS-10, 11, 12, and 37, 38 and 39) with added Am-241.

- About 75 mg of Am-241 as a soluble salt was added to the Portland Cement test containers LS-10, 11 and 12, and the Pyrochemical Salt tests LS-37, 38 and 39. In both cases, the Am precipitated in the basic brine solution and was not re-solubilized during the entire test period.

- Fe mesh was added to each STTP liter-scale and drum-scale test container except the three sets LS-7, 8, 9; 10, 11, 12; 37, 38, and 39. The Fe mesh was packed into flow through polypropylene bottles to allow brine to have free access to the Fe mesh. However, D&D of the liter-scale test containers showed that most of the Fe mesh containers were filled with finely divided sludge that limited the contact between the brine and the Fe mesh. **A hard black coating, identified as magnesioferrite, formed on the surface of the Fe mesh that prevented corrosion or dissolution of the Fe mesh. This occurred in all test containers**.

- Fe mesh did not appear to maintain a reducing environment in most test containers. Pu (V) and (VI) was present in four test containers with Fe mesh present.

- A mixed microbial inoculum (100-150 ml) of anaerobic brine-containing sediments consisting of 20% lake brine and 30% muck pile salt solution from the WIPP environs along with 50% G-Seep Brine from the WIPP was added to each test container. The microbes appeared to die off rather quickly in the STTP test containers.

- Nitrate and phosphate were added to three drum-scale tests (DS-10, 11 and 12). Nitrate was essentially totally destroyed in the two Brine A experiments (DS-10 and 11) and was not affected in the Castile Brine experiment (DS-12). The mechanism for destruction of nitrate was thought to be from alpha-particle activity that radiolytically destroyed the nitrate that was in solution. **The reason the Brine A experiments resulted in destruction of nitrate and the Castile Brine had no effect is not known.**

- Organic solvents were added to LS-13, 14, and 15. The organic solvents generated very high concentrations of particles and colloids that did not contain actinides. Nitrates in the two Brine A experiments (LS-13 and 14) were totally destroyed and the nitrate in LS-15 with Castile Brine was less affected. This finding points to an energy transfer that may include Mg in the Brine A test. Higher concentrations of H_2 and CO_2 were present in LS-13 and 14 and not so high levels were in the headspace of LS-15, a Castile Brine experiment. Once again, this points to an energy transfer mechanism that could include Mg in Brine A and lack of a radiolytic energy transfer in Castile Brine. **These results accentuate one of many differences in Brine A and Castile Brine chemistry.**

- Bentonite was added to LS-31, 32, and 33 and to DS-4, 5, and 6. Bentonite was effective in maintaining a very low concentration of soluble actinides in all six test containers. The tests with added bentonite had relatively lower concentrations of particles (colloids) that ranged from 10^8 to 10^{10} particles per liter. Typical particle concentrations ranged from 10^{10} to10^{11} particles per liter.

- Envirostone tests with high levels of nitrates (30,000 to 36,000 ppm) also had very high concentrations of N_2O (20 to 40 $^v/_o$) but not high levels of CO_2 in the headspace of the test containers. These test containers with high concentrations of N_2O had lower levels of H_2 in the headspace.

- The drum-scale tests with massive metals did not result in significantly higher concentrations of Pu or other actinides. The soluble Fe concentration increased from <0.1 ppm to 558 ppm in LS-13 (Brine A) and <0.1 to 110 ppm in LS-14 (Brine A), and did not increase (<1 ppm) in LS-15 (Castile Brine). The pcH decreased in LS-13 from pcH 8.19 to 5.45 and in LS-14 from 7.78 to 6.62. The pcH in the Castile Brine test LS-15 did not significantly decrease during the test period (7.86 to 7.74). These results show the Brine A resulted in greater concentrations of soluble Fe than Castile Brine. The pcH in Brine A tests decreased while the pcH in Castile Brine did not. **These results strongly point out the difference in the chemistry of Brine A and Castile Brine.**

- The STTP tests contained comminuted homogeneous wastes and a selection of heterogeneous wastes immersed in brine, therefore, the experiments are applicable to WIPP Disposal Rooms that would be partially or completely filled with brine. **Such a brine-filled containment in the WIPP would require a geologic upheaval or an extensive human intrusion scenario. The probability of either of these two scenarios is very low.**

- Pu present as a salt or non-fired oxide in the waste is probably the major form that would be soluble in WIPP brines. Medium-fired or high-fired Pu oxides would have minimal solubility in basic WIPP brines. Metallic Pu is not expected to be in the waste.

- The wastes included in the STTP studies to determine the chemical behavior of the waste and associated actinides Th, U, Np, Pu and Am, were comminuted forms of the homogeneous wastes Portland Cement, Envirostone and Pyrochemical Salts. This effectively speed up chemistry in the repository by several hundred or thousand years. The heterogeneous waste forms were a mixture of combustible wastes and three tests contained massive metal.

- Actinides were not solubilized in brine in contact with Portland Cement or were solubilized and immediately precipitated. Soluble concentrations in Portland Cement tests were in the low ppb range.

- Only U was solubilized to any extent in tests with comminuted Envirostone. Pu, Am, Np, Th, and Nd were essentially not solubilized in the Envirostone tests.

- Envirostone tests with added organic solvents resulted in increased actinide solubilization but concentrations were low relative to pyrochemical salt tests. **Organic solvents resulted in much higher particle concentrations (~10^{13} particles/liter) but the particles did not contain actinides.**

- There were two forms of pyrochemical salt wastes tested, Direct-Oxide Reduction (DOR) salts and Oxygen Sparging (OS) salts. The chemistry of the two salt wastes were considerably different as shown later in this report.

- Test containers with Pyrochemical salt wates contained higher loadings of Pu (0.38 to 11.1 gm) relative to other STTP tests. The concentration of soluble actinides in pyrochemical salt wastes was significantly higher than other STTP tests.

- The liter-scale pyrochemical salt tests with added bentonite resulted in very low levels of soluble actinides and relatively low particle concentrations (10^9 to 10^{10} particles/liter). These tests also had very low Ca and Fe concentrations.

- Pyrochemical salt tests with added chelators and calcium hydroxide (96 gm) resulted in significant solubilization of actinides in Castile brines but much lower concentrations in Brine A experiments. The high Mg concentration in the two Brine A tests (LS-34 and 35) combined with chelators to lessen the impact while in the Castile Brine test, LS-36, the chelators were free to solubilize actinides because of the low Mg content. The concentration of Mg in LS-36 at a pcH of 11.2 was < 20 ppm because of the formation of $Mg(OH)_2$. The Ca concentration of 9000 ppm, 90,000 ppm and 65,000 ppm in LS-34, 35 and 36, respectively did not have an impact on solubilization. The ionic strength of all these pyrochemical salt tests, especially Brine A, was very high. Overall, the impact on solubilization of actinides with chelators in comminuted homogenous wastes was considerably less effective than the heterogeneous wastes in the drum-scale tests.

- Pyrochemical salt tests with added soluble Am-241 (75 mg) did not result in significant solubilization of actinides (LS-37, 38, 39). The Am was immediately precipitated in all three tests and did not resolubilize.

- The highest levels of soluble actinides in the STTP was found in LS-27, a Castile Brine experiment with DOR pyrochemical salt wastes at a pcH of ~11.0. D&D of the test container showed that <u>all</u> of the comminuted pyrochemical salts were available to the brine because the interaction of comminuted waste with brine did not form a cemented mass as was seen on many of the other pyrochemical salt waste tests. LS-27 had relative high concentrations of soluble Fe (16-243 ppm) during the test period. Pu (V) was identified in LS-27 but not Pu (VI). An explanation for the presence of Pu (V) is given in this report.

- The highest levels of Pu (VI) were identified in LS-26, a Brine A experiment with DOR pyrochemical salt at a pcH range of ~7.5 to 8.4. The Pu concentration increased slowly at first but more rapidly after about one year and Pu (VI) was identified that persisted for about one year. LS-26 was unique in that only Pu and Am increased in concentration while all other actinides and Nd remained at low levels. In contrast to LS-27, LS-26 had very low levels of soluble Fe (0.1 to 4 ppm) during the test period. LS-26 was the only test that exhibited a positive Eh. An explanation for the presence and eventual reduction in Pu (VI) is given for this test container.

- LS-28 was a DOR pyrochemical salt test in Brine A with ~60 bar of CO_2 pressure added to the headspace of the test container. The pcH of LS-28 had decreased to 4.48 while the Pu had increased to 90,942 ppb. All other actinides and Nd increased during the same period. A slurry of MgO was added to the test container which increased the pcH to 7.7 and the concentrations of Pu and all other actinides were reduced by 90 to 95%. However, a year after addition of MgO, the concentrations of Pu and Am with all the other actinides had increased significantly (Pu from 18,097 to 197,984 ppb) and Pu (VI) was identified in one sample about 27 months after addition of MgO. LS-28 had soluble Fe concentrations that ranged from 1 to 165 ppm during the test period and ~50 ppm in the sample with Pu (VI). An explanation for the presence of Pu (VI) in LS-28 is given in this report.

- LS-36 was a DOR pyrochemical salt test in Castile Brine with a rather high pcH of 11.2. Six chelators each at a concentration of 100-154 ppm was added to the test container. The concentration of soluble actinides, especially Pu, in LS-36 was relatively high and the Fe concentration typically ranged from 30 to 100 ppm. **Pu (V) was identified in LS-36 and this was somewhat surprising because the test had to overcome 101 ppm of added ascorbate as a chelator and a strong reductant and the reducing strength of the added microbial inoculum to achieve an oxidizing environment. The soluble Fe concentration did not maintain a reducing environment.**

- The drum-scale tests were not opened up as part of the D&D process and the condition of the waste or Fe mesh was not established. This decision was based on the increased time and effort as well as the considerable cost for accomplishing this D&D effort.

- The drum-scale tests with combustible and massive metal wastes all contained very low levels of actinide activity. The exception was the three drums (DS-7, 8 and 9) with chelators. **The chelators were considerably more effective at solubilizing all actinides in the drum-scale tests relative to the liter-scale tests with added chelators.**

- The drum-scale tests with massive metal (DS-13, 14 and 15) developed very high levels of H_2 during the entire test period.

- Phosphate added to DS-10, 11 and 12 as a microbial nutrient disappeared rather quickly after the beginning of the experiment. Phosphate concentrations for the two Brine A experiments were reduced to less than detectable within one month while detectable levels of phosphate persisted for about two months in Castile Brine experiment DS-12. **This may have been**

influenced by the higher Mg content in Brine A experiments and exemplified the difference in the radiolytic behavior in Brine A and Castile Brine.

- Phosphate added to the drum-scale tests containing chelators near the end of the test period was very effective in reducing the concentration of all actinides by > 90%. **It was interesting that Fe was also significantly reduced (>90%) in the Castile Brine experiment with chelators but was not effective in reducing the soluble Fe concentration in the DS-7 and 8 with Brine A.** This finding could explain the effectiveness of higher concentrations of Mg in lessening the effectiveness of chelators in solubilizing actinides in the WIPP.

- Radiolysis of brine resulted in the production of much H_2 that accumulated in the headspace of all test containers. **H_2 was found to not have an influence in maintaining a reducing environment.** H_2 is quite insoluble in brine and rises to the headspace of the test container rather rapidly. N_2O is very soluble in brine and is expected to be a reducing agent when nitrate is radiolytically converted to N_2O. Radiolytically generated O_2 remained in the brine as a combined radical and rarely was seen in the headspace except in tests with high loadings of Pu or Am.

- H_2 was a radiolytically generated gas that was the primary gas found in the headspace of STTP test containers except in the tests with high levels of nitrates. All other gases were in trace quantities relative to H_2 and N_2O.

- CO_2 was a radiolytically produced gas from alpha-particle irradiation of organics within the brine. The alpha-particle range in brine is a few microns and does not generate much CO_2 as evidenced by the < 1% CO_2 in the headspace of all test containers except LS-13 and 14 with > 4000 ppm total organic carbon added as organic solvents. LS-13 and 14 accumulated 4-5 $^v/_o$ and LS-14 about 3 $^v/_o$ CO_2 in the headspace of the test containers. **Test containers with < 2000 ppm organics typically generated < 1 $^v/_o$ CO_2.**

- Radiolytic generation of hypochlorite in concentrated brine (~5 M NaCl) is a well known process as reported in the literature. Formation of hypochlorite is dependent on the radiation levels (> 2 GBq/l) and the concentration of chloride (> 4 molar) in the brine. Alpha activity from Pu soluble in brine plus Pu loading in the waste for Pyrochemical Salts would achieve a level of 2 to 10 GBq/liter. So production of hypochlorite is certain to occur in the STTP test containers that contain > 1 gm of Pu-239. Hypochlorite can act as a powerful oxidant in acid (hypochlorous acid) or basic solution (hypochlorite). Both have been shown to stabilize Pu (VI) in Brine A and Castile Brine.

- Radiolytic generation of peroxide in high concentration brines occurs because of the dissociation of the H_2O molecule in brine to form peroxides. Peroxide is a strong oxidant in weak acid and basic solutions of Brine A and Castile Brine and will stabilize Pu (VI) in both solutions but is less effective in neutral solutions. An excess of peroxide can result in reducing Pu (VI) or reducing the concentration of Pu as a precipitate in Brine A and Castile Brine. This may be the cause of the eventual diminution of Pu (VI) in LS-26 and 28.

- A combination of radiolytically generated hypochlorite and peroxide could well serve as an oxidant to oxidize Pu (IV) to Pu (V) and (VI) in weak acid, neutral and basic Brine A and Castile Brine solutions. As the hypochlorite and peroxide concentrations become greater and greater, Pu can be either reduced or act as precipitants to reduce the Pu activity in an STTP test. **This mechanism could limit the concentration and lifetime of Pu (VI) in specific environments in the WIPP.**

- An explanation for the formation of Pu (VI) is STTP Pyrochemical Salt tests is given in a sequential manner as follows.

Formation of Pu (V) and Pu(VI) in STTP Pyrochemical Salt Tests; Sequential Order of Reactions

Pyrochemical Salt Wastes Consist of:

1. DOR (Direct-Oxide Reduction)
2. OS (Oxygen Sparging)

↓

1. **DOR: High concentration of Ca and Cl^-**
OS : High concentration of Na and K and Cl^-

↓

2. **DOR: High loading of Pu and Am; high activity**
OS : Lower loading of Pu and Am

↓

3. **DOR: Pu (V) and Pu (VI) Identified**
OS : No oxidation Observed

↓

4. **Pu (IV) is stabilized by $SO_4^{=}$**

↓

5. **Sulfate in DOR tests precipitated as $CaSO_4$**
K_{sp} of $CaSO_4$ is 7.1 x 10^{-5}

↓

6. **Nitrates as source of nitrite and N_2O**
Not available in pyrochemical salt tests

Continued on next page

Formation of Pu (V) and Pu(VI) in STTP Pyrochemical Salt Tests; Sequential Order of Reactions (continued)

7. **High chloride (6 to 11 Molar) predominates in Pyrochemical salt tests**

8. **DOR: Fe concentrations are high; F^- complexation of Fe in acid solution strong; metal hydrolysis effect and amphoterism effect in high basicity solutions.**
OS : Fe concentrations are low

9. **DOR: Total colloid concentration high**
OS : Total colloids 10x to 100x lower than DOR
DOR: Colloids high in Pu, Sr, Ca, SO_4
OS : Colloids low in Pu, Sr, Ca, SO_4

10. **DOR: High Ca and Mg release Pu from $SO_4^=$ to Cl^-**
OS : Sulfate remains to stabilize Pu (IV)

11. **DOR: High loading of Pu and Am produce radiolytic OCl^- and peroxides in basic solution and > 5 M chloride**

12. **DOR: Pu (IV) is susceptible to oxidation**
OS : Pu not so susceptible to oxidation

13. **Pu (V) and Pu (VI) Identified in DOR tests**

14. **Pu (VI) Concentration Disappeared**

- A comprehensive study was conducted to determine the concentration and stability of colloids in the STTP experiments. The data showed there was a very low population of Pu bearing colloids. Field Flow Fractionation studies verified this finding and further showed for one test container (LS-27) that there was no activity in the different particle sizes outside of what was defined as a soluble species (<10 nm diameter particles). **This was considered to be an important finding because colloids as a vehicle for transport of actinides does not appear to be a problem for the WIPP. Also, colloids do not seem to be stable in the Brine A and Castile Brine environment of the WIPP.**

- The liter-scale tests were loaded with about 2.5 liters of brine and the pressured tests were loaded with ~ 2 liters of brine. The drum-scale tests were loaded wit about 50 gals (190 liters) of brine. All tests were rotated to agitate the brine and waste to achieve mixing to optimize the amount of leaching that could occur during the rotation period. Agitation was conducted weekly for about 5 years. During the final one to two years, the test containers were left in a quiescent mode. Recognizing that the brine in the repository would be in a relatively quiescent mode, a study comparing the analytical results for actinides after the rotation mode was compared with results after the quiescent mode. Most test containers showed little change between the two modes with concentrations in general being a little lower to significantly lower after the quiescent mode. The test containers showing greater concentrations were as follows: LS-16 showed a significant increase of most actinides; LS-25 showed a Pu increase from 40 ppb to 250 ppb; LS-34 showed a Pu increase from 13.5 ppb to 87 ppb; and LS-37 showed a significant Pu increase from 194 to 5500 ppb. The drum-scale test DS-12 showed a significant increase of all actinides while DS-09 showed a significant decrease of all actinides.

- Sulfate is considered to be an anion that stabilizes Pu (IV), especially when the sulfate concentration predominates over other anions. The concentration of sulfate ranged in Portland Cement tests up to 14000 ppm, Envirostone tests up to 18000 ppm, Pyrochemical Salt tests with Oxygen Sparging waste up to 9000 ppm and Direct Oxide Reduction waste had a range of 50 to 250 ppm. The drum-scale tests showed sulfate from 4700 to 48000 ppm. It is apparent that Direct Oxide Reduction Pyrochemical Salt wastes had concentrations of sulfate that were far lower than other wastes. The high Ca concentration in the DOR salt tests (30,000 to 120,000 ppm) reduced the sulfate concentration by precipitation of the sulfate as $CaSO_4$. The addition of $Ca(OH)_2$ to LS-34, an OS test, resulted in a lower sulfate concentration (800 ppm) than the other OS tests (4600 to 9000 ppm).

- The pressurized liter-scale tests with Portland Cement (LS-4, 5 and 6) showed higher concentrations of U and LS-6, a Castile Brine experiment, showed a higher concentration of Pu (up to 638 ppb) than other Portland Cement tests. The U was expected to increase because of the higher carbonate concentrations in the tests with CO_2 pressure. **Interestingly, the pcH of the Portland Cement did not decrease and go acid as was thought might happen.** The buffering capacity of comminuted Portland Cement must be significant to remain basic after 5-6 years with 60 bars of CO_2 pressure.

- The pressurized liter-scale tests with Pyrochemical Salt wastes showed significantly higher concentrations of all actinides. LS-28 showed a relatively higher Pu concentration after addition of MgO (up to 197,000 ppb of Pu). Th, Np, U, and Am also had higher than usual concentrations in the presence of CO_2. The pcH decreased to slightly acid conditions in all three Pyrochemical Salt tests. The headspace gas in LS-28 showed a concentration of ~ 50% H_2 after being pressurized with 60 bars of CO_2 for over two years. The H_2 is believed to be from radiolytic degradation of brine. The Pyrochemical Salt tests with added CO_2 pressure were all DOR salt tests. The presence of Pu colloids or microprecipitates was evident by the spectroscopic analyses of filters and Pu was associated with $SrSO_4$, however, the concentrations of colloidal-bearing Pu were very small.

- The two liter-scale tests with Pu (VI) were LS-26 and LS-28. LS-26 was a Pyrochemical Salt test with a loading of 4.06 grams of Pu and 2.25 mg of Am in a Brine A. The pcH for LS-26 ranged from a pcH of 7.5 to 8.4 with an average pcH around 8.0 The Pu concentration started at 42.9 ppb and in creased to 3996 after one year of testing. The Pu and Am concentration increased rapidly to 70,826 ppb on 12/02/96 and a sample was analyzed and found to contain 63,413 ppb Pu and Pu (VI) was identified on the 03/24/97 sample. Pu (VI) persisted for about 1 ½ years till 11/02/98 when the total Pu concentration dropped to 5642 ppb. The upward trend that occurred was attributed to the presence of soluble Pu (VI). The eventual downward trend in concentration is attributed to precipitation of Pu (VI) or reduction of Pu (VI) to Pu (IV) and subsequent precipitation of Pu (IV) as a hydrated PuO_2 or Pu hydroxide. According to the results of experiments conducted at LANL by Runde and VanPelt, Pu (VI) can be reduced or precipitated by peroxide within 18 months in Brine A at pH 7-10. Also, peroxide generated by alpha radiolysis that exceeds a few ppm will result in precipitation of Pu as a Pu (VI) hydroxide or a reduced form of Pu hydroxide. The stability or instability of Pu (VI) in the presence of peroxide or hypochlorite in acid, neutral and basic solutions of 5m NaCl Brine A and Castile Brine is summarized below.

Table 1. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

Because LS-26 was a Brine A experiment at a pcH of 7.6 to 8.1, Pu (VI) is shown to be unstable on a long-term basis in the presence of peroxide and hypochlorite with the formation of white precipitate at neutral and basic pH. Pu (VI) is more stable in basic pcH than neutral and LS-26 may have been on the verge of being basic enough to be stable. LS-28 was on the acid side of neutral where Pu (VI) is much more stable in Brine A with both hypochlorite and peroxide.

- There were several liter-scale tests that showed a cemented mass at the bottom of the test container. The cemented solid was very hard and resembled Sorel Cement (magnesium oxychloride). None of the Portland Cement or Envirostone tests had the cemented solid, but at least 7 Pyrochemical Salt tests had the cemented solid at the bottom of the test container as determined by visual examination of the test containers. The cemented mass was very hard and could not be penetrated with a sharp screwdriver. The hardened cement would have trapped actinides that also precipitated with the components of the Sorel Cement and would not be made available to the brine.

- Fe mesh was added to 30 liter-scale test containers and corrosion of the Fe wire strands was evident in LS-19, 22, 23 and 24, four Envirostone tests with a pcH range of 6.8 to 8.2. The Fe mesh was irretrievably embedded in hard cement in three Pyrochemical Salt test containers, LS-32, 34 and 36. **The Fe mesh in all test containers had a hard black coating that protected the Fe strands from corroding in both Brine A and Castile Brine.**

- Strontium present in STTP brines because of addition as part of the ingredients or as an impurity in Ca and Mg added to make Brine A and Castile Brine was a key carrier of Pu in Portland Cement, Envirostone, and Pyrochemical Salt tests, but showed no correlation in drum-scale tests. This conclusion was established by observing the correlation of Sr, S, and Pu in the 5 micron, 1.2 micron, and < 10 nm filters with a Wavelength Dispersive X-ray Fluorescence technique. The correlation between Pu and $SrSO_4$ was especially noted in the Pyrochemical Salt tests. Fe as a precipitate or colloid was essentially not present in the Pyrochemical Salt tests and did not have a correlation with Pu filtered out on the filters. $SrSO_4$ is expected to be an efficient carrier of Pu because $BaSO_4$ is a classic method of scavenging and carrying Pu in aqueous systems. $SrSO_4$ could be a most important compound for entrainment (not precipitation) of Pu in certain wastes within the WIPP. Of course, Sr would have to be present in the WIPP salt formations.

II. Applicability of STTP; Chemical Actinide Transport in the WIPP

The primary concern of actinides in the WIPP is the concentration and transport of the soluble or colloidal form actinides in the wastes emplaced in the WIPP Disposal Rooms by any mechanism or process that results in concentrations of actinides in the accessible environment or outside the administrative boundaries of the WIPP. Probably the two primary mechanisms or processes of transporting actinides are by chemical or physical means. Establishing the possibilities of physical transport of actinides in the WIPP was beyond the scope of the STTP. However, establishing the dynamics of actinide transport by chemical means, namely, as soluble actinide species or colloids, was considered to be within the scope of the STTP. Three conditions that could be present in the WIPP after waste has been placed in the WIPP Disposal Rooms could be characterized as follows. The condition of WIPP disposal rooms:

1) could be essentially dry or free of brine pockets;
2) could be partially brine loaded or contain enough free brine to moisten the waste; or
3) could be significantly brine loaded so the waste would be partially or completely immersed in brine.

The most conservative condition would be the third condition of partial or complete immersion because this would require future human intrusion scenarios or a geologic upheaval that would change the characteristics of the entire area.

The first condition would result in a condition of no chemical transport because a chemical carrier that could transport soluble chemical species or colloids from the repository would not exist.

The second condition would be similar to the first because there would be insufficient liquid pressure or driving force to sustain a continuous or semi-continuous flow of brine carrier and therefore soluble actinides or colloid bearing actinides out of the repository.

The third condition, which has a rather low probability, presents the possibility of solubilizing actinides within the waste by free flow brine and transporting the soluble or colloidal species to the accessible environment. It was this condition for which the STTP was designed to provide experimental information, according to an established technical requirements document and test plan. The experiment was to use only actual homogeneous and heterogeneous waste forms. The experiments were to be conducted with brine that was similar to the brine found in the Salado Formation (Brine A) and also brine found in the Castile Formation (Castile Brine). The 36 non-pressurized homogeneous waste experiments were conducted in 3 liter vessels, while the 15 heterogeneous waste experiments were conducted in 246 liter (65 gallon) vessels. Six tests were pressurized to 60 bars with CO_2 and contained in 2-liter vessels. The experiments were conducted in sets of three (2 Brine A and 1 Castile Brine). Several chemical additives were added to different tests to gain technical information on the influence of certain chemicals that might be found on actual waste to solubilize, transport, or alternatively to immobilize otherwise transportable or mobile actinide species. The three major transuranic content codes (TRUCON codes) used for the homogeneous wastes were TRUCON 111-211 as Portland Cement tests, TRUCON 112/212, 113/213, 114/214, and 126/226 as Envirostone tests, and TRUCON 124/224 as Pyrochemical Salt tests. All tests were maintained at 30 °C, the approximate temperature in the WIPP, for the entire test period of 5-6 years.

Significant Transport Parameters

Solubility of Pu and Am in TRU waste

The transport of mobile species of Pu and Am require that the two actinides are solubilized to some extent in the brine phase to be available for transport as a soluble or colloidal species. The solubility of the Pu and Am in brine under WIPP relevant conditions can be governed by the form of the Pu. STTP data has shown that soluble Am concentrations followed or tracked the soluble Pu concentrations in essentially every test that had higher Pu concentrations. In six liter-scale tests (LS-10, 11, 12, 37, 38, and 39) with Am-241 added in a soluble form, the Am-241 precipitated immediately after addition and did not resolubilize at any time during the test period. The concentration of Am followed the increase and decrease of Pu in all tests including the six tests pressurized with 60 bars of CO_2. This indicates that as Pu present in the actual waste solubilized, Am was solubilized by the same mechanism from the same matrix. The forms of Pu that can be present in the TRU waste shipped to the WIPP can be categorized as follows:

1) Pu metal – This form is not expected to be in most TRU waste and has probably oxidized to a non-fired Pu oxide. Pu, as a finely divided metal or non-fired Pu oxide, is solubilized quite easily by strong anions or chelators.

2) Pu salt – Pu present as a salt such as chloride, nitrate, sulfate, or fluoride is soluble to a large extent based on the anion or chelating species in the brine. This form of Pu is not expected to represent a significant portion of the waste streams except for select canisters. Pyrochemical salt wastes could have significant quantities of Pu salts.

3) Pu oxide (non-fired) – This is the form of Pu that can be a major source of contamination in both homogeneous and heterogeneous TRU waste streams. The first three Pu waste forms are the most likely to solubilize in WIPP type brines. This waste stream consists of Pu that has oxidized at ambient temperatures or less than 200 °C.

4) Pu oxide (medium-fired) – This is a waste form that is generated by oxidizing Pu of > 400 °C which can be the primary contaminant in both homogeneous and heterogeneous wastes. This waste form will not dissolve in a slightly acidic, neutral, or basic medium or with strong chelators. This form of Pu is refractory and generally requires a strong anion such as fluoride in a > 1 Molar acid heated to greater than 40 °C for an extended period of time (several hours). Based on the STTP results, the only waste that showed significant solubilization of Pu was certain experiments with pyrochemical salt wastes and the heterogeneous waste stream with added chelators.

5) Pu oxide (high fired) – This waste stream is a specialized form of highly refractory Pu oxide that is difficult to dissolve even in concentrated nitric acid with fluoride. This form of Pu is not soluble in WIPP type brine under WIPP conditions.

The forms of Pu that can be solubilized in WIPP brines under WIPP conditions will probably precipitate as Pu hydrate or polymer that reduce the concentrations of soluble Pu to much lower levels. However, once solubilized the Pu can remain solubilized in an anionic, chelated, or oxidized form. Certain soluble species of Pu can be present as or associated with colloids that are readily transportable. The conditions and chemistry of the brine must be favorable for colloids to form rather than non-transportable precipitates. Soluble Pu species that precipitate are generally no longer available to be metathesized to a transportable form. The enhancement of transportability of actinides by major influencing variables has been summarized for the major waste streams tested in the STTP in Table I. A review of the solubilization level is categorized on a relative basis as follows:

Designation	Solubilization Level
Very Low (VL)	< 50 ppb
Low (L)	50-500 ppb
Medium (M)	500-5000 ppb
High (H)	5000-100,000 ppb
Very High (VH)	>100,000 ppb

The categorization and designation of total colloid particles per liter of brine is as follows:

Designation	Total Particles/Liter
VL	10^9
L	10^9-10^{10}
M	10^{10}-10^{11}
H	10^{11}-10^{12}
VH	10^{12}-10^{13}

The two above designation will be used in the following data tables for liter-scale and drum-scale tests according to the test matrix.

Table 2. STTP Liter-Scale test Matrix

	LS-01	LS-02	LS-03		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic process sludge	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	LS-04	LS-05	LS-06		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge with CO_2	
Brine	A	A	CASTILE	Portland Cement	10:1 / 3:1 / 2:1

Continued on next page

	LS-07	LS-08	LS-09		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge without Fe	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	LS-10	LS-11	LS-12		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge w/o Fe; Am-241 added	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	LS-13	LS-14	LS-15		
TRUCON	112/212	112/212	112/212	Absorbed organic liquids	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-16	LS-17	LS-18		
TRUCON	113/213	113/213	113/213	Absorbed aqueous laboratory waste	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-19	LS-20	LS-21		
TRUCON	114/214	114/214	114/214	Cemented inorganic particles	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-22	LS-23	LS-24		
TRUCON	126/226	126/226	126/226	Cemented organic sludge	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-25	LS-26	LS-27		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-28	LS-29	LS-30		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with CO_2	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-31	LS-32	LS-33		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with brine – equilibrated bentonite	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-34	LS-35	LS-36		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with $Ca(OH)_2$ and chelators	
Brine	A	A	CASTILE		3:1 / 3:1 / 3:1
	LS-37	LS-38	LS-39		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts without Fe; Am-241 added	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1

Table 3. STTP Drum-Scale Test Matrix

	DS-01	DS-02	DS-03	
TRUCON	116/216	116/216	116/216	Combustibles
Brine	A	A	CASTILE	
Waste (lbs)	43	59.1	47.2	
Total (lbs)	740.2	728.4	720	

	DS-04	DS-05	DS-06	
TRUCON	116/216	116/216	116/216	Combustibles and brine – equilibrated bentonite
Brine	A	A	CASTILE	
Waste (lbs)	72.6	85.5	76.6	
Total (lbs)	765	723	746	

	DS-07	DS-08	DS-09	
TRUCON	116/216	116/216	116/216	Combustibles with chelators
Brine	A	A	CASTILE	
Waste (lbs)	122.6	51.55	56.65	
Total (lbs)	783.4	726	720.6	

	DS-10	DS-11	DS-12	
TRUCON	116/216	116/216	116/216	Combustibles and sodium nitrate/phosphates
Brine	A	A	CASTILE	
Waste (lbs)	66.4	48.6	66.4	
Total (lbs)	728	754.6	717	

	DS-13	DS-14	DS-15	
TRUCON	117/217	117/217	117/217	Metals
Brine	A	A	CASTILE	
Waste (lbs)	171.4	136.8	162.2	
Total (lbs)	867.4	846.2	860	

Table 4. Factors That Influence Actinide Transport
PORTLAND CEMENT

	Liter-Scale ID								
Soluble Pu Concentration Level	*1*	*2*	*3*	*7*	*8*	*9*	*10*	*11*	*12*
VL	X	X	X	X	X	X	X	X	X
L									
MED									
H									
VH									
Pu Solubilization Basis									
Added Chelators	0	0	0	0	0	0	0	0	0
Radiolytic Oxidants	0	0	0	0	0	0	X	X	X
Unknown	-	-	-	-	-	-	-	-	-
*Colloid Formation**									
Pu	0	0	1	0	0	0	0	0	0
Fe	0	11	15	0	2	7	0	7	7
Sr	4	13	15	3	15	12	2	15	8
Total Particles/Liter	L	M	M	L	L	L	L	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

No Fe mesh added to LS-7, 8, 9, 10, 11, 12
No Nd added to LS-10, 11, 12
^{241}Am added to LS-10, 11, 12

Table 5. Factors That Influence Actinide Transport
ENVIROSTONE

	Liter-Scale ID											
Soluble Pu Concentration Level	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*	*23*	*24*
VL					X		X	X	X	X	X	X
L	X	X	X			X						
MED				X								
H												
VH												
Pu Solubilization Basis												
Added Chelators	0	0	0	0	0	0	0	0	0	0	0	0
Radiolytic Oxidants	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	-	-	-	X	-	-	-	-	-	-	-	-
Added Organics	X	X	X	0	0	0	0	0	0	0	0	0
High Nitrate					X		X	X	X	X	X	X
*Colloid Formation**												
Pu	14	11	0	6	14	12	6	0	0	6	6	5
Fe	17	14	5	10	16	8	9	16	3	15	12	13
Sr	2	4	1	8	7	10	7	7	2	16	9	13
Total Particles/Liter	VH	VH	VH	L	L	L	L	M	L	M	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Fe mesh added to all tests
Organic solvents added to LS-13, 14, 15

Table 6. Factors that Influence Actinide Transport
PYROCHEMICAL SALT

	Liter-Scale ID											
Soluble Pu Concentration Level	*25*	*26*	*27*	*31*	*32*	*33*	*34*	*35*	*36*	*37*	*38*	*39*
VL							X				X	
L	X			X	X	X				X		
MED								X				X
H		X							X			
VH			X									
Pu Solubilization Basis												
Added Chelators	0	0	0	0	0	0	X	X	X	0	0	0
Radiolytic Oxidants		X							X	X	X	X
Unknown		X	X									
DOR (X) or OS (0)	X	X	X	0	0	0	0	X	X	X	0	0
*Colloid Formation**												
Pu	9	17	16	8	10	14	11	2	16	8	0	13
Fe	0	0	0	3	5	6	0	0	2	6	1	0
Sr	15	13	16	0	4	3	0	3	14	15	2	5
Total Particles/Liter	M	H	H	L	L	L	L	M	M	L	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Bentonite added to LS-31, 32, 33
Chelators and Calcium hydroxide added to LS-34, 35, 36
^{241}Am added to LS-37, 38, 39
No Fe or Nd added to LS-37, 38, 39
Pu (V) and (VI) identified in LS-26, 28, 36

Table 7. Factors that Influence Actinide Transport
PRESSURIZED TESTS

	Liter-Scale ID					
	Portland Cement			*Pyrochemical Salt*		
Soluble Pu Concentration Level	*4*	*5*	*6*	*28*	*29*	*30*
VL						
L	X	X	X			
MED			X			X
H					X	
VH				X		
Pu Solubilization Basis						
Added CO_2	X	X	X	X	X	X
Radiolytic Oxidants				X		
Unknown				X	X	
MgO				X		
*Colloid Formation**						
Pu	0	0	0	3	3	3
Fe	1	1	0	1	2	1
Sr	0	0	0	3	0	0
Total Particles/Liter	M	M	L	VH	H	M

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Pu (VI) identified in LS-28
MgO added to LS-28

Table 8. Factors That Influence Actinide Transport
DRUM-SCALE TESTS (D1-9)

	Drum-Scale ID								
Soluble Pu Concentration Level	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
VL	X	X	X	X	X	X			
L									
MED							X	X	X
H									
VH									
Pu Solubilization Basis									
Added Bentonite				X	X	X			
Added Chelators							X	X	X
NO_3 Decrease	X	O	X	X	X	O	O	O	O
*Colloid Formation**									
Pu	0	0	0	1	0	1	13	13	3
Fe	15H	17H	18H	15H	19H	19H	12L	14	11L
Sr	0	0	0	0	0	2	0	0	1
Total Particles/Liter	L	M	L	M	M	L	M	H	H

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

10 kg of Bentonite (Brine equilibrated) added to DS-4 and DS-5
10 kg of Bentonite (non-equilibrated) added to DS-6
Chelators added to DS-7, 8, 9
$NaNO_3$ (159 g) and NaH_2PO_4 (258 g) added to DS-10, 11, 12

Table 9. Factors that Influence Actinide Transport
DRUM-SCALE TESTS (D10-15)

	Drum-Scale ID					
Soluble Pu Concentration Level	*10*	*11*	*12*	*13*	*14*	*15*
VL		X	X	X	X	X
L	X					
MED						
H						
VH						
Pu Solubilization Basis						
Added metals				X	X	X
Added $NaNO_3$ and NaH_2PO_4	X	X	X			
NO_3 decrease*	X*	X*	0			X*
*Colloid Formation***						
Pu	12L	14L	10L	1L	9L	1
Fe	20VH	23VH	18H	19MED	20MED	18MED
Sr	1	0	0	0	0	0
Total Particles/Liter	MED	MED	L	H	L	L

* NO_3 reduction rapid and complete

** Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

$NaNO_3$ (159 g) and NaH_2PO_4 (258 g) added to DS-10, 11, 12
DS-13, 14, and 15 were massive metal tests

III. STTP Test Matrix

Liter-scale Tests

This sludge is described as Los Alamos 111A, concreted aqueous waste. This waste was a mixture of radioactive liquid waste from analytical operations in the CMR, process waste from TA-55, and industrial waste from throughout the Laboratory. It began as a corrosive and radioactive liquid waste that was neutralized essentially to a basic slurry with powdered $Ca(OH)_2$, ferric sulfate, and a flocculation aid. This treatment precipitated and carried the actinides and other soluble metal ions into a slurry. This slurry was solidified in 55-gallon drums with various portions of Portland Cement, vermiculite, and sodium silicate. The pH of the Portland Cement waste was driven by the calcium hydroxide concentration and is generally 9-11.

LS-1, 2, 3

Solidified Aqueous Inorganic Process Sludge, TRUCON 111/211, (LS 1-3)

These experiments would establish the effectiveness of Portland Cement to retain actinides precipitated by addition of ferric sulfate and $Ca(OH)_2$ and a flocculation aid. The comminuted Portland Cement immersed in Brine A and Castile Brine should have a different basicity in the two brines; pcH 8-10 in Brine A and pcH 10-13 in Castile. The results from this experiment will allow comparison between a Brine A test with a brine to solid ration of 10:1 and 2:1. There was an addition of Fe mesh, Th, U, Np and Nd. These experiments should establish a reference background of Eh from basic Portland Cement tests.

LS-4, 5, 6

Solidified Aqueous Inorganic Process Sludge, TRUCON 11/211 with CO_2 at 60 Bar (LS 4-6)

The composition of these sludges is similar to LS 1-3. These tests will be conducted with a headspace pressure of about 60 atmospheres (870 psig) with CO_2. The pressurized test containers will be sampled for brine at pressure and filtered at pressure. It is reasonable to assume that the actinide solubilities, especially U, could be affected by carbonate complexation and decreased pcH. The increased carbonate complexation might solubilize the ferric sulfate, which would increase the concentration of soluble iron and provide more chemical sites for entrainment of $Fe(OH)_3$. The results from these tests could be directly compared with LS 1-3.

LS-7, 8, 9

Solidified Aqueous Inorganic Process Sludge, w/o Fe, TRUCON 111/211, (LS 7-9)

Corroding steel in the disposal rooms provides a possible sink for actinides through sorption. However, CO_2 in the rooms might passivate steel by forming a surface layer of siderite ($FeCO_3$), which would render much less iron oxide available for actinide sorption. These experiments test the effect the removal of iron oxides from the system, elimination sorption of actinides by the Fe oxide phases. These experiments would be similar to LS 1-3 but without added Fe mesh and could be directly compared with LS 1-3 to determine the effect of Fe under these conditions.

LS-10, 11, 12

Solidified Aqueous Inorganic Process Sludge w/o Fe, TRUCON 111/211; ^{241}Am added (LS 10-12)

In addition to providing a source of sorbants, corrosion of steel also lowers brine Eh in its vicinity. Without steel (or other active metals), the oxidizing effects of radiolysis may dominate the Eh of the system. These experiments measure actinide concentration, and possibly speciation, under the most toxic conditions reasonably attainable in the rooms. The addition of about 75 mg (257 mCi) of Am-241 to each test container would be expected to increase radiolytic decomposition of brine to yield greater concentrations of peroxide and hypochlorite. The basicity of the Portland Cement is expected to precipitate the actinides including the added Am-241 and higher Eh may solubilize some of the precipitated actinides. The extent of radiolysis may be determined by the rate of hydrogen generation and eventual accumulation in the headspace.

Envirostone Liter-scale Tests

Envirostone is the commercial name of Envirostone gypsum cement and is a white solidification agent that was used to solidify evaporator bottoms and other sludge wastes that could contain both inorganic and organic solvents or salts. The composition of Envirostone is 80-90% calcium sulfate, 15-20% melamine-formaldehyde resin and 0-0.1% ammonium chloride. Envirostone is not as basic as Portland Cement and the results of these experiments should provide information about the effect of a high calcium and sulfate matrix with mild basicity on actinide chemistry.

LS-13, 14, 15

Absorbed Organic Liquids, Envirostone, TRUCON 112/212 (LS 13-15)

The experiments with Envirostone have added organic solvents and residues and will determine if high concentrations of organic solvents and reagents in the brine significantly promote dissolution or suspension of actinides. If the waste contains exclusively solvent residues, their effect will be minimal. However, if chelating agents, extractants, or detergents are present, their effect on actinide concentration could be significant. These experiments will also establish the effect of colloidal suspensions on actinide concentrations.

LS-16, 17, 18

Absorbed Aqueous Laboratory Waste in Envirostone, TRUCON 113/213 (LS 16-18)

These are laboratory wastes that have been neutralized or made slightly basic and solidified with Envirostone. The high salt content and possible high organic content including chelating agents may increase actinide solubility. The possible high nitrate content in these wastes should provide information on the effect of radiolytic degradation of nitrates.

LS-19, 20, 21

Cemented Inorganic Particulates (Sludge) in Envirostone, TRUCON 114/214 (LS 19-21)

This waste form is process residue from evaporator bottoms and other discardable solutions, process leach solids, ash, filter cakes, salts, metal oxides, fines, etc. These tests will determine the effect of increased pcH and particulate from process waste streams. Similar to LS 16-18, there may be high concentrations of nitrate in these experiments.

LS-22, 23, 24

Cemented Organic Sludge Solidified with Envirostone, TRUCON 126/226 (LS 22-24)

These wastes are process residues from evaporator bottoms and other discardable solutions, process leached solids, ash, filter cakes, salts, metal oxides, fines, etc. This waste has been immobilized in Envirostone with a possible presence of chelators. These tests have the potential for high concentrations of nitrates.

Pyrochemical Salt Liter-scale Tests

The Pyrochemical Salt waste added to the STTP test containers was obtained directly from TA-55 (the technical area where LANL's nuclear materials are handled) waste drums. The Pyrochemical salt waste streams were from two major operations, direct oxide reduction and oxygen sparging of electrorefined plutonium metal and salts. The Pyrochemical salt waste contained high-fired MgO crucibles entrained with salts used for direct oxide reduction. For the STTP, the crucibles and any salt lumps were comminuted, including other salt flux ingredients. It was expected that the Pyrochemical salt waste would be high in sodium chloride, potassium chloride, calcium chloride, magnesium oxide, magnesium chloride, fluorides, and some residual unreacted calcium metal and calcium oxide.

The Pyrochemical salt process was initiated to directly reduce PuO_2 to Pu metal by heating to ~800 °C with Ca metal in a MgO – Y_2O_3 crucible containing $CaCl_2$ or some other salt matrix. The direct oxide reduction was followed by an electrorefining process including oxygen sparging to eliminate Na or K developed at the electrorefining cathode. The Pyrochemical salts used for STTP contained higher concentrations of ^{239}Pu and ^{241}Am relative to Envirostone and Portland cement tests.

LS-25, 26, 27

Pyrochemical Salt Wastes, TRUCON 124/224 (LS 25-27)

The Pyrochemical waste forms used for the STTP tests were the wastes developed from the Direct-Oxide Reduction (DOR) process or the Oxygen Sparging process and included pieces of MgO crucibles that had been ground up.

The waste from the DOR process could contain $CaCl_2$, CaF_2, Ca metal, CaO, and magnesia (MgO) from the MgO crucible. The Pyrochemical salt wastes from DOR and O_2 sparging processes generally contain relatively higher levels of Pu and Am which could result in increased levels of brine radiolysis and perhaps more oxic conditions from oxidizing products of radiolysis. If unreacted Ca remains in the waste or if higher concentrations of CaO or $Ca(OH)_2$ are in the waste, the brine become more basic upon dissolution of the Ca or Ca compounds. LS-25, 26, and 27 were Pyrochemical salts from the DOR process.

LS-28, 29, 30

Pyrochemical Salt Wastes with Added CO_2, TRUCON 124/224 (LS 28-30)

This test has Pyrochemical salt wastes from the DOR process as discussed in "Pyrochemical Salt Wastes" just above, but with added CO_2 pressure at about 60 bars (~870 psig). Any basicity from the Ca compounds should be neutralized by the CO_2 headspace. The bicarbonate and carbonates formed from the CO_2 may increase the solubility of actinides, especially uranium, but may also increase solubility of iron.

LS-31, 32, 33

Pyrochemical Salt Wastes with Brine-Equilibrated Bentonite, TRUCON 124/224 (LS 31-33)

These tests contain wastes from the oxygen-sparging process with added brine-equilibrated bentonite. The O_2 sparging process resulted in wastes as discussed in the “Pyrochemical Salt Wastes with Added CO_2” section above but also contained oxidized salts (Ca, Na, K) generated by the electrorefining process. The results from these tests could indicate the effectiveness of brine-equilibrated bentonite, a potential backfill material, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids. These tests could also determine the effectiveness of bentonite as an actinide sorbent in the presence of high concentrations of divalent ions (particularly Ca^{2+}), which compete with the actinides for sorption sites on the clay particles.

LS-34, 35, 36

Pyrochemical Salt Wastes with $Ca(OH_2)$ & Chelators, TRUCON 124/224 (LS 34-36)

This set of tests consists of LS-34 with Pyrochemical salt wastes from the O_2 sparging process and LS-35 and 36 with wastes from the DOR process. All three tests have added $Ca(OH)_2$ to increase the basicity of the brine and to determine the effect of the basic solution on generated CO_2 and increased carbonate production. Major chelators have been added to the three test containers. These tests should indicate the solubilizing effect of major chelators on actinides in a basic solution. The results of these experiments can be compared to the results of the drum-scale tests with added chelators, DS 7-9.

LS-37, 38, 39

Pyrochemical Salt Wastes with added ^{241}Am, TRUCON 124/224 (LS 37-39)

This set of tests consists of LS-37 with Pyrochemical salt wastes from the DOR process and LS-38 and 39 with wastes from the O_2 sparging process. All three tests have added ^{241}Am, which may render the system more oxic and provide an indication of Pu-238 effects on brine chemistry. The oxidizing products of radiolysis such as O_2, H_2O_2, or OCl^- if they are stable in the high brine solutions may enhance corrosion of iron that could in turn actually provide a reducing effect on the system. These tests may provide an indication of the redox chemistry with increased radiolysis. Fe mesh was excluded from these tests.

The test matrices for drum- and liter-scale test containers include all combinations of solubility-influencing variables judged sufficiently different to require testing. The two test matrices were developed by collaborative effort between SNL and LANL.

IV. Drum-Scale Test Waste and Pu Content

The waste loaded into the drum-scale tests were Transuranic Content Code 116 (Heterogeneous Combustible or debris type waste) and 117 (Massive metal wastes). The criteria for the drums was that the waste must contain greater than 5 grams of Pu in a 55-gal drum. Also, the entire contents of a single 55-gal waste drum was to be loaded into each STTP all-titanium drum-scale test which had a volume of ~65 gal. There was to be no mixing of waste from different 55-gal waste drums. The waste that was selected for each test drum to meet the type of waste and the total Pu content is given below.

Table 10. STTP Drum-Scale Pu Contents

Drum #	LA No.	TRUCON Code	Pu-52 (gm)
DS-1	54546	116	7.10
DS-2	52896	116	8.15
DS-3	54129	116	8.19
DS-4	52114	116	9.11
DS-5	53565	116	9.38
DS-6	52410	116	10.78
DS-7	52047	116	11.60
DS-8	54409	116	14.94
DS-9	54174	116	16.25
DS-10	52878	116	16.44
DS-11	53217	116	16.45
DS-12	53211	116	16.70
DS-13	54371	117	12.74
DS-14	52109	117	8.19
DS-15	54871	117	16.22
		Total	182.24

Drum-Scale Tests

DS-1, D2, D3

Combustibles, TRUCON 116/216 (DS 1-3)

Of significance in these drum-scale tests are the effects of cellulose degradation on actinide concentration. Aerobic oxidation and fermentation will lower system Eh. Denitrification may produce complexing agents such as citrate and lactate. Complexing agents from decontamination activities may already be present in the waste and will make up the bulk of complexing agents withdrawn in the leachate at early times.

DS-4, D5, D6

Combustibles with Bentonite Backfill (DS 4-6)

The results from these experiments can be compared directly with those from tests, DS 1-3. These results will indicate the effectiveness of brine equilibrated bentonite, a reference backfill, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids.

DS-7, 8, 9

Combustibles with Added Chelation Agents (DS 7-9)

Although fermentation and denitrification of cellulose are predicted to yield complexing agents, this condition conceivably may not occur during the time frame of the STTP. These experiments test how actinide solubility is affected by a system containing both "naturally occurring" ligands (such as lactate) and ligands introduced as part of the waste stream (such as EDTA). As it is not reasonable to assay drums for chelating agents as part of waste selection, these drums must be prepared by spiking the ordinary combustible waste with the major chelators described in "Addition of Chelators."

These tests will follow ligand concentration over time to observe if microbial activity can act as a sink or source of complexing agents.

DS-10, 11, 12

Combustibles with Added Nitrate and Phosphate, TRUCON 116/216 and 111/211 (DS 10-12)

In denitrification, cellulose or its fermentation products are oxidized by bacteria capable of using nitrate as an electron acceptor. The NO_3 is in turn reduced to N_2 or NH_3. Denitrifying bacteria can oxidize organic acids to α-hydroxy acids, which are effective complexing agents. The presence of nitrate in process sludges may be significant in promoting this process in combustible waste.

In these experiments, nutrients in the form of sodium nitrate and sodium phosphate are added to the test containers to study their effect on microbial activity. $NaNO_3$ and NaH_2PO_4 was added at the 0.01M level for the 210 liter volume, 180 and 300 grams, respectively.

DS-13, 14, 15

Metals, TRUCON 117/217 (DS 13-15)

Metals capable of corroding under anoxic conditions can reduce system *E*h below the stability limit of water, possibly stabilizing Pu(III) in solution. Both iron (from mild steel) and aluminum will anoxically corrode in brines. Less active metals such as copper and lead may also corrode if H_2S (from sulfate reduction) is present. A protective polyethylene liner was added to these drums to prevent damage to the test container walls during rotation.

V. Commentary on STTP Liter-Scale Tests

PORTLAND CEMENT

The soluble actinides and Pu in the Portland Cement tests were all categorized as "very low" for all non-pressurized tests. Am-241 was added to LS-10, 11, and 12, and no apparent solubilization occurred as a result of enhanced oxidation from radiolytically produced oxidants. Nitrate reduction occurred in all Portland Cement tests. Calcium concentrations were very high for all Brine A tests and very low for Castile Brine tests. Sulfate was very high for Castile Brine tests and relatively low for Brine A tests. There were essentially no Pu bearing colloids in any Portland Cement tests although there were Fe and Sr bearing colloids without actinides. The concentration of total particles per liter was categorized as low (7 tests) and medium (2 tests), but the particles did not contain actinides.

Overall Comment: There was no analytical evidence that there was significant actinide solubilization or production of mobile colloids in Portland Cement tests.

ENVIROSTONE

The analytical results from Envirostone show the Pu concentrations were categorized as "very low" (7 tests), "low" (4 tests), and "medium" (1 test; LS-16). LS-16 is perhaps the only test that was on a trend of actinide increase (except for U which was on a definite decrease, (14583 ppb to 182 ppb) with Pu increasing from 208 to 1187 ppb. The Pu concentration of 1187 ppb in LS-16, is the highest of the Envirostone tests but can be considered to be relatively low overall. LS-13, 14, and 15 had added organic solvents that had increased total particles per liter that did contain a significant number of Pu bearing colloids, but these were at relatively low levels. Most of the colloids were Fe bearing, and some were associated with Sr. In general, the Envirostone Brine A tests had 1100-2700 ppm of soluble Ca while the Castile Brine test had 600-780 ppm Ca. The sulfate concentrations of the Brine A tests were 4000-9000 ppm, while the Castile Brine tests were 12000-17000 ppm. The nitrate concentrations all decreased during the test period. And certain tests such as LS-13, 14, and 18 showed very large decreases so that the nitrates were essentially totally destroyed. The destruction of nitrate, an oxidant, to nitrites N_2O and N_2 by chemical, microbial, or radiolytic degradation is significant because the intermediate species are reductants that will maintain a reducing environment during the nitrate destruction process. Nitrous oxide, a gaseous product from the radiolytic degradation of nitrate is very soluble in brine and will promote a reducing condition during the test period. The Envirostone tests were noted for the high starting concentrations of U that in all cases decreased to very low levels at the end of the test period. Np was initially high in LS-15 (7753 ppb), LS-18 (1557 ppb), and LS-21 (5311 ppb), but these three tests ended up at <100 ppb.

Overall Comment: There was no analytical evidence that Envirostone tests resulted in significant solubilization of Pu and other actinides. Except for LS-17 and 18, there was minimal production of Pu bearing colloids, and even LS-17 and 18 had sporadic concentrations on the filter papers. Fe was a very prevalent colloid and Sr was present in most tests for colloids.

PYROCHEMICAL SALTS

The tests with pyrochemical salts had the highest content and concentration of Pu and Am in both what was in the waste and what was solubilized. The concentrations of soluble Pu in the non-pressurized tests were categorized as follows:

Very Low	2 tests (LS-34 and 38)
Low	4 tests (LS-25, 31, 33, and 37)
Medium	3 tests (LS-32, 35, and 39)
High	2 tests (LS-26 and 36)
Very High	1 test (LS-27)

To understand the chemistry that occurred in the pyrochemical salt tests, it is necessary to recognize the difference in the two major pyrochemical salt waste forms, namely, Direct Oxide Reduction (DOR) and Oxygen Sparging (OS).

The waste from the DOR process was obtained from a process that mixed and heated PuO_2 in a salt flux of $CaCl_2$, CaO, and Ca metal in a ceramic crucible made of refractory MgO and 3% Y_2O_3. This mixture was heated up to about 840 °C to convert the PuO_2 to Pu metal. The Pu metal button was removed from the mixture, and for STTP, the crucible, $CaCl_2$, and residual Ca metal was comminuted and became DOR pyrochemical salt waste in LS-25, 26, 27, 28, 29, 30, 35, 36, and 37. The key to this waste is that the $CaCl_2$ is very high leading to a high concentration of Ca and chloride ions.

The waste from the OS process was obtained during the process of purifying impure Pu in a heated NaCl-KCl salt flux by electrodepositing the Pu on the cathode electrode of the electro-refiner. After a pure Pu metal product was electro-deposited on the cathode, some K and Na from the NaCl-KCl mixture were also reduced to metallic Na and K on the cathode. This mixture was sparged with oxygen to oxidize the K and Na metal to the oxide and eventually converted back to the chloride. After removal of the Pu metal, the remainder of the salts became the OS waste stream that was comminuted and used for STTP tests. Some OS experiments also contained $CaCl_2$ from O_2 sparging experiments that had $CaCl_2$ as part of the salt flux.

The pyrochemical salt tests with DOR wastes were very high in $CaCl_2$ and may have had some residual Ca metal or CaO. The OS wastes were very high in KCl and NaCl and may have had some Ca as $CaCl_2$ or CaO.

As part of the preparation for the tests with pyrochemical salt wastes, Brine A and Castile Brine were added to the comminuted waste forms. Brine A is principally $MgCl_2$ but also contains lower quantities of sulfate as sodium sulfate, bromide as NaBr, and Ca chloride and Sr chloride as salts. Castile Brine is primarily NaCl but there is a high concentration of sulfate as $NaSO_4$.

When DOR experiments with very high levels of $CaCl_2$ were mixed with Brine A and Castile Brine, the very high Ca concentrations resulted in precipitation of most of the sulfate as $CaSO_4$ and other Group II cations, such as Ba and Sr sulfates. This would result in DOR pyrochemical salt tests with low sulfate concentrations and very high Ca and chloride concentrations. The concentrations of nitrate in pyrochemical salts were very low for all tests because this is not a part of the waste stream. Also, if any nitrate had been resent, it would be destroyed by heating with Na, K, or $CaCl_2$. The sulfate concentrations in the OS tests that were not so high in $CaCl_2$ except for LS-34 and 38 were as high as expected based on the relative sulfate concentrations in Brine A and Castile Brine. So basically, sulfate was at low concentrations for DOR salt tests and at higher levels of OS salt tests.

Pu sulfate ($Pu(SO_4)_2$) is a strong Pu complex that tends to stabilize Pu in the Pu (IV) oxidation state especially, in a basic medium. However, the absence or very low concentration of sulfate in the DOR tests reduced the potential for stabilization of Pu as Pu (IV) sulfate in these tests. Oxidized forms of Pu as Pu (V) and (VI) were identified in LS-26, 27, 28 and 36. All four of these tests were DOR salt tests with very high calcium and low sulfate concentrations. None of the OS wastes showed oxidized Pu species. Any low concentration of nitrate was quickly destroyed as a source of radiolytic nitrite and N_2O which are both reductants. The very high chloride content in the DOR tests enhances the possibility of oxidation to the Pu (V) and (VI) states in the absence of a stabilizing anion. The presence of Pu bearing colloids or microprecipitates was a characteristic of essentially all the pyrochemical salt tests. The filters from DOR tests had high concentrations of Ca whereas the filters from OS tests had low concentrations of Ca. The filters from DOR tests were all high Pu bearing filters with Sr and sulfate associated with the Pu while filters from OS tests had lower Pu, Sr, and sulfate concentrations. The high concentration of all actinides in LS-27, a DOR experiment with Castile Brine, was surprising initially because no explanation was established for this test. LS-27 had a high Fe concentration (generally 100-200 ppm) and Pu (V) was identified in this test container. The pyrochemical salt tests were characterized by the absence of Fe in most of the filters even though the presence of soluble Fe in many tests was significant. The high radiolytic activity in the pyrochemical salt tests could have produced sufficient oxidants to oxidize the Fe^{2+} to the Fe^{3+} state which is much more insoluble and will not act as a reductant in the chemistry of soluble and insoluble Fe.

Liter-scale test number 27 was anomalous in that this test container had high concentrations of all actinides from the start of the experiment. This can be explained by the D&D observation that in LS-27 (and LS-26) there was no solidified or cemented mass and all the comminuted waste was available to all the brine throughout the test period. This was not the case in most pyrochemical salt tests. Soluble Fe was high in LS-27 but very low in LS-26 which had high levels of Pu (VI). Liter-scale tests LS-31, 32, and 33 were oxygen-sparging tests that had added bentonite that may have been the reason for the lower concentrations of Pu in these tests. LS-31 had a definite trend up from 1.4 ppb at the start to 275 ppb near the end of the test period. LS-32 started very low (3.9 ppb) and peaked at 697 ppb half-way through the test and then trended down to 156 ppb near the end of the test. Liter scale test LS-33 in Castile Brine started very low at 2.7 ppb and leveled off at about 135 ppb through the end of the test period. Liter-scale tests

LS-34, 35, and 36 contained added chelators and calcium hydroxide. LS-34 was an oxygen-sparging test while the other two tests with chelators and $Ca(OH)_2$ were Direct Oxide Reduction tests with very high levels of calcium (9000, 80000, and 80000 ppm, respectively). LS-34 and 35 had very high levels of Mg while LS-36 had very low levels of Mg. The high Ca and Mg in LS-34 and 35 appeared to mitigate the solubilizing effect of the chelators, but L36 had very high levels of solubilized Pu. The combination of low Mg content and very high levels of chloride allowed the chelators to be effective in solubilizing actinides in LS-36. The combination of high Ca, Mg, and chloride did not enhance solubilization of actinides by the chelators.

The addition of Am-241 to LS-37, 38, and 39 did not seem to enhance solubilization of Pu significantly.

Overall Comment: There were several unknown factors about the chemical and radiolytic behavior of the pyrochemical salt wastes including the presence of Pu (VI) in LS-26 and 28. However, a comprehensive examination of the test data including observations from the D&D process has led to explanations of why these tests acted as they did. It is now understandable why the Direct Oxide Reduction tests were the only tests that had oxidized forms of Pu and why the oxygen sparging tests did not. The overall impact of these tests experiments has shown that the presence of oxidized forms of Pu is limited to a very small percentage of wastes under very specific conditions that are rather unique. The lessons learned from the behavior and chemistry of DOR and OS pyrochemical waste forms can be extended to mitigate the oxidative potential of other high level wastes including high Pu-Am content oxide residues. The effect of chelators in LS-34 (OS and Brine A), LS-35 (DOR and Brine A), and LS-36 (DOR and Castile Brine) provides a diverse set of conditions to establish that LS-34 and 35 did not significantly solubilize Pu and other actinides whereas LS-36 (OS and Castile Brine) showed the effectiveness of chelators solubilizing Pu under the conditions of high Ca and chloride and low Mg.

PRESSURIZED TESTS

The STTP pressurized liter-scale tests were conducted in specifically designed containers with a 2-liter volume and a pressure of 60 bars (870 psig) of CO_2. The 6 pressurized tests consisted of three Portland Cement tests and three pyrochemical salt tests. The pyrochemical salt tests were all from the Direct Oxide Reduction (DOR) processes conducted at TA-55.

Portland Cement

The three Portland Cement tests contained different amounts of waste; LS-4 (204 g), LS-5 (612 g) and LS-6 (907 g). The brine to solid ratio was 10:1. 3:1, and 2:1, respectively. The Pu concentration in LS-4 started very low (1.6 ppb) and increased with each sampling period to 255 ppb; LS-5 did not have a trend and varied to 184 ppb; and LS-6 had an up and down trend with a maximum of 638 ppb. The U concentration was about 10000 ppb, 500 ppb, and 4000 ppb, respectively. There were very low concentrations of all other actinides. The pcH range was 7.2-7.4, 7.0-7.4, and 7.5-7.9 for the three tests, respectively. There were no filters with Pu colloids or microprecipitates. There was a medium level of particles per liter in the three tests. The three different quantities of wastes did not seem to have an impact on these tests.

Overall Comment: The pressurized Portland Cement tests showed that there was essentially no significant solubilization of actinides other than U. Even with 780 psig of CO_2, the pcH remained above pcH 7.0 for all the tests. There were no mobile Pu bearing colloids identified during the test period.

Pyrochemical Salts

The three pressurized pyrochemical salt tests, LS-28, 29, and 30, contained 920 g, 920 g, and 902 g of Direct Oxide Reduction process waste, respectively. The brine to solid ratio was 2:1 for all three tests. LS-28 and LS-29 were both Brine A experiments and had very high levels of Pu concentrations. LS-28 contained one of the highest inventories of Pu on the STTP (10.61 g) and LS-29 was also very high with 4.34 g. LS-30 had a considerably lower inventory of 2.01 g. LS-30 was a DOR waste experiment with Castile Brine at a pcH range of 5.9-6.6. Generally, Castile Brine experiments are low Ca and low Mg experiments, but LS-30 was a high Ca, high Mg experiment with a Pu concentration that leveled off at about 1000 ppb with no apparent trend.

LS-29 was a DOR waste experiment with Brine A at a pcH range on the acid side of neutral of 4.7 to 5.7. This test had a very high content of Ca (180000 ppm) as $CaCl_2$ and about 22000 ppm of Mg. The high Ca concentration resulted in a low sulfate concentration. The Pu concentration increased from 161 ppb to 8444 ppb as the pcH dropped to 4.73.

LS-28 become one of the most notorious experiments of the STTP matrix because it had a very high Pu inventory with a high soluble Pu concentration that was rapidly increasing. MgO was added to this test in February 1997, and the pcH increased from 4.48 to 7.70, and the concentrations of actinides and Fe decreased substantially. However, in time, actinides and Fe concentrations increased rather rapidly, and Pu (VI) was identified on May 17, 1999 when the Pu concentration achieved a peak of 197,984 ppb. All other actinides increased in concentration during the same period. LS-28 was a DOR experiment with Brine A with a very high Ca concentration (120,000 ppm) and Mg concentration (16,000 ppm) and a very low concentration of sulfate (60 ppm) and nitrate (21 ppm). With a low sulfate and nitrate concentration and a very high Ca and chloride concentration as $CaCl_2$, the Pu in LS-28 was susceptible to oxidation. The question concerning LS-28 was whether the addition of MgO enhanced the potential for oxidation of Pu.

The presence of mobile colloids or microprecipitates was evident in essentially all filters. The Pu in the filters was associated with $SrSO_4$ and was less associated with Fe precipitates. The number of particles per liter of brine in the 3 pressurized liter-scale tests was very high for LS-28, high for LS-29, and medium for LS-30. The addition of MgO to a brine pool in LS-28 resulted in precipitation of the MgO as sorel cement that blocked the test container and about half-way down and effectively divided it into two parts.

Overall Comment: The pressurized tests with pyrochemical salts (DOR) showed that Pu was solubilized in the three tests. The buffer capacity of Portland cement to maintain the pcH in the basic range was not characteristic of pyrochemical salt wastes as had been observed in the Portland Cement tests. LS-28 had the highest concentration of soluble Pu after LS-27. It had very high concentrations of Ca and chloride as $CaCl_2$ and very low concentrations of sulfate and nitrate. The Fe soluble concentration had increased from 19 to 165 ppm prior to addition of MgO, but Pu (VI) was identified during a period of 1.1 to 2.5 ppm Fe. LS-28 was the only test other than LS-26 that showed Pu (VI). It was the only test with added MgO. The MgO was solidified by the Brine A in such a way that there was no communication of the top portion of brine with the brine near the bottom of the test containers. This isolation led to a small brine pool near the top of the test container that was radiolytically very active and with other chemical additions resulted in the formation of oxidized Pu as Pu (VI). The pressurized tests with pyrochemical salts did have Pu colloids available for transport.

VI. Commentary on STTP Drum-Scale Tests

The 15 drum-scale tests utilized the total content from individual drums for each test. The 15 tests consisted of four sets of three drums of combustible wastes (TRUCON 116) and one set of massive metal tests (TRUCON 117). The drum-scale tests with heterogeneous or debris waste including the three massive metal tests were all categorized as tests with “very low” levels of soluble Pu except for the tests with added chelators and $Ca(OH)_2$ were categorized as “medium” wastes based on results from the tests. The first four sets of drum-scale tests were designed to study the chemical and radiolytic degradation effects of cellulose and carbonaceous materials in TRU wastes immersed in brine and how the degradation intermediates or products might influence the concentrations of soluble or colloidal forms of actinides. The last set of experiments in the drum-scale matrix was to determine the effects of massive metal on the chemistry and concentration of actinides in brine. Drum-scale tests DS-1, 2, and 3 were tests with combustibles in Brine A (DS-1 and 2) and Castile Brine (DS-3). Drum-scale tests DS-4, 5, and 6 were tests with combustibles with added bentonite. DS-4 and 5 in Brine A had 10 kg of brine-equilibrated bentonite, while DS-6 in Castile Brine had 10 kg of bentonite that was not brine-equilibrated. DS-7, 8, and 9 were tests with combustible wastes with added chelators without $Ca(OH)_2$. The five chelators added to DS-7, 8, and 9 at a concentration of about 160 ppm were:

1) Acetamide,
2) Sodium acetate,
3) Trisodium citrate dihydrate,
4) Oxalic acid dihydrate, and
5) Ammonium thiocyanate.

Ascorbic acid was added to the liter-scale tests as a chelator but was not added to the drum-scale tests. Calcium hydroxide was added to the liter-scale tests to assure the pcH was basic so all the chelators would dissolve.

DS-10, 11, and 12 were tests with combustibles with added $NaNO_3$ and NaH_2PO_4 which were to be nutrients for the microbial inoculum added to the test containers. There were 159 g of added $NaNO_3$ and 258 g of added NaH_2PO_4. DS-13, 14, and 15 were massive metal tests in Brine A and Castile Brine.

The drum-scale tests with combustible waste only (DS-1, 2, and 3) gave results that showed essentially no solubilization of Pu for all three tests. DS-1 had <10 ppb Pu; DS-2 had <30 ppb Pu; and DS-3 had <10 ppb Pu for the entire test period. The pcH ranged from 7.0-8.0 for all three tests. There was no Pu bearing colloids or microprecipitates in DS-1, 2, or 3 and also no Sr bearing colloids. Fe was prevalent in high quantities in essentially all filters but Pu was not carried with the Fe.

The drum-scale tests with combustible waste with added bentonite (DS-4, 5, and 6) showed essentially no solubilization of actinides (generally <10 ppb) at a pcH range of 7.0-7.7. There did not appear to be any difference in the chemistry of the brine-equilibrated and non-brine-equilibrated bentonite. The non-brine-equilibrated bentonite in Castile Brine generally showed <10 ppb in all actinides while the brine-equilibrated tests (DS-4 and 5) showed some solubilization of U and Np. There was essentially no Pu bearing colloids or microprecipitates in the filters from these tests.

The drum-scale tests with combustibles with added chelators and calcium hydroxide (DS-7, 8, and 9) showed great solubilization of all actinides throughout the test period. All the actinides were solubilized to high levels at the beginning of the tests and remained at high levels for the entire test period. The major decrease in concentration for all actinides in DS-7, 8, and 9 occurred when phosphate was added to these drum-scale tests. The added phosphate was quickly reduced in concentration due to precipitates of elemental phosphates. The presence of mobile colloids or microprecipitates was very evident in the drum-scale tests with added chelators in that most of the filters contained Pu bearing colloids. Fe bearing colloids were at lower levels than the rest of the drum-scale tests. Phosphate additions were made to the drum-scale tests with chelators to reduce the actinide concentrations for waste disposal purposes. Drum-scale 7 was an experiment in Brine A and chelators that contained 700 ppm Ca, 32000 ppm Mg, 4700 ppm sulfate, and 33 ppm nitrate. The Pu concentration was generally high for most actinides. Drum-scale test 8 was a Brine A experiment with chelators that contained 800 ppm Ca, 32000 ppm Mg, 48000 ppm sulfate, and 836 ppm nitrate. The Pu concentration peaked at 4310 ppb, and all other actinides were very high as well. Drum-scale 9 was a Castile Brine experiment with chelators that contained 600 ppm Ca, 700 ppm Mg, 17000 ppm sulfate, and 540 ppm nitrate. The Pu concentration peaked at 2667 ppb, and all other actinides were very high as well.

The drum-scale tests with combustible wastes with added sodium nitrate and sodium dihydrogen phosphate showed the effect of three major processes on the chemistry of these wastes.

The addition of phosphate to the drums reduced and maintained actinides at a very low level. However, the phosphate tended to complex all cations and precipitated and disappeared within a few weeks.

The addition of nitrate to these tests showed a very interesting process that was later found to exist in most liter-scale and drum-scale tests. The nitrate in DS-10 and 11 (Brine A) essentially disappeared due to either radiolytic, chemical, or microbial degradation or a combination of all three processes. The degradation products of nitrate, an oxidizing agent, are nitrites and N_2O, which are reductants. An associated by-product is N_2 which has no chemical effect. The addition of nitrates and phosphates as nutrients for the microbial inoculum added to the drums was not conclusive. There did not seem to be significant microbial activity that affected the chemistry of the tests other than the reduction of nitrate. The drum-scale tests with added nitrate and phosphate did show a significant population of filters with Pu bearing colloids or microprecipitates. There was a very large population of Fe bearing colloids. There was essentially no Sr bearing colloidal particles.

The drum-scale tests with massive metals were conducted to establish the effect of massive metals on the chemistry of the actinides in brine and to establish the rate of corrosion of massive metals in brine. DS-13, 14, and 15 showed essentially no solubilization of Pu during the entire test period. There was some solubilization of U and Np in all three tests but at low levels. The pcH dropped from 8.1 to 5.95 in DS-13 and from 7.78 to 6.71 in DS-14 during the test period. DS-15 in Castile Brine did not show a similar decrease in pcH (7.9-7.7). The Fe concentrations in the Brine A tests from DS-13 increased to a concentration of 558 ppm. In DS-14, the Fe concentration increased to 110 ppm during the test period. DS-15 in Castile Brine did not show any solubilization of Fe (<1 ppm) for the entire test period. There was a reduced level of Pu bearing colloids in the three tests and the Fe bearing colloids were very high as could be expected.

VII. Brine Replacement During Sampling

Samples of about 40-50 ml of brine were periodically taken from each test container in the STTP. Some samples were less in volume because of plugging of the sampling syringe needle that occurred during sampling and some were sampled fewer times during the test period because of the difficulty in sampling. Pressurized liter-scale samples were only sampled 7 or 8 times during the test period and the sample volume varied from 10 to 30 ml. There was no replacement brine added to the pressurized tests. A maximum of about 27 samples of brine was taken from each of the non-pressurized test containers and the volume of sample extracted was replaced with fresh Brine A or Castile brine as appropriate. This means that a maximum of about (50) (27) = 1350 ml of brine was sampled from an estimated volume of about 2,500 ml or about 54%. So the soluble contents of the waste such as nitrate would be diluted by 54% by the replacement brine. However, the soluble constituents in the brine would be replenished by the replacement brine and any constituents that precipitated early in the test would be continually replaced by the fresh brine.

VIII. Addition of Actinides to STTP Test Containers

The waste streams added to the STTP test containers were all from the Los Alamos National Laboratory inventory of wastes. The criteria for waste drums to be used for the STTP matrix is that each waste drum must contain at least 5 grams of Pu. ^{241}Am should accompany the total Pu but a criteria is not established for Am. There is no criteria to limit the quantity of ^{240}Pu and ^{241}Pu. There is no need to include waste containing ^{238}Pu because of the added difficulty in handling, sampling, and analyzing samples with the very high radioactivity levels of ^{238}Pu. The chemical effects expected to result from ^{238}Pu in the wastes will be induced by addition of about 75 mg of ^{241}Am to six different liter-scale test containers. Because the WIPP is expected to have wastes contaminated with Th, U, and Np, all the liter-scale and drum-scale tests are spiked with soluble salts of these actinides. Neodymium was also added to select test containers as a chemical analogue or surrogate for ^{241}Am.

The following is a list and description of the added actinides and neodymium:

Neodymium

Neodymium was added as $NdCl_3$ directly to the test containers at the WCRRF. The glass vial containing the $NdCl_3$ was not added to the test container.

Thorium

Thorium was added as a water solution of $Th(NO_3)_4 \cdot 4H_2O$ to a glass vial containing other actinides. The glass vial was placed in each test container. The Th was 99.99% pure and was present as ^{232}Th.

Uranium

Uranium was added as a nitric acid solution from a high purity specimen of depleted U metal (100%). The metal was dissolved in 16 N HNO_3 heated with a trace of HF. An aliquot of the U solution was placed in a glass vial containing other actinides. The glass vial was placed in each test container. The U was ^{238}U.

Neptunium

Neptunium was added as a Np salt solution after dissolution of NpO_2 by a sealed reflux dissolution system. Concentrated HCl with a few drops of HNO_3 and HF was used to dissolve the NpO_2. Aliquots of the dissolved oxide were added to glass vials containing other actinides. An aliquot of the solution was placed in a glass vial with other actinides. The glass vial was placed in each test container. The Np was ^{237}Np. The Np solution from the dissolved NpO_2 was added to each liter-scale test container, the Np added to the drum-scale tests was dissolved form specimens of Np metal. The metal was dissolved in concentrated HCl with a few drops of HNO_3 and HF. The 15 specimens of Np metal weighed 5 gm.

Americium

Americium was added as an Am solution after dissolution of AmO_2 in 0.5 ml 12 N HCl with two drops 16 N HNO_3 and two drops of HF. An aliquot of the solution was placed in a glass vial and evaporated to damp dryness. Each of the six glass vials had a radiation reading of about 800 mR/hr β, γ at contact. The AmO_2 was about 82.2% Am and remainder Pu. The vials with Am were added to each select test container along with the vials containing the other actinides.

Table 11. Actinides Added to STTP Liter-Scale Test Containers

Test Containers	*Nd (mg)* *	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	45	75	75	75	0
4, 5, 6	30	75	75	75	0
7, 8, 9	45	75	75	75	0
10, 11, 12	0	75	75	75	75
13, 14, 15	45	75	75	75	0
16, 17, 18	45	75	75	75	0
19, 20, 21	45	75	75	75	0
22, 23, 24	45	75	75	75	0
25, 26, 27	45	75	75	75	0
28, 29, 30	30	75	75	75	0
31, 32, 33	45	75	75	75	0
34, 35, 36	45	75	75	75	0
37, 38, 39	0	75	75	75	75

[*] Nd added as $NdCl_3$ for a concentration of about 15 mg/L for nonpressurized tests, assumption of 3L; 15 mg/L for pressurized tests, assumption of 2L.

Table 12. Actinides Added to STTP Drum-Scale Test Containers

Test Containers	*Nd (mg)* *	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	3.69	5	5	5	0
4, 5, 6	3.69	5	5	5	0
7, 8, 9	3.69	5	5	5	0
10, 11, 12	3.69	5	5	5	0
13, 14, 15	3.69	5	5	5	0

[*] Nd added as $NdCl_3$ for a concentration of about 24.37 mg/L, assuming 151.4 L (40 gal).

IX. Addition of Chelators to STTP Tests

The effect of chelators on chemicals with complexing functional groups was expected to be present in a portion of the wastes destined for the WIPP. Most of these complexing agents are expected to be in the combustible or debris waste but some complexing agents could be solidified in the Envirostone waste so to study the impact of chelators on the chemistry of the tests, a set of complexing agents were added to both the homogeneous wastes (pyrochemical salt tests LS-34,35, and 36) and the heterogeneous wastes (DS-7, 8, and 9). The chelators were the same for the two wastes except the pyrochemical salt waste tests had added ascorbate, a strong reducing agent, and the drum-scale tests did not have ascorbate. The chelators were added in acid or neutral salt form to a separate vessel and dissolved in a slightly basic medium prior to addition to the 3 liter-scale tests and 3 drum-scale tests. The chelators, especially citrate, were expected to solubilize actinides that otherwise might not have solubilized in the basic medium in the test containers.

Calculation of Concentration of Chelators in STTP Liter and Drum-Scale Test Containers

Liter-scale test containers with added chelators and 96.2 gm of $Ca(OH)_2$ are:

LS-34 Oxygen sparging pyrochemical salts
LS-35 Direct oxide reduction pyrochemical salts
LS-36 Direct oxide reduction pyrochemical salts

The concentration of chelators added to the liter-scale test containers assume a brine volume of 2000 ml.

The drum-scale containers with added chelators are DS-7, 8, and 9, which are loaded with TRUCON Code 116/216, combustibles. The concentration of chelators added to the drum-scale test containers assume a brine volume of 200L.

Table 13. Chelators Added to STTP Tests:

Liter-Scale Tests

Chelator	*LS-34 (mg)*	*LS-35 (mg)*	*LS-36 (mg)*
Acetamide	200	200	202
Sodium Acetate	277	276	277
Trisodium Citrate Dihydrate	308	307	311
Oxalic Acid Dihydrate	285	288	286
Ascorbic Acid	201	202	198
Ammonium Thiocyanate	295	294	295

Continued on next page

Drum-Scale Tests

Chelator	***DS-7 (mg)***	***DS-8 (mg)***	***DS-9 (mg)***
Acetamide	30.2	30.2	30.3
Sodium Acetate	42.0	42.0	42.0
Trisodium Citrate Dihydrate	46.6	46.6	46.6
Oxalic Acid Dihydrate	43.3	43.3	43.3
Ammonium Thiocyanate	44.4	44.4	44.4

Calculations for Liter-Scale Test Containers

Acetamide

$$\frac{(200\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 100\text{ ppm}$$

Sodium Acetate

$$\frac{(277\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 139\text{ ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(308\text{ mg})(1000\text{ ug/ml})}{2000\text{ ml}} = 154\text{ ppm}$$

Oxalic Acid Dihydrate

$$\frac{(285\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 143\text{ ppm}$$

Ascorbic Acid

$$\frac{(201\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 101\text{ ppm}$$

Ammonium Thiocyanate

$$\frac{(295\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 148\text{ ppm}$$

Calculations for Drum-Scale Test Containers

Acetamide

$$\frac{(30.2\ \text{gm})(1000\ \text{mg/gm})}{200\ \text{L}} = 151\ \text{ppm}$$

Sodium Acetate

$$\frac{(42.0\ \text{gm})(1000\ \text{mg/gm})}{200\ \text{L}} = 210\ \text{ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(46.6\ \text{gm})(1000\ \text{mg/gm})}{200\ \text{L}} = 233\ \text{ppm}$$

Oxalic Acid Dihydrate

$$\frac{(43.3\ \text{gm})(1000\ \text{mg/gm})}{200\ \text{L}} = 217\ \text{ppm}$$

Ammonium Thiocyanate

$$\frac{(44.4\ \text{gm})(1000\ \text{mg/gm})}{200\ \text{L}} = 222\ \text{ppm}$$

X. Addition of Fe to STTP Test Containers

An important parameter that could have a significant effect on the Redox potential in the repository is the presence of iron from the mild steel 55-gallon drums containing the waste. The STTP experiments were designed to be conducted in Ti vessels because high ionic strength brine was expected to dissolve to different degrees many of the proposed containment vessels that might be used to contain the experiments with brine at 30 °C for up to 5 years. Because titanium was not dissolved by the synthetic Brine A and Castile Brine formulations, a means of trying to determine the effect of Fe in the mild steel drums had to be tested. Consequently, all test containers were fabricated from Ti metal and a high surface area mesh was added to each test to simulate the amount of Fe that would be present if the waste were in a 55-gallon drum. The corrodable surface area in a 55-gallon drum was calculated to be about 4 m^2. To simulate this surface area of Fe, an Fe mesh with wire strands of a small diameter and therefore a large surface area was procured and prepared by Sandia National Laboratory for addition to the STTP test containers. The procured material was a No. 10 mesh made with 20 gauge wire and procured from Aggregate and Mining Supply Company of Albuquerque, New Mexico. The material came in rolls three feet wide and had a nominal analyses of elements as follows:

Fe	98.453 %
C	0.679 %
Mn	0.620 %
Si	0.230 %
P	0.012 %
S	0.006 %

It was determined that 2748 in^2 of this mesh would provide about 4 m^2 of surface area in a 55-gallon or 210-liter test drum. For the liter-scale vessels, about 39.25 in^2 would be required. The Fe mesh was cut in approximately 1.25 inch width and 30.0 inch length sections, with a target mass of 102.01 g selected to provide the necessary surface area for the experiments in three liter-scale test containers. This amounted to 39.25 in^2 with an average weight to surface area ratio of 2.599 g/in^2. These cut samples were packaged in 4 ounce Qorpak polypropylene jars with one inch diameter holes cut on the top and bottom of each jar to allow inflow and outflow of brine.

The Fe mesh for the 6 pressurized test containers with a two-liter volume were cut to a target mass of about 68 g and placed in 2-ounce Qorpak polyethylene jars.

The Fe mesh prepared and packaged for the drum-scale tests were cut into 6 pieces that were 36 inches by 12 inches plus one additional piece that was 12 inches by 12.9 inches for a target surface of 2748 square inches. The target weight of Fe mesh was about 7142 g to achieve about 4 m^2 of corrodable steel surface. The accumulated Fe mesh sections were placed in a 5 gallon polyethylene bucket that had 5-inch diameter holes cut in the top and bottom to allow flow of brine through the Fe mesh.

A spectroscopic analysis of the Fe mesh with a Wavelength Dispersive X-ray Fluorescence Spectrometer showed an average constituent analysis of five wires, giving the following data:

Fe	95.4 %
Zn	1.5 %
P	1.43 %
Mn	1.28 %
Si	0.29 %
Cr	0.14 %
C	not analyzed

The presence of zinc was disturbing because it might be a galvanizing constituent or a protective layer. A surface analysis was performed to determine the property of the zinc in the wire by Auger Electron Spectroscopy. The zinc was determined to be a loose protective layer that was discontinuous over the Fe based wire strands. Corrosion on the unprotected Fe strands was visible where the zinc layer was very thin (~200 angstroms) and did not provide total protection of the wire.

XI. Addition of Mixed Inoculum

A batch of mixed inoculum was prepared for addition to each of the 39 liter-scale tests and 15 drum-scale tests. The inoculum consisted of a mixture of ingredients sampled from the WIPP site that contained a diverse mixture of halotolerant microorganisms that survive in the surfacial and supersaline conditions of the WIPP environments. The mixed inoculum batch consisted of the following components.

Table 14. Composition of Mixed Inoculum and Amounts Added to STTP Tests

Component	Quantity %	Liters/drum
Lake Brine and sediment mixture	20 %	1.06
Muck-pile salt solution	30 %	1.59
G-seep Brine	50 %	2.65
	Total	5.30

The inoculum solution was to be added to the test containers to establish and maintain an anaerobic environment. The anaerobic environment was established by purging the mixed inoculum for 30 minutes with N_2. The mixed inoculum was continually mixed and maintained under a N_2 atmosphere prior to addition to the liter-scale and drum-scale tests. About 100-150 ml of inoculum was added to the liter-scale tests, and about 5.3 liters was added to the drum-scale tests. For the pressurized liter-scale tests, 80-100 ml of inoculum was added to each of the 6 pressurized tests. The quantity of chemical reducing agents added as part of the inoculum injection was not known.

XII. Addition of Nitrate/Phosphate; Effect of Brine Type on Nitrate Reduction

Nitrate was added to three drum-scale test containers along with phosphate as nutrients for the added microbes. Nitrate was added as sodium nitrate ($NaNO_3$) and phosphate was added as sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$). Approximately 159 gm of $NaNO_3$ and 258 gm of $NaH_2PO_4 \cdot H_2O$ was added to each of the three drums. Assuming 50 gallons of brine in each drum, that would give a concentration of 159000 mg/189.25 liters = 840 mg/liter of $NaNO_3$ and 613 mg/liter (613 ppm) of added nitrates. The concentration of nitrate in the waste prior to addition of the nitrate injection is unknown. Nitrate could be expected to be totally soluble in the tests.

Table 15. Reduction of Nitrate in STTP Tests

	DS-10	**DS-11**	**DS-12**
Select Dates	**Nitrate, ppm**	**Nitrate, ppm**	**Nitrate, ppm**
06/19/95	683	441	620
08/21/95	620	325	620
10/10/95	584	260	570
04/15/96	545	31	482
01/21/97	334	**5**	542
06/16/97	103	**6**	477
06/22/98	**20**	**<5**	571
02/08/99	**8**	**<5**	554

The trends apparent in the above data show that nitrate was essentially totally destroyed in the Brine A experiments (DS-10 and 11) and was not affected in the Castile Brine experiments (DS-12). The major difference in the constituents in the Brine A and Castile Brine tests is that there is ~ 30,000 ppm Mg in the Brine A experiments (DS-10, 11) and only ~ 600 ppm Mg in the Castile Brine experiments (DS-12). Another difference is that the sulfate concentration in DS-10 and 11 was ~ 5000 ppm whereas DS-12 (Castile Brine) has a sulfate concentration of 17,000 ppm. It appears that the reduction in the nitrate concentration in the Brine A experiments could be due to lower sulfate concentration or, most likely, the much higher Mg concentration in DS-10 and 11. The mechanism responsible for this reduction may be chemical, radiochemical, or microbial but the overall assessment of the data points to a radiolytic/chemical reduction. There is no explanation why microbes would not be effective in DS-12 and be very effective in DS-10 and 11 for total destruction of nitrate in the brine. The Pu loading for the three drums were quite similar as below.

Table 16. Pu Loading vs. Soluble Pu Concentration

	DS-10	DS-11	DS-12
Pu Loading	16.44 gm	16.45 gm	16.70 gm
Pu Concentration Potential	* 87,000 ppb	87,000 ppb	88,000 ppb
Soluble Pu Concentration Measured	0-30 ppb	<5 ppb	<5 ppb

* Assumes 50 gal (189.25 Liter) of Brine in test

The above data shows that if the reduction in nitrate was a result of radiolysis that the radiolysis process must have been from alpha particles in the waste that were not dissolved or that dissolved and reprecipitated. If the Pu oxides did not dissolve, they could still be present in the waste as dispersed oxides or be released as dispersed oxides or be released and settled to the bottom of the drum. If the Pu contaminants dissolved and precipitated as hydrated Pu oxide, the precipitate would have settled to the bottom of the drum. Rotation of the drum contents would have enhanced settling of the Pu oxide and precipitates to the bottom of the drum. Any radiolytic degradation of nitrate would have to occur at the bottom of the drum or from Pu particles that are dispersed in the waste.

Assessing the data that shows the destruction of nitrate in the drum-scale tests DS-10 and 11 with Brine A indicates that Mg could have played a key role in enhancing this reaction. The actual mechanism of Mg as an energy transfer agent of radiolytic processes is not known.

The other instance in the STTP where nitrate was essentially totally destroyed was in LS tests with added organics such as LS-13 and 14 (Brine A experiments and less prominent in LS-15, Castile Brine experiments).

XIII. Pu (V) and (VI) in the STTP; An Explanation

The pyrochemical salt tests of the STTP consisted of two principal waste streams from pyrochemical salt processes at TA-55. The two major pyrochemical salt processes were Direct Oxide Reduction (DOR) and Oxygen Sparging (OS). The two waste streams had significantly different processes that yielded parameters that impacted the chemistry of the two different sets of STTP tests with DOR and OS wastes.

The waste from a typical DOR run was to add approximately 200 gm of PuO_2 to a refractory MgO – 3% Y_2O_3 crucible with about 1000 gm of $CaCl_2$ salt and 85 gm of Ca metal. The furnace was heated to ~ 840 °C and the PuO_2 was reduced to Pu metal while the Ca was oxidized to CaO. The Pu metal button would accumulate at the bottom of the crucible and was removed for further processing. The crucible with $CaCl_2$ salts and residual calcium metal and unreacted PuO_2 or $PuCl_3$ would be the DOR waste stream that was comminuted for the STTP DOR experiments. An important parameter was that the waste had a high concentration of $CaCl_{2,}$ high concentrations of Pu salts, and a low concentration of nitrate because nitrate would be destroyed during the high temperature process step with $CaCl_2$ and Ca. The high Ca and chloride concentrations were to be important chemical parameters in the chemistry of the STTP pyrochemical salt tests.

The waste from the OS process was generated during the process of purifying the Pu metal by electrodeposition with a cathode-anode electrode immersed in a heated NaCl-KCl salt flux. During the electrolytic process, NaCl and KCl was also reduced at the cathode to yield Na and K metal. This heated mixture was sparged with O_2 to convert the K and Na to K_2O and Na_2O and eventually the K_2O and Na_2O was converted back to KCl and NaCl.

The salt tests with DOR were characterized by high concentrations of $CaCl_2$ that may have had some residual Ca metal or CaO. The OS wastes were characterized by high concentrations of NaCl and KCl and may have had some K_2O, Na_2O, and CaO.

Preparation of the salt wastes for the STTP at the LANL Waste Characterization, Reduction and Repackaging Facility consisted of comminution of the crucibles, salts, and oxides and weighing out ~ 1320 gm of waste (920 gm for pressurized tests LS-28, 29, and 30; 880 gm for the tests with chelators, LS-34, 35, and 36). Brine was added to the test containers loaded with pyrochemical salt wastes and additives were added prior to final placement and fixing of the lid. A visible reaction of the Ca or CaO was noted during the addition of brine to some of the test containers. Later, a microbial inoculum was added to the sealed test containers at the CMR Building where the tests were to be conducted.

Brine A was added to the two test containers in each set of three tests and Castile Brine was added to the remaining test container from each set so a total of 10 tests had Brine A and 5 tests had Castile Brine. Brine A primarily consists of $MgCl_2$, NaCl, and KCl with some $NaSO_4$, $CaCl_2$, and NaBr. A small amount of $SrCl_2$ and $FeCl_2$ is included in the Brine A experiments. Castile Brine primarily consists of NaCl, $NaSO_4$, KCl, and $MgCl_2$. Lesser amounts of $CaCl_2$ and NaBr are added to the Castile Brine experiments.

The pyrochemical salt tests with Brine A and Castile Brine contain the following soluble constituents contributed by addition of brine.

Table 17. Total Constituent Content in Brine A and Castile Brine Tests

	Brine A			Castile Brine		
Brine Constituent	**Total gm/2.5L**	**Salt ppm**	**Element ppm**	**Total gm/2.5L**	**Salt ppm**	**Element ppm**
$MgCl_2 \cdot 6H_2O$	730	292,000	3,5000	9.7	3880	464
NaCl	250	100,000	40,000	654	261,600	103,000
KCl	143	57,200	30,000	18	7,200	3,775
$NaSO_4$	15.5	6,200	5,200	59.3	23,720	20,000
$CaCl_2$	4.2	1,680	607	3.3	3,300	1,200
NaBr	1.3	520	116	2.8	1120	250
$SrCl_2$	0.038	15	8	0	0	0
$FeCl_2$	0.031	12	5	0	0	0

NOTE: The pressurized tests (LS-28, 29, 30) contain about 1500 ml of brine or ~ 60% of the constituents in the non-pressurized tests.

It is evident that the addition of Ca to the DOR pyrochemical salt tests from brine is negligible relative to the Ca added as $CaCl_2$ in the waste. However, the amount of Mg added to each DOR test by the brine A is significant; castile brine tests contained low concentrations of Mg as does the brine. The sulfate concentrations of all tests was very low because of the high Ca content which resulted in precipitation of the sulfate. The K_{sp} for $CaSO_4$ is 7.1×10^{-5}.

The Ca ion concentration in DOR tests varied from 2-4 molar (80,000 to 160,000 ppm). The sulfate concentration in Castile Brine tests due to the brine was ~ 20,000 ppm and about 5,200 ppm in brine A tests. The sulfate concentration in OS tests was generally 5,000-16,000 except when higher Ca concentrations reduced the sulfate to lower concentrations such as LS-38 with a Ca concentration of 60,000 ppm.

Typically, the DOR tests with high Ca ion concentrations precipitated the sulfate to yield tests with sulfate concentrations that were generally less than 200 ppm from a beginning Castile brine concentration of 20,000 ppm and Brine A test concentration of 5,200 ppm.

One of the strongest anionic complexes for Pu in both acid and basic solution is fluoride. The STTP Portland cement tests had fluoride concentrations from 0-40 ppm depending on the test and the Envirostone tests contained fluoride concentrations from 0-250 ppm. The Pyrochemical salt tests contained fluoride concentrations from 0-325 ppm and many of the tests showed a reduction in the concentration of fluoride with time.

Table 18. Fluoride and Fe Concentrations in Pyrochemical Salt Tests

ID	Characteristic	Range of F^-, ppm	pcH	Fe Concentration
25	DOR	50-40	7.8-8.1	<1-6
26	DOR	65-45	7.8-8.1	<1-4
27	DOR, Castile	**39-5**	10.7-11.2	20-240
28	DOR, CO_2	80-70	4.7-7.7	20-165
29	DOR, CO_2	70-80	4.7-5.1	50-1468
30	DOR, CO_2,, Castile	12-20	5.9-6.3	1967-9
31	OS, Bentonite	<10	8.7-9.0	0
32	OS, Bentonite	<10	8.7-9.0	0
33	OS, Bentonite, Castile	<10	9.5-9.8	0
34	OS, Chelators	**325-5**	8.7-9.1	0
35	DOR, Chelators	60-25	8.1-8.3	0
36	DOR, Chelators	**22-2**	11.1-11.4	30-103
37	DOR, ^{241}Am	90-34	7.6-8.0	1-5
38	OS, ^{241}Am	30-17	7.7-8.0	0
39	OS, ^{241}Am, castile	**<10**	9.4-9.8	0

The reduction in fluoride concentration appeared to be most evident in tests with a pcH > 9.0. Castile Brine tests with higher pcH (except the pressurized tests) resulted in reduction of fluoride down to <10 ppm. Bentonite, a clay composed of montmorillonite and beidelite minerals, was effective in eliminating fluoride after the beginning of the test. The high Al content of montmorillonite could be the active agent that complexed fluoride because fluoride has a high affinity (stability constant) for Al at neutral and basic pH.

The concentration of Fe in the pyrochemical salt tests may seem to be sporadic but there is a pattern of chemistry that emerges when the Fe data is evaluated against the parameters of other variables. Fe concentration in the pyrochemical salt experiments is greatest under two different conditions: when the pcH is acidic as in the tests pressurized with CO_2 (LS-28, 29, 30) and when the pcH is very high (> 10.5) in DOR tests in Castile Brine (LS-27 and 36). It was thought that Fe would maintain the repository in a reducing condition but some of the tests with significant concentrations of Fe had oxidized Pu as below.

Table 19. Fe Concentrations in Pyrochemical Salt Tests

ID	Pu Oxidation State	Fe Concentration Range	pcH
LS-26	Pu (VI)	Fe = <1 – 4 ppm	7.8 – 8.1
LS-27	Pu (V)	Fe = 20 – 240 ppm	10.7 – 11.2
LS-28	Pu (VI)	Fe = 20 – 165 ppm	4.7 – 7.7
LS-36	Pu (V)	Fe = 30 – 103 ppm	11.1 – 11.4

One of the puzzling questions concerning Fe in the STTP is that soluble Fe is present in a basic solution at the same time that Pu is soluble and in an oxidized form. This seems like the concentration of Fe and Pu is in contradiction with the K_{sp} of the two cations.

The solubility product constant, K_{sp}, of various reactants shows the solubility that can be achieved by each of the reaction ions relative to the formed solid compound.

Table 20. K_{sp} of Ca, Mg, Fe, and Ba for Relative Comparison

Ca	K_{sp}	Mg	K_{sp}
$Ca(OH)_2$	4.7×10^{-6}	$Mg(OH)_2$	5.6×10^{-12}
$CaSO_4$	7.1×10^{-5}	$MgSO_4$	-
$CaSO_3$	5.0×10^{-6}	$MgCO_3$	6.8×10^{-6}
CaF_2	1.5×10^{-10}	MgF_2	7.4×10^{-11}

Fe	K_{sp}	Ba	K_{sp}
$Fe(OH)_2$	4.9×10^{-17}	BaF_2	1.8×10^{-7}
$Fe(OH)_3$	2.6×10^{-39}	$BaSO_4$	1.1×10^{-10}
FeF_2	2.4×10^{-6}	$BaCO_3$	5.0×10^{-9}

However, the mass action expression for reactants and formed solid compounds requires a heterogeneous equilibrium because more than one phase enters into the expression. The calculated product of ion concentrations given above, are the result from experiments conducted at ideal conditions in low ionic strength solutions with known activity coefficients at neutral pH. The STTP solutions are at extremely high ionic strength solutions with unknown and perhaps indeterminate activity coefficients in a multiple and dynamic electrolyte system that is different for each test. Also, the pcH for each test container is different and certainly not neutral. So we must recognize that the normal equations of state at standard conditions do not apply to the STTP tests (nor to the WIPP). Also, the molar concentration of reactant ions are complicated by the common ion effect as in the case of excess Ca ions relative to sulfate in the following reaction:

$Ca^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow CaSO_4(s)$ *(aq) = aqueous

Theoretically, any reaction equilibrium may be shifted in one direction or another if sufficient reactant or product is added or removed. Perhaps the greatest complication in STTP high ionic strength solutions with multiple reactant ions and salts is the reactions that are competing to form precipitates and reactions that form soluble complexes. The formation of soluble complex ions by the addition of negatively charged ions (ligands) to a central metal ion will compete with the equilibrium that is established between reactant ions to form precipitates. So the formation constants or instability constants for complexation are in competition with the solubility product expression for precipitation.

The above discussion on complexation and precipitation is included in this report to provide an explanation of how an ion like Fe^{3+} in a basic solution can exist in solution with a K_{sp} of 10^{-39}. In solutions with high pcH values, as in some Castile Brine experiments, amphoterism enters into the already complex chemistry as compounds that are highly insoluble in neutral to slightly basic (pcH 7 to 9) conditions begin to solubilize in the more basic solutions. Also, the stability or formation constants of certain ligands compete with the hydroxide radical as the pcH of a test is more or less basic. Generally, the stability constant for inorganic ligands such as fluoride, carbonate and phosphate become stronger as the pH becomes more basic but, sulfate forms strong complexes at neutral pcH and relatively weaker complexes at more basic pcH's (pcH >10). For example, in the presence of EDTA, Ba, Sr, Ca, and Pb precipitate as sulfates at pH 5, but only BaSO4 is precipitated at pH 10. Generally, the hydroxide radical predominates at the higher pH's to either precipitate the metal ion or lead to solubilization due to ion complexation or amphoterism. The presence of high concentrations of Ca and Mg will tend to release Pu from ligand interaction toward the highest anion concentrations, namely, chloride.

XIV. An Explanation of Pu(V) and (VI) in STTP Pyrochemical Salt Waste Stream

Direct-Oxide Reduction (DOR)

$$PuO_2 \xrightarrow[840°C]{CaCl_2,CaO,Ca} Pu \quad + \quad Ca\ Salts$$

Oxygen Sparging (OS)

$$Pu/PuO_2 \xrightarrow[\Delta,\ emF]{NaCl,KCl} \underset{cathode}{Pu + K + Na} \xrightarrow[\Delta]{O_2} Pu + K_2O + Na_2O$$

INFLUENCING PARAMETERS

	DOR	OS
1. Pu(V) and Pu(VI)	LS-26, 27, 28, 36	None
2. Soluble Pu Concentration	Medium -Very High	Very Low-Low
3. Calcium	Very High	Low
4. Sulfate	Very Low	Higher
5. Chloride	Very High	High
6. Pu & Am loading	Very High	Lower
7. Nitrate	Very Low	Very Low
8. Mg (Brine A)	High	High
Mg (Castile Brine)	Low	Low
9. Na and K	Lower	High
10. Soluble Fe concentration	High	Very Low
11. Colloids	High	Low

Parameter No. 1 Pu(V) and Pu(VI)

DOR	OS
Pu(V) LS-27, 36	None
Pu(VI) LS-26, 28	None

Parameter No. 2 Pu Concentration

DOR		OS	
ID	Peak Pu Concentration, ppb	ID	Peak Pu Concentration, ppb
LS-25	127	LS-31	275
LS-26	70, 826	LS-32	697
LS-27, Castile	243, 438	LS-33, Castile	190
LS-28	197, 984	LS-34	50
LS-29	8446	LS-38	19
LS-30, Castile	2226	LS-39, Castile	2599
LS-35	1458		
LS-36, Castile	19963		
LS-37	381		

Parameter No. 3 Calcium
Parameter No. 4 Sulfate

DOS			OS		
ID	Ca, ppm	Sulfate, ppm	ID	Ca, ppm	Sulfate, ppm
LS-25	83000	30	LS-31	1200	4600
LS-26	70000	70	LS-32	800	4800
LS-27, Castile	80000	180	LS-33, Castile	800	9000
LS-28	120000	60	LS-34	9000	800
LS-29	18000	50	LS-38	60000	140
LS-30, Castile	30000	250	LS-39, Castile	700	16000
LS-35	80000	100			
LS-36, Castile	80000	200			
L37	120000	50			

Note: K_{sp} for $CaSO_4$ is about 7×10^{-5}

Parameter No. 5 Chloride Content

DOR		OS	
ID	Chloride, Molar	ID	Chloride, Molar
LS-25	9.1	LS-31	6.3
LS-26	9.0	LS-32	6.3
LS-27, Castile	6.7	LS-33, Castile	5.7
LS-28	10.43	LS-34	6.5
LS-29	10.81	LS-38	7.2
LS-30, Castile	6.4	LS-39, Castile	4.9
L35	7.7		
LS-36, Castile	6.1		
LS-37	9.3		

Parameter No. 6 Pu and Am Loading

DOR			OS		
ID	Pu, g	Am, mg	ID	Pu, g	Am, mg
LS-25	0.38	0.40	LS-31	0.81	0.65
LS-26	4.06	2.25	LS-32	4.10	2.92
LS-27	3.41	1.56	LS-33	1.14	1.10
LS-28	10.61	1.24	LS-34	2.05	2.69
LS-29	4.34	2.38	LS-38	2.77	7.43
LS-30	2.01	2.38	LS-39	4.42	11.50
LS-35	0.45	0.07			
LS-36	11.07	4.94			
LS-37	4.35	1.10			

Note: Portland Cement Pu average = 0.077
Envirostone Average = 1.12

Parameter No. 7 Nitrate Concentration

DOR			OS		
	Nitrate, ppm			Nitrate, ppm	
ID	Start	End	ID	Start	End
LS-25	30	20	LS-31	5250	50
LS-26	40	40	LS-32	1030	28
LS-27	80	35	LS-33	9100	33
LS-28	58	21	LS-34	1020	22
LS-29	15	10	LS-38	30	77
LS-30	26	10	LS-39	2000	219
LS-35	940	20			
LS-36	25	120			
LS-37	960	85			

Parameter No. 8 Mg Concentration

DOR		OS	
ID	Mg, ppm	ID	Mg, ppm
LS-25	22000	LS-31	28000
LS-26	21000	LS-32	30000
LS-27, Castile	<10	LS-33, Castile	400
LS-28	16000	LS-34	23000
LS-29	20000	LS-38	28000
LS-30, Castile	22000	LS-39, Castile	1400
LS-35	24000		
LS-36, Castile	<10		
LS-37	23000		

Parameter No. 9 Na and K Concentrations

DOS			OS		
ID	Na, ppm	K, ppm	ID	Na, ppm	K, ppm
LS-25	7000	20000	LS-31	60000	50000
LS-26	10000	21000	LS-32	70000	55000
LS-27, Castile	44000	5000	LS-33, Castile	100000	40000
LS-28	4000	10000	LS-34	60000	42000
LS-29	2000	12000	LS-38	22000	30000
LS-30	40000	4000	LS-39, Castile	80000	7000
LS-35	20000	26000			
LS-36, Castile	50000	5000			
LS-37	8000	22000			

Parameter No. 10 Soluble Fe Concentration

DOR		OS	
ID	Fe, ppm	ID	Fe, ppm
LS-25	0.1-10	LS-31	0.1-3
LS-26	0.1-4	LS-32	0.1-1
LS-27, Castile	16-243	LS-33, Castile	0.1-1
L28	1-165	L34	0.1-2
LS-29	34-1468	LS-38	0.1-3
LS-30, Castile	10-1967	LS-39, Castile	0.1-1
LS-35	0.1-3		0.1-3
LS-36, Castile	10-103		0.1-1
LS-37	1-20		

Parameter No. 11 Colloids

DOR							
ID	Total Particles	Pu	Sr	Fe	Sulfate	Ca	pcH
LS-25	2×10^{11}	9L	14H	0	15H	High	8.0
LS-26	10^{11}-10^{12}	17H	13M	0	13M	High	8.0
LS-27, Castile	10^{11}-10^{12}	16VH	16H	0	15H	High	11.0
LS-28, CO_2	10^{12}-10^{13}	3H	3M	1L	3M	High	5.0
LS-29, CO_2	2×10^{12}	3H	0-	2L	4M	High	5.0
LS-30, CO_2	3×10^{11}	3M	0-	1M	3M	High	6.4
LS-35, Chelators	10^{10}-10^{11}	1L	3VL	O	15VH	High	8.3
LS-36, Castile/ Chelators	10^{10}-10^{11}	16VH	14H	2M	14H	High	11.2
LS-37, ^{241}Am	10^{9}-10^{10}	8L	15H	6M	13H	High	7.8

OS							
ID	Total Particles	Pu	Sr	Fe	Sulfate	Ca	pcH
LS-31, Bentonite	10^{9}-10^{10}	8M	0	3M	10M	Low	8.8
LS-32, Bentonite	10^{9}-10^{10}	10H	4M	5M	12M	Low	8.8
LS-33, Bentonite	10^{9}-10^{10}	14H	3VL	6M	16M	Low	9.7
LS-34, Chelators	10^{10}	11M	0	0	12M	Med	8.7
LS-38, ^{241}Am	10^{9}-10^{10}	0	2VL	1L	15L	Med	7.8
LS-39, ^{241}Am	10^{9}-10^{10}	13H	5L	0	12H	Low	9.5

Note: L=Low, M=Medium, H=High, VH=Very High

Parameter No. 12 Oxidation Potential

ID	Total Activity, mCi	Cl^-, Molar	pcH
LS-25	25	9.1	8.0
LS-26	259	9.0	8.0
LS-27	217	6.7	11.0
LS-28	662	10.43	5.0
LS-29	277	10.81	5.0
LS-30	133	6.4	6.4
LS-35	28	7.7	8.3
LS-36	703	6.1	11.2
LS-37	531	9.3	7.8

NOTE:
1. pcH < 4 radiolysis of brine yields Cl_2
2. pcH 4 – 7 radiolysis of brine yields HClO
3. pcH > 7 radiolysis of brine yields OCl^-
4. The higher the α-activity the greater the Eh increases
5. > 3 M NaCl + radiolysis oxidizes Pu (IV) to (VI) and Am (111) to (V) in basic solution but not acid solution
6. Pu and Am hydroxide can be solubilized by oxidation
7. Pu α-particle path length in water is ~ 74 microns

Parameter No. 13 Downward Trend of Pu (VI)

The two liter-scale tests with Pu (VI) were LS-26 and LS-28. LS-26 was a Pyrochemical Salt test with a loading of 4.06 grams of Pu and 2.25 mg of Am in a Brine A. The pcH for LS-26 ranged from a pcH of 7.5 to 8.4 with an average pcH around 8.0 The Pu concentration started at 42.9 ppb and in creased to 3996 after one year of testing. The Pu and Am concentration increased rapidly to 70,826 ppb on 12/02/96 and a sample was analyzed and found to contain 63,413 ppb Pu and Pu (VI) was identified on the 03/24/97 sample. Pu (VI) persisted for about 1 ½ years till 11/02/98 when the total Pu concentration dropped to 5642 ppb. The upward trend that occurred was attributed to the presence of soluble Pu (VI). The eventual downward trend in concentration is attributed to precipitation of Pu (VI) or reduction of Pu (VI) to Pu (IV) and subsequent precipitation of Pu (IV) as a hydrated PuO_2 or Pu hydroxide.

According to the results of experiments conducted at LANL by Runde and VanPelt, Pu (VI) can be reduced or precipitated by peroxide within 18 months in Brine A at pH 7-10. Also, peroxide generated by alpha radiolysis that exceeds a few ppm will result in precipitation of Pu as a Pu (VI) hydroxide or a reduced form of Pu hydroxide. The stability or instability of Pu (VI) in the presence of peroxide or hypochlorite in acid, neutral and basic solutions of 5m NaCl Brine A and Castile Brine is summarized on the next page.

Table 21. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

Because LS-26 was a Brine A experiment at a pcH of 7.6 to 8.1, Pu (VI) is shown to be unstable on a long-term basis in the presence of peroxide and hypochlorite with the formation of white precipitate at neutral and basic pH. Pu (VI) is more stable in basic pcH than neutral and LS-26 may have been on the verge of being basic enough to be stable.

LS-28 was on the acid side of neutral where Pu (VI) is much more stable in Brine A with both hypochlorite and peroxide.

Table 22. Anion Behavior and Influence on Actinides

ID	Ca, ppm	Mg, ppm	Sulfate, ppm	Nitrate, ppm		Chloride, Molar	Remarks
				Start	End		
LS-01	18000	21000	600	280	150	5.4	
LS-02	40000	<1	400	1550	560	4.8	
LS-03	130	<10	13000	1670	990	4.2	
LS-07	12000	25000	700	250	160	5.5	No Fe mesh
LS-08	36000	2000	400	1800	670	5.0	No Fe mesh
LS-09	120	<10	14000	1300	800	4.3	No Fe mesh
LS-10	12000	22000	800	250	160	5.4	No Fe mesh; ^{241}Am
LS-11	40000	<10	400	1300	660	4.9	No Fe mesh; ^{241}Am
LS-12	120	<10	13000	1300	700	4.3	No Fe mesh; ^{241}Am
LS-13	1150	30000	7000	792	11	5.5	Organic solvent
LS-14	1300	30000	7000	600	8	5.5	Organic solvent
LS-15	650	1000	16000	471	163	4.6	Organic solvent
LS-16	1300	30000	6500	60	10	5.4	
LS-17	1500	30000	6500	23000	11000	5.4	
LS-18	700	1000	16000	3400	134	4.6	
LS-19	1100	25000	9000	51000	28000	5.0	
LS-20	1200	30000	9000	46000	24000	5.4	
LS-21	600	800	17000	47000	28000	4.4	
LS-22	2300	30000	4500	60000	31000	5.3	
LS-23	2700	34000	4000	40000	26000	NA	
LS-24	780	2000	12000	44000	28000	4.4	
LS-25, DOR	83000	22000	30	30	20	9.1	
LS-26, DOR	70000	21000	70	40	40	9.0	
LS-27, DOR	80000	<10	180	80	35	6.7	
LS-28, DOR	120000	16000	60	58	21	10.43	60 bars CO_2; MgO
LS-29, DOR	180000	20000	50	15	10	10.81	60 bars CO_2
LS-30, DOR	30000	22000	250	26	10	6.4	60 bars CO_2
LS-31, OS	1200	28000	4600	5250	50	6.3	Bentonite
LS-32, OS	800	30000	4800	1030	28	6.3	Bentonite
LS-33, OS	800	400	9000	9100	33	5.7	Bentonite
LS-34, OS	9000	23000	800	1020	22	6.5	Chelators and $Ca(OH)_2$
LS-35, DOR	80000	24000	100	940	20	7.7	Chelators and $Ca(OH)_2$
LS-36, DOR	80000	<10	200	25	120	6.1	Chelators and $Ca(OH)_2$

Continued on next page

ID	**Ca, ppm**	**Mg, ppm**	**Sulfate, ppm**	**Nitrate, ppm**		**Chloride, Molar**	**Remarks**
				Start	**End**		
LS-37, DOR	120000	23000	50	960	85	9.3	No Fe or Nd; ^{241}Am
LS-38, OS	60000	28000	140	30	77	7.2	No Fe or Nd; ^{241}Am
LS-39, OS	700	1400	16000	2000	219	4.9	No Fe or Nd; ^{241}Am
DS-01	700	32000	18000	312	34	5.3	Combustibles
DS-02	500	30000	5000	100	42	5.6	Combustibles
DS-03	400	500	17000	390	40	4.9	Combustibles
DS-04	600	32000	5000	90	20	5.5	Bentonite
DS-05	700	33000	5000	100	20	5.5	Bentonite
DS-06	600	800	18000	140	145	5.0	Bentonite
DS-07	700	33000	4700	38	33	5.5	Chelators and $Ca(OH)_2$
DS-08	800	32000	48000	804	836	5.6	Chelators and $Ca(OH)_2$
DS-09	600	700	17000	503	540	4.9	Chelators and $Ca(OH)_2$
DS-10	600	32000	4900	683	8	5.4	Nitrate/Phosphate
DS-11	500	32000	4900	440	5	5.4	Nitrate/Phosphate
DS-12	300	700	17000	620	554	4.9	Nitrate/Phosphate
DS-13	600	32000	4700	8	0	5.6	Metals
DS-14	700	33000	4900	62	15	5.4	Metals
DS-15	400	800	16000	234	0	4.8	Metals

XV. A Comparison of STTP Final Results for Radioactivity

During the D&D process of STTP test containers, a final sample of brine was taken from each vessel during the disassembly process and total alpha and Am-241 activity was measured on each sample. A comparison of the results of radiochemistry from the final brine sample taken during the D&D disassembly process relative to the final samples taken after rotation of the test containers was terminated is presented. The goal of the comparison was to ascertain whether there were any major changes, particularly significant increases, in activity during the period that the test containers set in a quiescent mode to the D&D timeframe as determined by the total alpha and Am-241 activities in the brine.

The overall result of this comparison was that there was not any significant increase in activity based on total alpha and Am-241 activity except for the results noted in the summary below.

Summary of Comparison

Portland Cement: No increase in activity during final period.
Envirostone: LS-16 showed an increase in radioactivity during the final quiescent period.
Pyrochemical salt: LS-25, 26, 28, 29, and 34 had increases in either total alpha activity or Am-241 activity during the quiescent period.
Drum-scale tests: No increase in activity during the final period.

Table 23. Comparison of Portland Cement Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-01	10/14/99	0	0.06	0.06	<0.12	<0.12	8.74
	10/7/99		0.06	0.06	<0.12	<0.12	8.74
LS-03	[*1] 2/22/99	26	0.01	<0.01	<0.12	<0.12	12.92
	[*2] 4/27/01		0.01	0.01	0.17	0.46	12.9
LS-04 CO$_2$ pressure	9/21/98	32	**15.29**	–	0.92	–	7.34
	5/15/01		0.08	0.21	0.23	0.18	7.20
LS-05 CO$_2$ pressure	9/21/98	32	0.71	–	0.14	–	7.35
	5/15/01		0.03	0.04	<0.12	0.31	7.02
LS-06 CO$_2$ pressure	9/21/98	32	**28.01**	–	1.12	–	7.56
	4/27/01		0.07	0.07	0.21	0.44	7.74
LS-07	3/15/99	25	0.26	0.24	<0.12	<0.12	8.75
	4/16/01		0.18	0.14	0.52	0.21	8.85
LS-08	3/15/99	25	0.11	0.09	<0.12	<0.12	9.25
	4/16/01		0.1	0.09	0.15	<0.12	9.44
LS-09	3/15/99	25	0.02	<0.01	<0.12	<0.12	12.97
	4/27/01		<0.01	<0.01	<0.12	0.27	12.92
LS-10 Am-241 added	3/15/99	23	4.29	3.86	3.11	3.04	8.74
	2/22/01		2.25	2.11	1.19	1.15	8.79
LS-11 Am-241 added	3/15/99	23	0.09	0.08	<0.12	<0.12	9.74
	2/22/01		0.05	0.03	0.39	0.3	10.52
LS-12 Am-241 added	3/15/99	23	0.01	<0.01	<0.12	<0.12	12.98
	2/22/01		0.01	<0.01	0.23	0.31	12.92

*1 Final sample taken when rotation of test containers was terminated.
*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: Pressurized test containers LS-04 and L06 showed a high coarse alpha activity that was not present in the sample taken 32 months later.

Table 24. Comparison of Envirostone Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-13 added organics	[*1] 3/1/99	24	4.04	1.71	0.57	0.31	7.07
	[*2] 2/22/01		5.86	5.56	1.1	0.71	7.01
LS-14 added organics	4/15/99	22	10.87	8.23	1.62	1.11	7.11
	1/25/01		13.3	12.91	2.43	2.4	7.22
LS-15 added organics	4/5/99	25	2.01	1.75	<0.12	0.14	7.58
	4/27/01		1.01	1.02	0.34	0.68	6.76
LS-16	2/22/99	23	**424**	**409**	**2.64**	**2.59**	**7.45**
	1/16/01		**1033**	**1027**	**11.0**	**10.2**	**7.47**
LS-17	2/22/99	24	0.70	0.25	0.25	0.18	7.82
	2/22/01		0.97	0.48	0.58	0.76	7.73
LS-18	3/8/99	22	2.34	0.77	1.73	0.94	7.82
	1/25/01		2.78	2.02	2.04	1.5	7.66
LS-19	3/01/99	24	1.56	1.41	1.09	1.13	7.93
	2/22/01		1.75	1.67	1.57	2.01	7.83
LS-20	10/18/99	0	0.17	0.11	<0.12	<0.12	7.81
	10/14/99		0.17	0.11	0.13	<0.12	7.81
LS-21	11/9/99	0	0.44	0.36	<0.12	<0.12	8.11
	11/15/99		0.44	0.36	<0.12	<0.12	8.11
LS-22	2/22/99	26	0.29	0.21	0.25	0.14	7.20
	4/16/01		4.14	0.29	3.87	0.96	7.50
LS-23	3/1/99	24	4.91	5.02	2.98	3.79	7.49
	3/16/01		3.61	3.0	3.61	3.04	7.29
LS-24	2/22/99	26	0.18	0.10	0.13	<0.12	7.76
	4/27/01		0.08	0.06	0.33	0.3	7.70

*1 Final sample taken when rotation of test containers was terminated.

*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: LS-16 showed a definite increase in activity during the 23 months of quiescent operation (non-rotation of test containers). This result is consistent with Np, U, Pu, and Am results from an ICP-MS analysis.

Table 25. Comparison of Pyrochemical Salt Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-25	[*1] 12/6/99	16	0.96	0.66	<0.12	<0.12	8.04
	[*2] 4/16/01		28.66	24.97	0.82	0.72	8.14
LS-26	12/6/99	14	292.1	275	1.3	0.80	8.01
	2/22/01		251	247	77	44.5	8.07
LS-27	12/6/99	14	2825	2277	15.7	15.9	11.16
	1/25/01		1492	1181	155.6	187.8	11.21
LS-28 CO_2 pressure	12/6/99	18	1337	–	19.3	–	5.03
	5/15/01		1683	1767	152.5	141.3	5.19
LS-29 CO_2 pressure	9/20/98	33	360	–	99.8	–	4.73
	6/20/01		1822	1746	56.2	49.9	5.01
LS-30 CO_2 pressure	9/20/98	33	68.4	–	5.8	–	6.59
	6/20/01		70.4	70	1.12	0.99	6.86
LS-31 Bentonite	11/4/99	0	21.12	20.33	1.01	<0.12	8.79
	11/15/99		21.1	20.3	15.19	0.15	8.79
LS-32 Bentonite	12/15/99	0	10.76	10.77	<0.12	<0.12	8.75
	12/15/99		10.8	10.8	1.26	1.16	8.75
LS-33 Bentonite	3/8/99	23	11.37	10.93	<0.12	0.19	9.63
	2/22/01		8.5	8.5	0.46	0.49	9.73
LS-34 Chelators	3/8/99	25	4.68	1.83	0.82	0.44	8.75
	4/16/01		37.6	36.9	1.12	1.13	8.93
LS-35 Chelators	3/8/99	24	13.0	10.1	2.69	2.03	8.31
	3/16/01		14.4	8.8	2.89	2.26	8.26
LS-36 Chelators	3/8/99	22	140.4	126.5	4.0	9.2	11.38
	1/16/01		133	39	40.35	41.17	11.35
LS-37 Am-241 added	3/15/99	22	**15.17**	**13.96**	**0.37**	**0.29**	**7.80**
	1/16/01		**529.5**	**511.5**	**10.59**	**8.05**	**7.76**
LS-38 Am-241 added	3/15/99	22	0.65	0.62	<0.12	<0.12	8.02
	1/16/01		1.32	1.29	0.63	0.22	7.97
LS-39 Am-241 added	3/15/99	22	179.3	175.3	44.70	42.60	9.50
	1/16/01		55.9	53.4	10.19	7.77	9.49

*1 Final sample taken when rotation of test containers was terminated.
*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: The radiochemistry results of LS-37 agree with similar increases in concentrations with ICP-MS results. Differences found in LS-26, 28, and 36 do not correlate for the two measurement techniques. LS-27 was interesting because the total alpha activity decreased and Am-241 activity increased.

Table 26. Comparison of Final Drum-Scale Test Activities

Drum Number	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
DS-01	[*1] 2/1/99	28	0.66	0.13	0.36	<0.12	7.70
	[*2] 6/20/01		0.15	0.10	0.35	0.40	7.71
DS-02	2/1/99	28	0.63	0.13	0.13	<0.12	7.70
	6/20/01		0.07	0.07	0.30	0.28	7.71
DS-03	2/1/99	28	0.01	<0.01	<0.12	<0.12	6.95
	6/20/01		<0.01	0.02	0.26	0.29	6.86
DS-04 Bentonite	2/1/99	28	0.07	<0.01	<0.12	<0.12	7.37
	6/20/01		<0.01	0.03	0.54	<0.12	7.36
DS-05 Bentonite	2/1/99	28	0.06	0.02	<0.12	<0.12	7.16
	6/20/01		<0.01	0.01	0.12	0.56	6.99
DS-06 Bentonite	2/1/99	28	0.02	<0.01	<0.12	<0.12	7.18
	6/20/01		0.02	0.02	0.46	0.64	7.27
DS-07 Chelators	10/18/99	20	6.3	3.7	0.12	0.12	4.99
	6/20/01		1.76	1.64	0.63	0.54	6.33
DS-08 Chelators	10/18/99	20	51.7	51.9	0.40	0.40	6.80
	6/20/01		21.28	20.56	2.71	2.50	6.98
DS-09 Chelators	10/18/99	20	34.2	34.1	0.40	0.30	7.35
	6/20/01		13.52	13.38	1.61	1.84	7.41
DS-10 nitrate, phosphate added	2/8/99	28	2.75	2.42	0.49	0.28	7.45
	6/20/01		0.66	0.49	0.40	0.55	7.31
DS-11 nitrate, phosphate added	2/8/99	28	0.08	0.01	<0.12	<0.12	7.42
	6/20/01		0.01	0.01	0.32	0.44	7.44
DS-12 nitrate, phosphate added	2/8/99	28	0.01	<0.01	<0.12	<0.12	6.21
	6/20/01		0.03	<0.01	0.29	0.23	5.72
DS-13 massive metal	2/8/99	28	0.32	0.29	0.13	0.22	**5.95**
	6/20/01		0.29	0.29	0.26	0.41	**4.34**
DS-14 massive metal	2/8/99	28	0.08	0.05	<0.12	<0.12	**6.71**
	6/20/01		0.07	0.06	0.66	0.69	**5.45**
DS-15 massive metal	2/8/99	28	0.04	0.05	<0.12	<0.12	7.74
	6/20/01		<0.01	0.03	0.63	0.26	7.95

[*1] Final brine sample taken when rotation of test containers was terminated.

[*2] Final brine sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: There was not much change in concentration during the 20 to 28 month quiescent period of STTP. There was a decrease in the pcH in DS-13 and 14 during that period.

XVI. Experimental Study of Pu (VI) Stability/Instability in the Presence of Peroxide or Hypochlorite as Applied to STTP Tests

The radiolytic production of hypochlorite and peroxide in 5 M NaCl has been extensively studied, reported in the literature, and demonstrated in both basic and acidic conditions in solutions with high alpha activity. Also, the effectiveness of hypochlorite in oxidizing precipitated Pu to a soluble form has been reported in experiments conducted in the Federal Republic of Germany. However, the radiolytic behavior of Pu in > 3 M NaCl has been found to significantly differ from the Brine A and Castile Brine solutions synthesized to duplicate WIPP brines. Experiments conducted at LANL by Wolfgang Runde have demonstrated the stability/instability and speciation of Pu (VI) in Brine A, Castile Brine, and 5 M NaCl containing peroxide and hypochlorite in acidic, neutral, and basic pHs.

The experiments were conducted by adding a measured amount (~ 10^{-4} M) of peroxide (3.4 ppm) or hypochlorite (5 ppm) to Pu (VI) in Brine A, Castile Brine, and 5 M NaCl in acidic, neutral, and basic solutions and measuring the UV/VIS spectra on a repetitive basis for several days and up to 18 months to establish the stability or instability of the Pu (VI) in the various solutions.

Table 27. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

The results of the experiments were pertinent in helping to provide an explanation of results that showed the presence of Pu (VI) under certain conditions STTP results and the following conclusions could be made:

1) The stability or instability of Pu (VI) was quite different in 5 M NaCl compared to Brine A and Castile brines, the synthetic brines used to mimic WIPP brines.

2) 5 M NaCl
    a) Hypochlorite effect – Pu (VI) was quite stable in acid, neutral, and basic solutions with hypochlorite for up to 18 months. Partial reduction occurred in basic solution.
    b) Peroxide effect – Pu (VI) was not stable in acid, neutral, and basic solutions with hydrogen peroxide. Pu (V) was detected in acid and neutral solutions but not basic solutions.

3) Brine A
    a) Hypochlorite effect
        1. Pu (VI) was very stable in acid solution for up to 18 months
        2. not stable in neutral solution
        3. somewhat stable in basic solution
    b) Peroxide effect
        1. Pu (VI) was somewhat stable in acid solution with partial reduction up to 18 months.
        2. Pu (VI) fairly unstable in neutral solution
        3. Pu (VI) stable for short term in basic solution but was reduced after 18 months

4) Castile Brine
    a) Hypochlorite effect
        1. Fairly stable in acid solution with partial reduction in 18 months
        2. Fairly stable in neutral solution with partial reduction in 18 months
        3. Fairly stable in basic solution with minimal reduction in 18 months
    b) Peroxide effect
        1. Very stable in acid solution for 18 months
        2. Fairly stable in with partial reduction in neutral solution in 18 months
        3. Very stable with some reduction in basic solution in 18 months

5) Hypochlorite and peroxide at the 10^{-4} M level (3-5 ppm) was added to each experiment; higher concentrations resulted in precipitation of Pu.

6) Precipitation of Pu with **hypochlorite** containing brine
    a) 5 M NaCl
        1. No precipitate in acid solution
        2. No precipitate in neutral solution
        3. A yellow-brown precipitate formed in basic solution

- b) Brine A
    1. No precipitate in acid solution
    2. White precipitate formed in neutral solutions
    3. White precipitate formed in basic solution (this was a voluminous precipitate)
- c) Castile
    1. Very small brown precipitate formed in acidic solution
    2. A brown to yellow amorphous precipitate forms in neutral and basic solutions with NaOCl

7) Precipitation of Pu with **peroxide** containing brine
    - a) 5 M NaCl
        1. No precipitate in acidic solution
        2. Small precipitate in neutral solution
        3. Yellow-brown precipitate in basic solution
        4. Green precipitate in one basic solution; may have had too much peroxide
    - b) Brine A
        1. No precipitate in acidic solution
        2. White precipitate in neutral solution
        3. Voluminous precipitate in basic solution
    - c) Castile Brine
        1. Perceptible yellow-brown precipitate in acidic solution
        2. Brown to yellow amorphous precipitate in neutral solution
        3. Brown to yellow amorphous precipitate in basic solution

8) LS-26 was a Brine A experiment with a pcH of ~ 8. Therefore, oxidation of Pu (IV) to Pu (VI) for about 24 months must have been from radiolytically produced hypochlorite in a slightly basic solution. At neutral pcH, hypochlorite was not effective in stabilizing Pu (VI). Hydrogen peroxide in neutral solution is also not effective in stabilizing Pu (VI) while basic solutions at pcH 9-10 are effected for short times but not on a long term basis. Also, it may be that in neutral solutions that both hypochlorite and peroxide precipitate Pu but can oxidize certain levels of Pu to Pu (VI).

9) LS-27 was a Castile Brine experiment with a pcH around 11.0 and identified Pu (V). Pu (VI) is stabilized by both hypochlorite and peroxide in strong basic solution or a mixture of the two oxidants.

10) LS-28 was a Brine A experiment with identified Pu (VI) for one sample at a pcH of 5.1. Pu (VI) was stabilized in acid solutions of Brine A with hypochlorite (hypochlorous acid) and transitorily stabilized with hydrogen peroxide.

11) LS-36 was a Castile Brine experiment with identified Pu (V) at pcH ~ 11.2. At that pcH level, both hypochlorite and peroxide or mixtures of the two are effective at stabilizing Pu (VI).

12) Addition of peroxide in excess of 10^{-3} to 10^{-4} M can result in immediate reduction of Pu (VI) and formation of a green precipitate that is presumed to be Pu (IV) hydroxide. Addition of excess hypochlorite can also result in precipitation of a Pu (VI) compound, perhaps Pu (VI) hydroxide.

Overall, the results of the experiments provided a better understanding of the STTP results that showed Pu (VI) in the Brine A experiments, LS-26 and 28 under basic and slightly acidic conditions, respectively. Also, the presence of Pu (V) in LS-27 and 36 in Castile brine at pcH ~ 11.1 could be attributed to either hypochlorite or peroxide formation or a mixture of both.

The results of the experiments accentuated the difference of redox chemistry in 5 M NaCl and both Brine A and Castile Brine. The results of the experiments also raises our awareness that serves as a precaution on the relevancy and applicability of explanations derived from experiments conducted under conditions different from what is reality in the WIPP.

XVII. Stability of Pu(VI) in Castile and Brine A

by Wolfgang Runde and Craig VanPelt, LANL

Formation of hexavalent plutonium in concentrated chloride media due to its own alpha radiation has been known for decades. Radiolysis causes the formation of oxidizing species, such as hypochlorite in basic solutions, which subsequently can oxidize plutonium in lower oxidation states to Pu(VI). The kinetics of this autoradiolytic oxidation process depends on many parameters, such as pH, specific activity, and chloride concentration. In the absence or presence of limited concentrations of any reducing agent, high alpha-activities in concentrated chloride solutions will generate oxidizing species that will stabilize Pu(VI). Most of the radiolysis studies reported in the literature have been performed in acidic solutions or in pure NaCl media. WIPP brines are more complex than pure NaCl solutions and contain other cations and anions (e. g. Mg^{2+}, K^+, SO_4^{2-}) that may contribute to solution speciation and redox stability of plutonium. To better understand the behavior of plutonium in high chloride media, we initiated experiments to study the stability of Pu(VI) in brines relevant to the WIPP. We used synthetic brines that were used for the STTP, Castile brine and Brine A, and 5 M NaCl for comparison and varied the pH in the presence of pertinent concentrations of hydrogen peroxide or hypochlorite. The redox agents were added to the brines to obtain approximately 10^{-4} M/L in hydrogen peroxide (3.4 ppm) or hypochlorite (5 ppm) and the pH was very slowly adjusted between pH 2 and 10 by addition of 1 M NaOH or 1 M HCl. Aliquots of an acidic (0.1 M) Pu(VI) stock solution were added to the samples and the absorbance spectra monitored as a function of time. The Pu(VI) concentration was between 10^{-4} and 10^{-5} mol/L (2.4 to 24 ppm) in order to avoid the well known autoradiolytic effects at higher plutonium concentrations.

In the presence of hypochlorite, Pu(VI) observed in the wavelength region 830 to 860 indicates that Pu(VI) in 5 M NaCl and Castile Brine remains stable in solution even after 18 months. The complexation of Pu(VI) and the formation of Pu(VI) hydrolysis products with increasing pH is reflected in the shift of the absorbance maximum towards higher wavelengths. These results confirm the reported effect of hypochlorite to stabilize Pu(VI). While Pu(VI) remains stable in 5 M NaCl and Castile Brine solution, the intensity of the absorbance signals generally decreased over a period of 18 months. This intensity decrease could be caused by changes in solution speciation, reduction of Pu(VI), or precipitation of a plutonium-bearing solid phase. Formation of brown precipitates is observed in Castile brine in acidic, neutral, and basic pH and in basic 5 M NaCl when hypochlorite is added to the solution. Shaking up the precipitate and taking the absorbance spectrum of the suspended solid in solution doubles the Pu(VI) absorbance intensity in comparison to the signal obtained in the absence of the solid phase. This finding reveals that Pu(VI) is contained in the brown solid phase and the precipitation of Pu(VI) contributes to the overall lower soluble plutonium concentration. **This result is very important in understanding the limitations of oxidized forms of plutonium as may occur in the STTP tests.** The formation of a Pu (VI) precipitate in the presence of hypochlorite provides a reasonable explanation of why the concentration of Pu (VI) in STTP LS-26 decreased with time. Further characterization (XRD, XPS, SEM) will provide more information on the nature of the brown solid phase.

In the presence of hydrogen peroxide, Pu(VI) exhibits a different chemistry than in the presence of hypochlorite where Pu(VI) is stabilized in Brine A, Castile, or 5 M NaCl solutions. Plutonium(VI) was observed to be instantly reduced by equimolar amounts of hydrogen peroxide present in 5 M NaCl. In 5 M NaCl, soluble Pu(VI) is observed only within days of reaction time and no absorbance of Pu(VI) is observed after 18 months. In acidic 5 M NaCl, the Pu(VI) signal at around 840 nm disappears and a small peak at about 560 nm suggests the formation Pu(V). The absence of an absorbance peak characteristic for Pu(V) complicates the oxidation state determination of plutonium at neutral and basic pH. In contrast to 5 M NaCl, Pu(VI) in Castile brine is observed in acidic, neutral, and basic conditions after 18 months. Under slightly acidic conditions, the Pu(VI) absorbance was totally stable for a period of 18 months. A measured reduction of Pu(VI) is observed within days of reaction time under neutral and basic conditions, however, between 20% and 40% of the initial Pu(VI) remain in solution after 18 months. In Brine A, Pu(VI) stays in solution only at slightly acidic (pH 3-5) conditions. At neutral and basic pH no absorbance of a Pu(VI) solution species is observed. **This result explains that the oxidation of Pu (IV) to Pu (VI) in the Brine A experiments, LS-26 and 28, was due to hypochlorite formation rather than hydrogen peroxide.** While no precipitation was observed in acidic Brine A, neutral or basic conditions result in the formation of a white solid phase in Brine A. The oxidation state of plutonium in this solid is under investigation. Only in one case was the formation of a green precipitate observed suggesting predominantly Pu(IV) in the solid phase. This precipitation occurred in 5 M NaCl at slightly basic conditions.

The described results indicate the complicated chemistry plutonium may exhibit under different conditions. It is established that the presence of hypochlorite stabilizes Pu(VI) and inhibits reduction of Pu(VI) to lower oxidation states in all investigated brines. The presence of Pu(VI) in the brown solid phase limits the soluble Pu(VI) concentration by the solubility product of this solid. Hydrogen peroxide, however, reacts with Pu(VI) and affects the stability of Pu(VI) significantly, especially in 5 M NaCl. In acidic 5 M NaCl, reduction of Pu(VI) to Pu(V) took place instantly and very low concentrations of Pu(VI) are observed after 18 months. In 5 M NaCl with peroxide, the oxidation state of plutonium is unclear because of the lack of absorbance peaks of Pu(IV) and Pu(V) species. Excess of hydrogen peroxide precipitates Pu(VI) and ultimately reduces Pu(VI) to a lower oxidation state. However, with limited amounts of hydrogen peroxide available, Pu(VI) may be only partly reduced and remains stable in solution for at least 18 months. Most interesting is the different behavior the Pu(VI) exhibits in 5 M NaCl, Brine A, and Castile. While Brine A seemed not to favor Pu(VI) and formation of a white solid phase occurred easily at neutral and basic pH, Pu(VI) was more stable than in 5 M NaCl. Pu(VI) was observed in Castile brine after 18 months independent of pH.

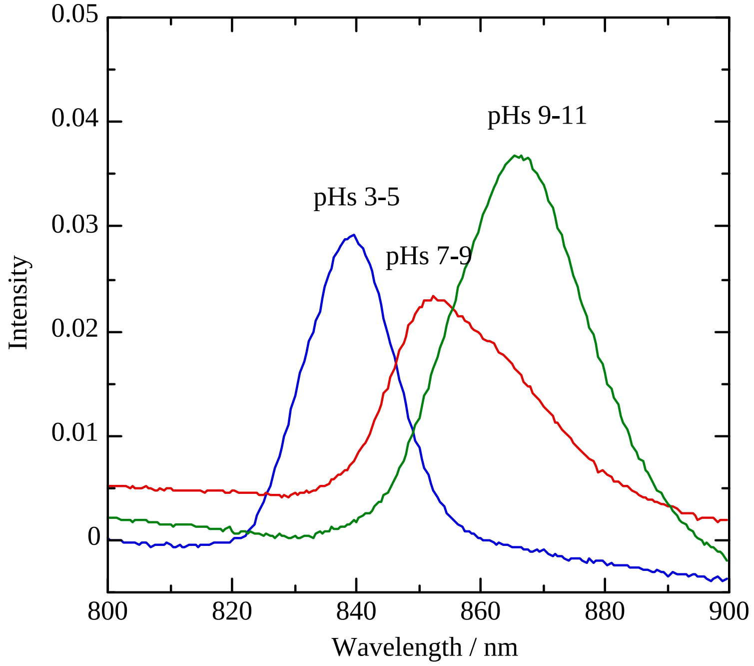


Figure 1. Characteristic absorbance bands for Pu(VI) with varying pH. With increasing pH, complexation of Pu(VI) with anionic ligands in solution shifts the absorbance maximum towards higher wavelength. In the absence of carbonate, formation of Pu(VI) hydroxo species are solution species that will form.

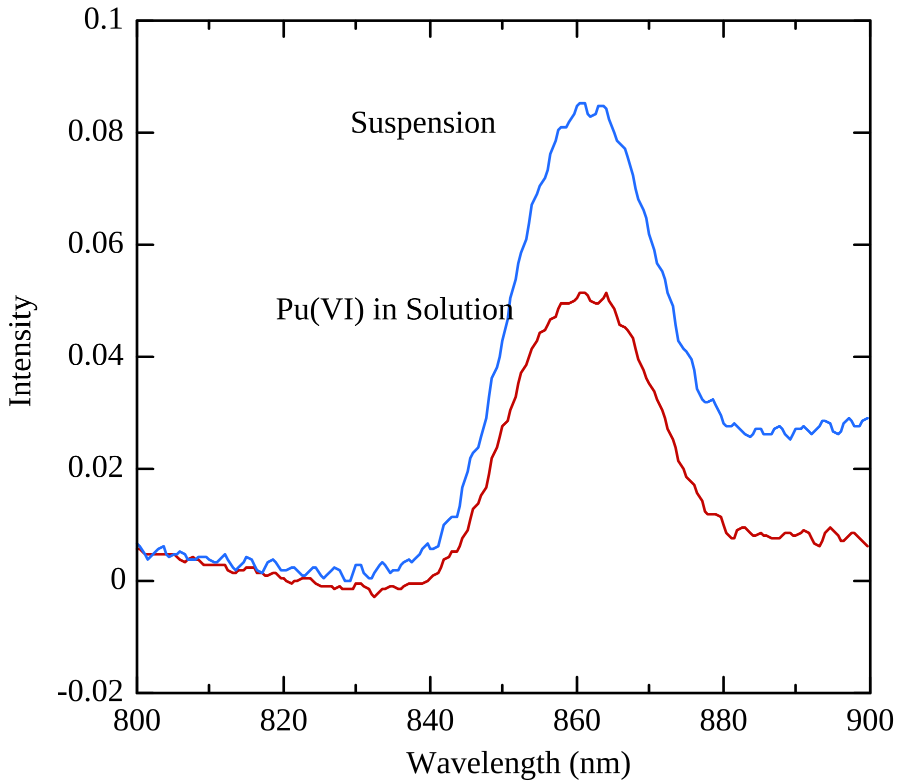


Figure 2. Pu(VI) absorbance in solution and in the presence of the brown solid phase precipitated in most of the Castile and in NaCl solutions. As an example, the Pu(VI) absorbance of alkaline Castile brine in the presence of hydrogen peroxide is shown. The increase in absorbance compared to that in solution indicates the presence of Pu(VI) in the solid phase.

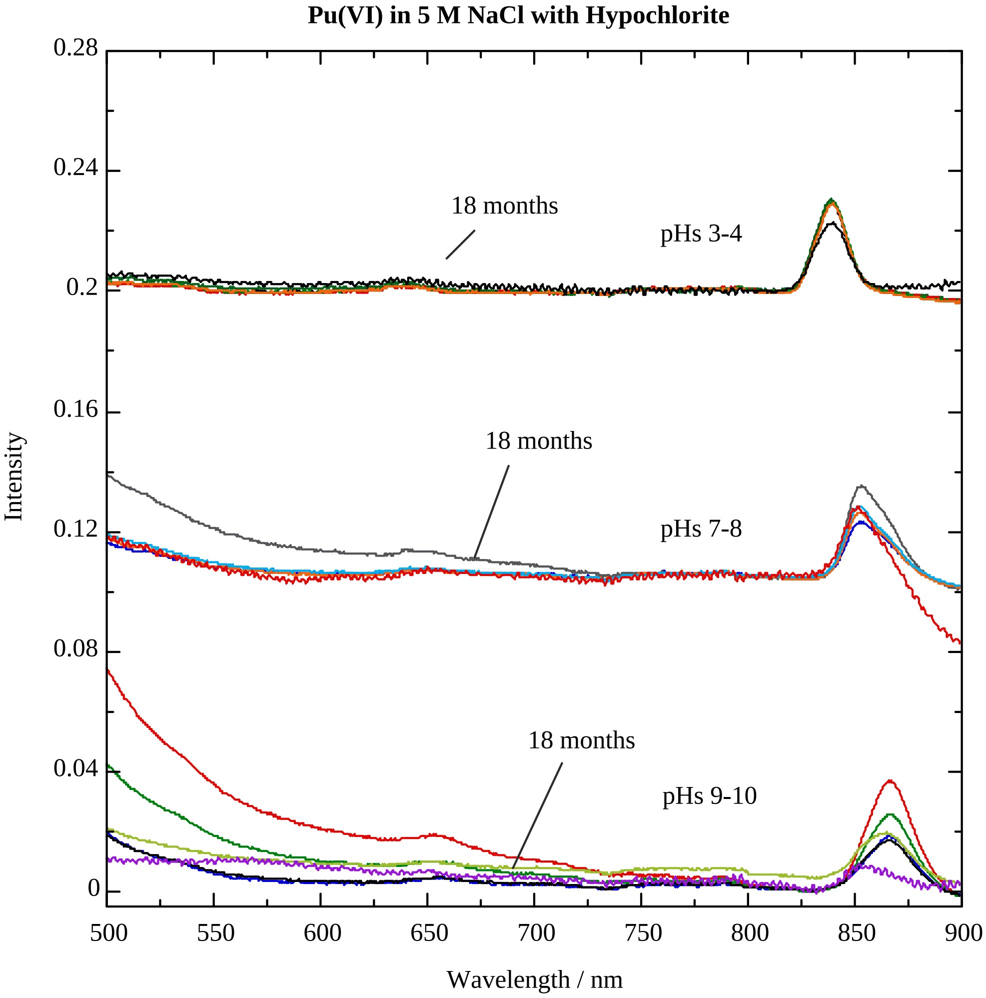


Figure 3. Pu(VI) absorbance spectra in 5 M NaCl in the presence of hypochlorite. The typical Pu(VI) bands are seen in all solutions even after reaction time of 18 months.

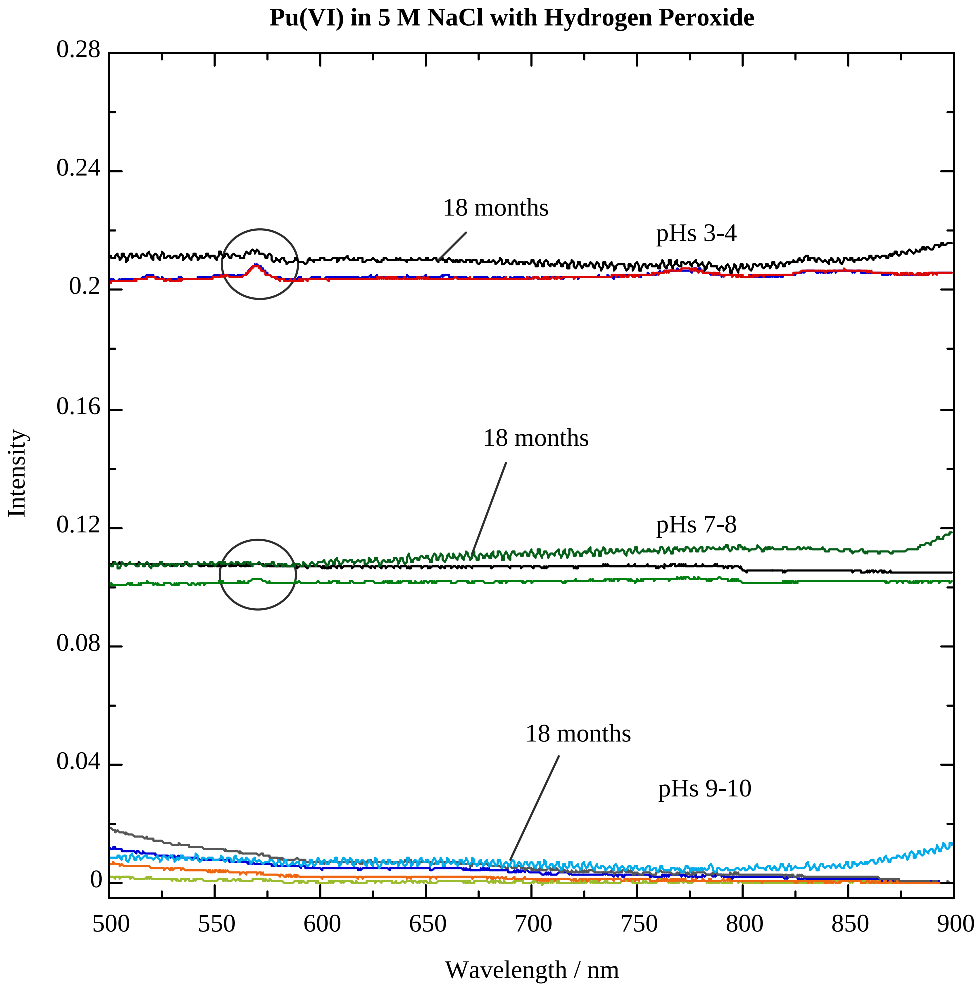


Figure 4. Pu(VI) absorbance spectra in 5 M NaCl in the presence of hydrogen peroxide. Reduction of Pu(VI) occurs instantly and the Pu(VI) bands disappear. The bands at about 550 nm indicate the formation of Pu(V).

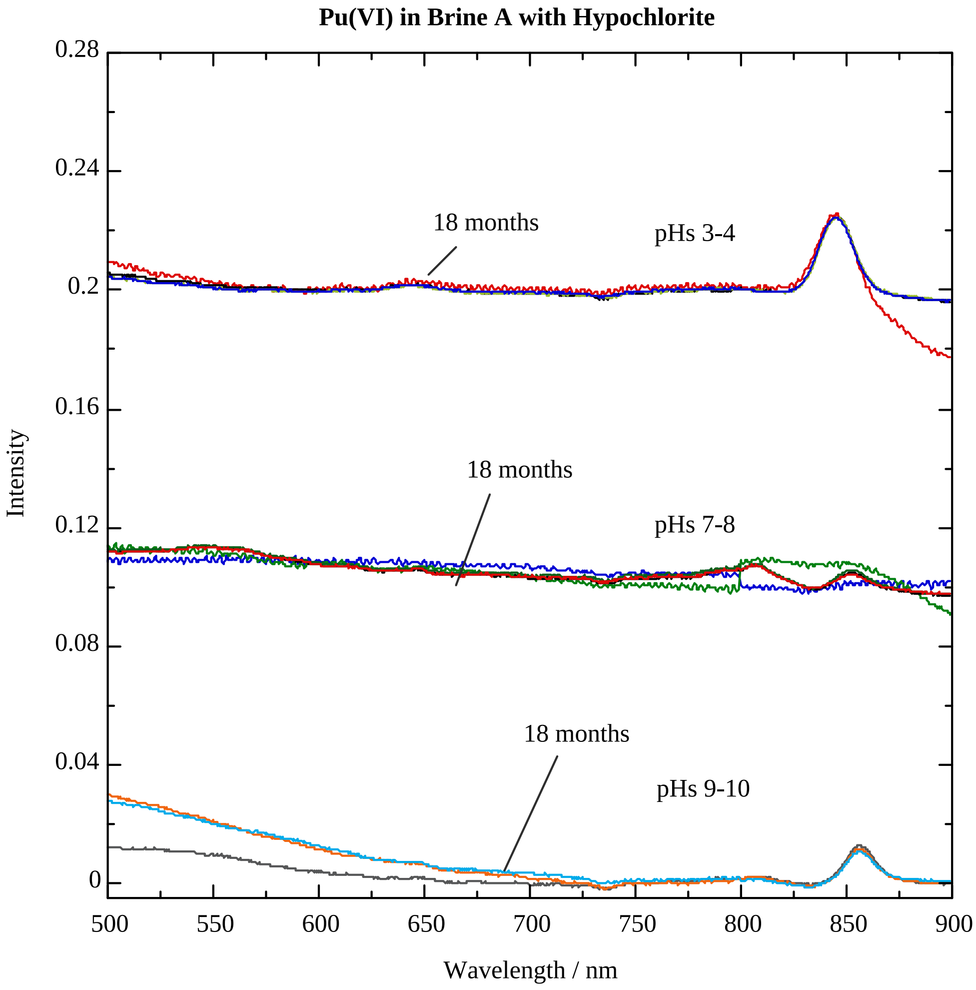


Figure 5. Pu(VI) absorbance spectra in Brine A in the presence of hypochlorite. Even after 18 months Pu(VI) remains in solution. White precipitation is observed at neutral and basic pH.

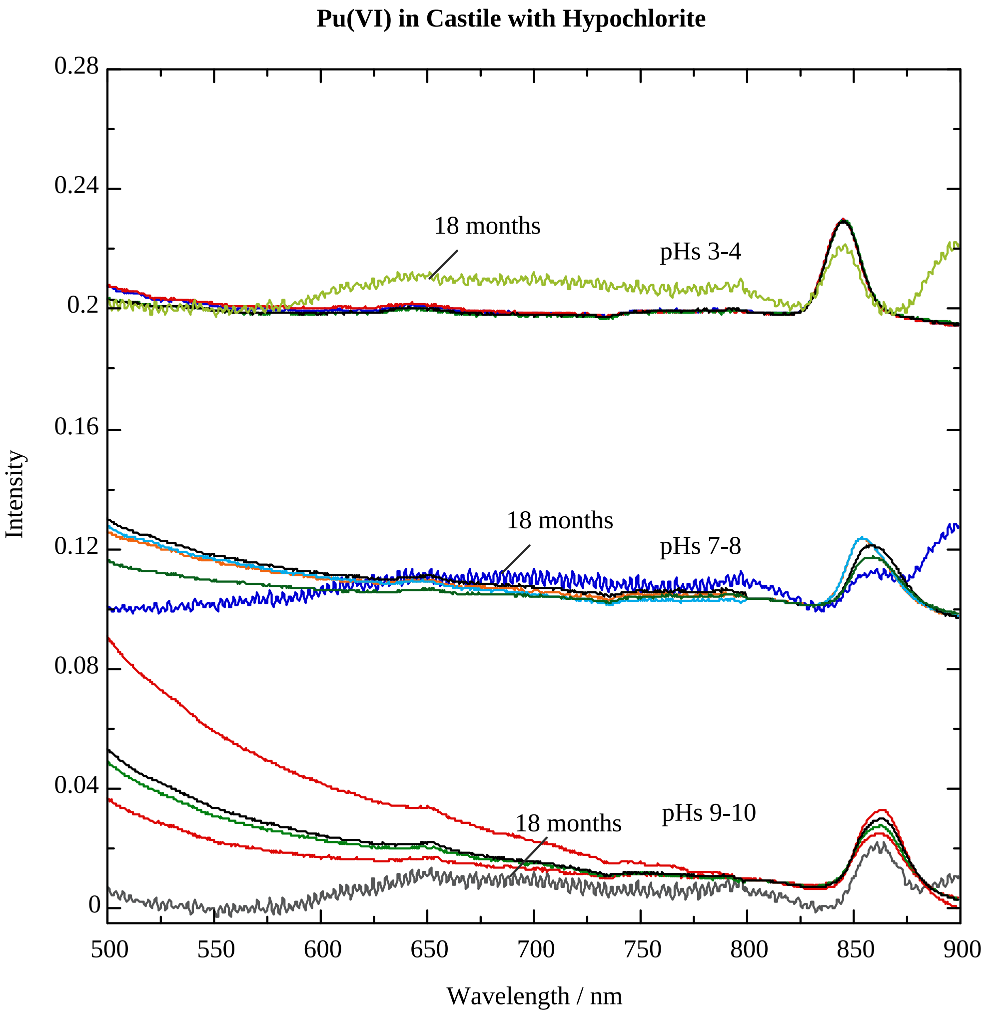


Figure 6. Pu(VI) absorbance spectra in Castile in the presence of hypochlorite. In contrast to Brine A, the characteristic Pu(VI) bands are observed in all Castile solutions with hypochlorite. Except at acidic conditions, precipitations of small amounts of brown Pu(VI)-containing solids are obtained.

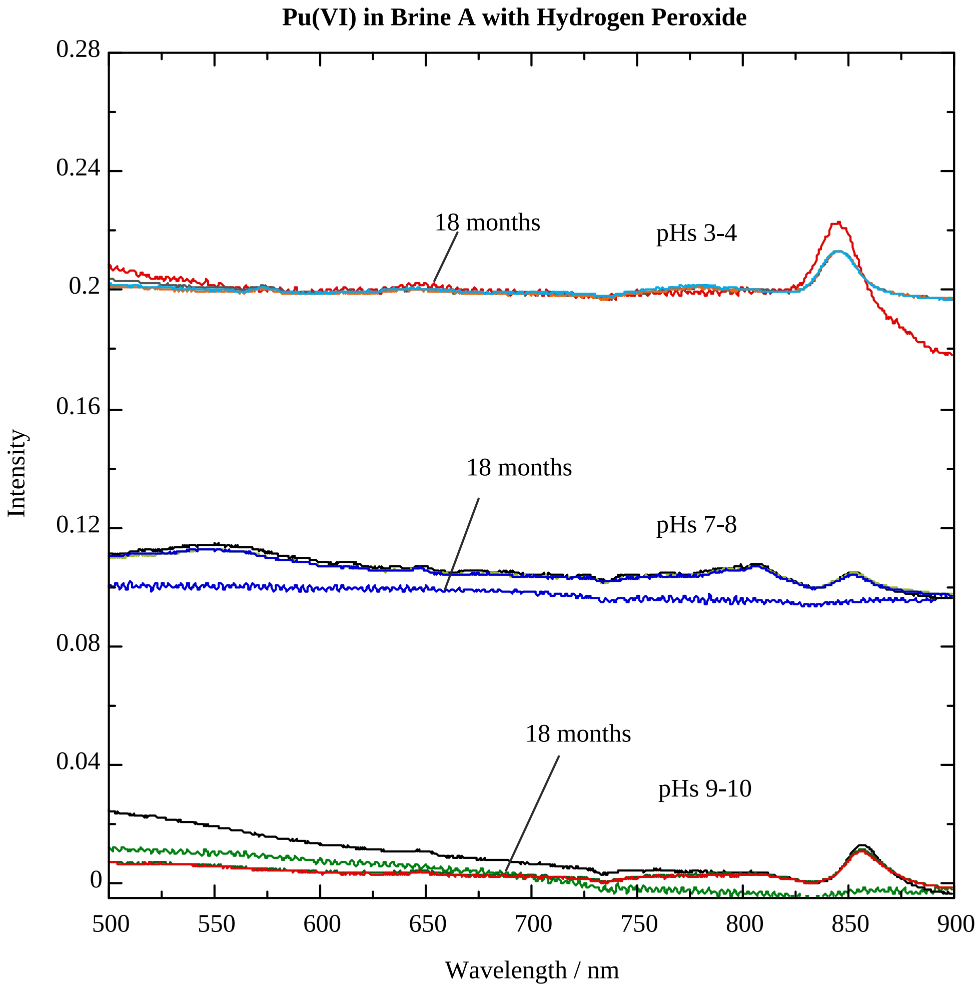


Figure 7. Pu(VI) absorbance spectra in Brine A in the presence of hydrogen peroxide. After 18 months, no Pu(VI) is observed in solution in neutral and basic pcHs; partial reduction in acidic solution at 18 months.

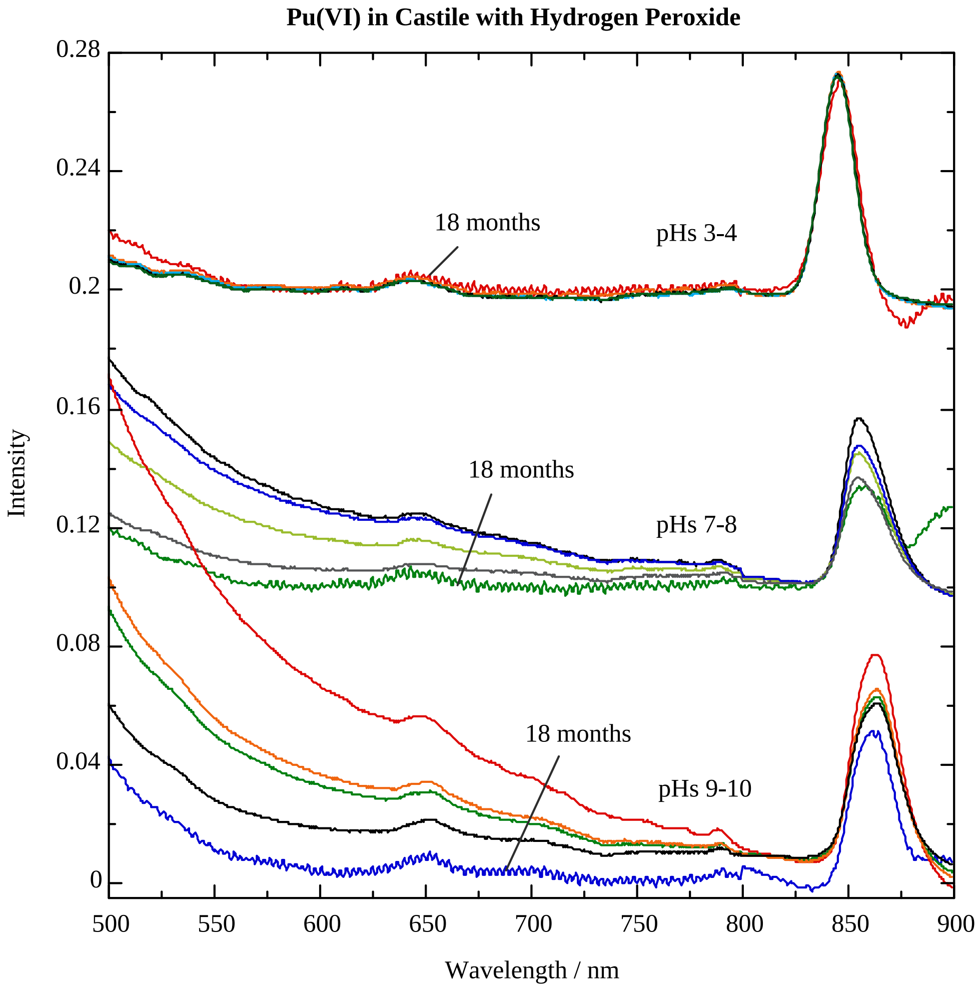


Figure 8. Pu(VI) absorbance spectra in Castile in the presence of hydrogen peroxide. After initial reaction of hydrogen peroxide Pu(VI) remains stable in solution. In contrast to Brine A, Pu(VI) is much more stable in Castile and can be found in solution after 18 months of reaction time.

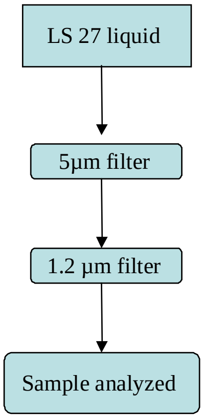
XVIII. Colloidal Study of LS-27 Brine with FFF and ICP-MS

The Castile Brine samples taken from the pyrochemical salt test, LS-27, contained some of the highest levels of actinide activities (except U) of the STTP. The concentration of Pu at 243,438 ppb and Am at 825 ppb on the same sample were the highest in the STTP. The concentrations of Nd, Th, Np, Pu, and Am were high from the first sample taken 5/8/95 and continued to increase to a peak concentration on 10/30/95, then slowly decreased for the remainder of the test. A large number of analyses of different kinds were conducted on LS-27 in an attempt to explain why this particular test had such high actinide activities, especially Pu and Am. The high Pu activity was determined by UV/VIS spectroscopy to have Pu (V) but not Pu (VI). The ratio of Pu (V) to Pu (IV) was not determined.

A sample of Castile Brine was specifically taken to measure the activity associated with colloids in each size fraction of the particle population (10^{11} to 10^{12} particles/liter) from 0 to 350 nm particle size diameters. Studies conducted by measuring the difference in activity of the brine fractions after coarse filtration (1.2 µm) and fine filtration (10 nm) showed that only a small fraction of activity associated with colloids was in the brine between the two filtrations. An attempt to determine the actual particle size fraction that contained the activity attributed to a colloidal fraction was made by isolating different size fractions by a Field Flow Fractionation (FFF) technique and measuring the soluble actinides in each size fraction with an Inductively-Coupled Argon Plasma – Mass Spectrometer (ICP-MS) instrument. The FFF-ICP/MS results showed that all the activity in the sample was associated with the soluble fraction only and that none of the activity was associated with a certain size fraction of particles. There was a rather comprehensive study conducted on LS-27 brine because it had the highest Pu and Am activity. These results verified the results of activities measured on filtered and centrifuged brine that there was essentially no activity associated with a definitive colloid fraction in both all the Brine A and Castile Brine experiments in the STTP. It appears that colloids in the STTP were not stable in the STTP brines because of the high ionic concentrations of a mixture of Group I and II cations and associated chloride anions and, perhaps, the organic content was so low. If the conditions of the STTP are applicable to the conditions in the WIPP, then there would not be stable Pu-bearing colloids or colloidally-based actinide transport mechanisms from the activity in the WIPP repository.

Figure 9.

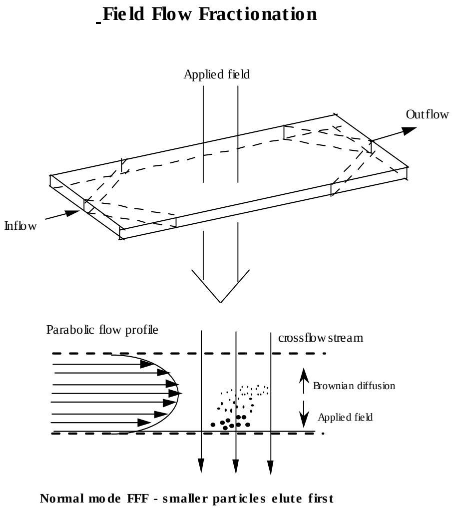
Analysis of liquid from liter-scale 27 from STTP
Field-Flow Fractionation
and
Inductively Coupled Plasma Mass Spectroscopy



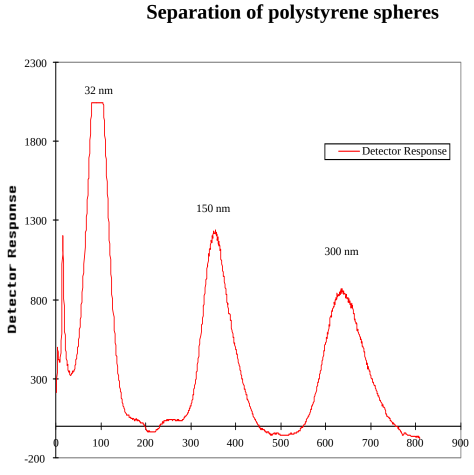
Doug Farr, MST-5

Figure 10.

Particle size determination - FFF


Field Flow Fractionation

Normal mode FFF - smaller particles elute first


Separation of polystyrene spheres

Doug Farr, MST-5

FFF separations are done by flowing a sample and carrier fluid within a flat open channel usually having a rectangular cross section and possessing triangular end pieces where the fluid enters and leaves. The channel dimensions are 20 to 100 cm long and about 1 to 3 cm wide, and 0.05 to 0.5 mm thick. A field, either gravitational, thermal, flow, electrical, or centrifugal, is applied perpendicularly the flat face of the channel. This field drives the sample molecules or particles across the thin channel towards the accumulation wall. The particles (or molecules) establish equilibrium positions in the channel that depend on factors such as how strongly the particles interact with the field and the sample diffusivity.

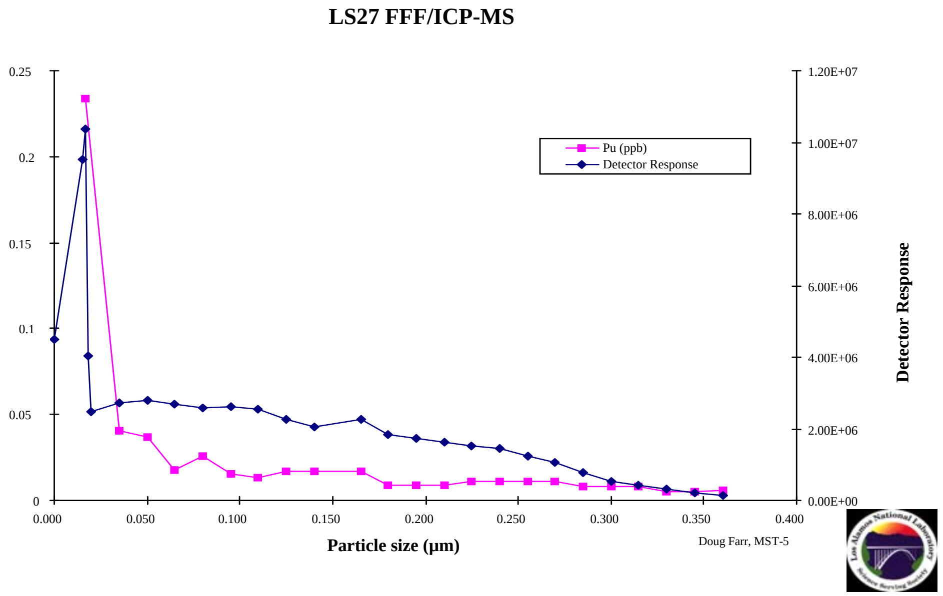
In flow FFF the channel and crossflow streams meet at right angles to each other and are blended. The parabolic channel stream carries the sample towards the outlet while the crossflow, which exits through the semipermeable membrane, drives the sample towards the accumulation wall. The force which drives particles towards the accumulation wall is the viscous force applied to the sample by the crossflow stream, described by Stoke's Law and the Stoke's-Einstein equation:

$$|F| = f|U| = kT|U|/D = 3\pi\mu|U|d$$

When the applied viscous force f|U| is equaled by the opposing effects of diffusion D, the particles equilibrate at a characteristic mean level above the accumulation wall. Each particle size has a different diffusion coefficient and thus will occupy different flow velocity streamlines and elute at different times.

Figure 11.

Solution phase Pu



Field Flow Fractionation (FFF) and Inductively-coupled plasma mass spectroscopy (ICP-MS) show that Pu is in the "soluble" fraction of the coarse-filtered aliquot from liter-scale 27. Pu concentrations were determined by ICP-MS from fractions that were collected as they eluted from the FFF channel. Detector response for the FFF system shows a strong "void peak" at the beginning of the run, around 25 nm. This peak arises from the unretained liquid in the sample and is seen in every fractionation run. The fraction collected from that region contained virtually all of the Pu that was in the sample. Any particles or molecular complexes in that fraction were less than 50 nm in size.

XIX. Reduction of Nitrate

There was a great diversity of starting concentrations of nitrate in the STTP tests as some tests were initiated with < 100 ppm whereas other tests had up to 60,000 ppm nitrate. Nitrate in contact with brine can be considered to be totally soluble in the brine. Many of the test containers showed a decrease in nitrate concentration of about 50% during the length of the test period. The reduction can be expected because about 54% of the brine in the test containers was replaced as part of the sampling and replenishment operation. However, there were certain tests that showed reduction of 80 – 100% of the nitrate and those are the tests that provided information on the destruction of nitrate. A listing of the tests that exhibited significant decreases is given below.

Table 28. Reduction of Nitrate in STTP Tests

Test Container ID	Influencing Variable	Nitrate Reduction, ppm	% Reduction
LS-13	Added organics	792 - 11	98.6
LS-14	Added organics	600 - 8	98.7
LS-18	Envirostone	3,400 - 134	61.0
LS-31	Bentonite	5,250 - 50	95.0
LS-32	Bentonite	1,030 - 28	97.3
LS-33	Bentonite	9,100 - 33	>99.0
LS-34	Chelators	1,020 – 22	98.0
LS-35	Chelators	940 – 20	98.0
LS-37	Am-241	960 – 85	91.0
LS-39	Am-241	2,000 – 219	89.0
DS-10	Added NO_3/PO_4	683 – 8	99.0
DS-11	Added NO_3/PO_4	440 – 5	99.0
DS-15	Metals	234 - 0	100

From the above listing of test containers with significant reduction of nitrates, it is apparent that the reduction occurred in a diversity of liter-scale and drum-scale tests. The cause of the reduction could be chemical, microbial, or radiolytic or a combination of all three. Six Envirostone test containers (LS-19, LS-20, LS-21, LS-22, LS-23, LS-24) had over 40,000 ppm (0.65 molar) of nitrate and up to 40% N_2O in the headspace of the test container. The reaction products of the destruction of nitrate can be different amounts of nitrite, N_2O and N_2 depending on the reduction mechanism. The production of nitrite and N_2O leads to a reducing environment in the brine because nitrite is a reducing agent very soluble in brine that stabilizes Pu in the Pu(IV) oxidation state. N_2O is a gas that has a solubility of ~ 1300 cm^3 per liter of water at 20ºC and is a reductant that would maintain Pu in the Pu(IV) state and preclude oxidation to higher oxidation states. Consequently, nitrate concentrations in the wastes would be a source of reducing agents under certain conditions. The pyrochemical salt tests had very low nitrate concentrations and would not be a source of reducing agents.

XX. Mg and Ca Concentration vs. pcH

Table 29. Mg and Ca Concentration vs. pcH

ID	pcH	Mg	Ca
LS-03	13.0	<10	130
LS-09	13.0	<10	120
LS-12	13.0	<10	120
LS-36*	11.2	<10	80,000
LS-27*	11.0	<10	80,000
LS-02	10.5	<1	40,000
LS-11	10.3	<10	40,000
LS-33	9.6	400	800
LS-39	9.6	1400	700
LS-08	9.1	2,000	36,000
LS-07	8.7	25,000	12,000
LS-01	8.8	21,000	18,000
LS-10	8.7	22,000	12,000
LS-34	8.8	23,000	9,000
LS-31	8.8	28,000	1,200
LS-32	8.7	30,000	800
LS-35	8.2	24,000	80,000
LS-19	8.0	25,000	1,100
LS-26*	8.0	21,000	70,000

* Pu(V) or (VI)

XXI. STTP Anion Results and Trends

Liter-Scale Tests

The anions routinely measured in STTP samples were fluoride, nitrate, phosphate, sulfate, and chloride. A trend in the concentrations of these anions would be indicative of some of the chemistry that would be occurring in the brine. A trend downward would be indicative that a soluble anion could be forming an insoluble precipitate that would settle out and thereby show a decrease in concentration. Also, radiolytic degradation could reduce the concentration of a soluble anion. An increase in the concentration of anions could be indicative of a solubilization of a waste yielding a higher concentration or that the anion was being produced as a radiolytic by-product. In the STTP liter-scale tests, only one increase in concentration of a soluble anion in the brine was found. LS-33, a pyrochemical salt experiment in Castile Brine that had added bentonite showed an increase in sulfate concentration from 6000 to 9000 ppm during the length of the test. No explanation is given for this increase.

Nitrate concentrations tended to decrease in all tests but was significant in at least 8 to 10 test containers as shown in TABLE 1. The decrease in nitrate concentrations in the Envirostone tests, which had the highest concentrations of nitrate, was generally accompanied by an increase in the N_2O concentration in the headspace. The reduction of nitrate concentrations is considered to be from chemical oxidation-reduction reactions, radiolytic degradation, or microbial activity. The significance of the radiolytic or chemical reduction of nitrate is that nitrous oxide, N_2O, and nitrite, which are by-products of the degradation of nitrate are compounds that contain the lower oxidation state of nitrogen and are reductants. This reaction could preclude the oxidation of actinides to higher oxidation states. The higher oxidation states of Pu were not found in Portland Cement and Envirostone tests. Pu (VI) was only found in Pyrochemical Salt wastes which were all low in nitrate salts.

Phosphate was initially present in several test containers but apparently quite rapidly formed precipitates that settled and resulted in the reduction in concentration of phosphate in liter-scale tests.

Fluoride was generally low in concentration and could have formed both insoluble and soluble fluoride complexes. LS-35, 36, 37 and 38 were examples of a significant trend, indicating a reduction in fluoride concentrations.

Table 30. Anion Trends in STTP Liter-Scale Tests

LS-ID	NO$_3^-$, ppm	SO$_4^{-2}$, ppm	F$^-$, ppm	TOC, ppm	pcH	Pu, g
LS-01	282-152 ↓	650-594	28	30	8.8	0.02
LS-02	1400-568↓↓	600-416	10	40	10.4	0.11
LS-03	1600-992	14000-12387	12	50	13	0.12
LS-07	256-158	749-800	40	30	8.7	0.03
LS-08	1180-673	700-400	10	60	9.3	0.12
LS-09	1300-816	16000-14000	8	60	13	0.11
LS-10*	250-150	650-770	36	38	8.8	0.02
LS-11*	1000-657↓	600-387	10	40	10.3	0.13
LS-12*	1100-750	14600-13163	8	50	12.9	0.11
LS-13	700-11↓↓	7600-7100	38	3200	7.1	3.39
LS-14	600-8↓↓	7600-6500	45	3500	7.1	3.47
LS-15	260-163	16000-1500	<10	1200	6.9	0.04
LS-16	60-10	6400-6400	<5	400	7.5	0.62
LS-17	20000-11000↓↓	6800-6600	<10	350	7.8	1.47
LS-18	3000-134↓↓	15000-15000	20	400	7.8	2.59
LS-19	45000-28000	12000-9000	50	600	7.9	0.51
LS-20	46000-24000	14000-7830↓	110	380	7.6	0.08
LS-21	47000-28000	18000-18000	12	310	8	0.25
LS-22	55000-31000↓	5000-4800	225	450	7.1	0.25
LS-23	38000-26000	3800-3800	250	480	7.3	0.23
LS-24	40000-28000	11000-12000	25	370	7.7	0.5
LS-25	30-30	80-80	36	20	7.9	0.38
LS-26	60-40	70-70	36	20	7.8	4.06
LS-27	40-37	140-170	10	50	11.1	3.4
LS-31	80-50	4800-4500	5	30	8.7	0.81
LS-32	70-30	4700-4800	5	38	8.7	4.08
LS-33	100-33	6000-9000↑	5	30	9.7	1.15
LS-34	73-22	1200-780	5-3	80	8.8	2
LS-35	50-21	103-106	52-25	60	8.3	0.45
LS-36	61-123	160-200	20-2↓	130-50	11.3	11.13
LS-37*	11-85	61-58	90-34↓	30	7.8	4.33
LS-38*	60-70	150-140	30-10↓	40	7.8	2.74
LS-39*	230-220	15000-16000	-	30	9.6	4.48

* Added 75 mg of Am-241

Drum-Scale Tests

The first 12 STTP Drum-Scale test containers contained heterogeneous waste (debris waste) with TRUCON code 116 and DS-13, 14, and 15 contained massive metal components (TRUCON code 117) with some plastic bags.

Three sets of three drum-scale tests (DS-04 through 12) contained additives that were added during the loading at the Waste Characterization, Repackaging, and Reduction Facility. Drum-scale tests D-04, 05, 06 had added bentonite; DC-07, 08, and 09 had added chelators and DS-10, 11, and 12 had added nitrate as $NaNO_3$ and phosphate as NaH_2PO_4. There was 159 g of $NaNO_3$ and 258 g of $Na_2H_2PO_4$ added to DS-10, 11, and 12.

The anions in the drum-scale tests remained fairly constant throughout the test period except for nitrate. Nitrate in most drum-scale tests decreased during the test period due to chemical, microbial, and/or radiolytic processes. The nitrate in DS-10, 11, and 15 were dramatically reduced from 680 to 10 ppm (DS-10) and 440 to 5 ppm (DS-11), and 234 to <5 ppm (DS-15) as shown in TABLE II.

The degradation by-products from reduction of nitrate are reducing agents that will have a significant role in maintaining the waste in the WIPP repository in a reducing condition.

The concentration of sulfate did not change in any of the drum-scale tests. Fluoride was at a very low level during the test period in all drums (1-26 ppm).

Total organic carbon (TOC) increased continuously in all drum-scale test containers, perhaps, due to the chemical or radiolytic degradation of organic-based materials in the waste. The effect of microbial activity on these brine-immersed materials is unknown.

Phosphate was added to DS-10, 11, and 12 and decreased in concentration within 1 to 2 months to less than detectable limits. The concentration of all actinides in the brine remained very low in the experiments with added phosphate.

Phosphate in the form of $NaH_2PO_4 \cdot H_2O$ at a concentration of ~ 3 g per liter was added to DS-07, 08, and 09 to reduce the concentrations of soluble actinides in the drums with added chelators. Typically, the soluble actinide concentrations were reduced by 87 to 95 %.

Phosphate as a soluble complex had a limited lifetime in the brine of these experiments because of the formation of insoluble phosphate precipitates along with actinide phosphates.

A detailed description of the phosphate addition to DS-07, 08, and 09 is given in the document, “Phosphate Addition to Drums 7, 8, and 9 and its Effect on Soluble Actinide Species,” LA-UR-01-3081, May 2001.

Table 31. Anion Trends in STTP Drum-Scale Tests

Drum-ID	Additives	NO_3^-, ppm	SO_4^{-2}, ppm	F^-, ppm	TOC, ppm	pcH	Pu, g
DS-01	none	300-34	5000-4800	2	120-190↑	7.8	7.1
DS-02	none	46-40	5000-5000	5	150-248↑	7.8	8.15
DS-03	none	48-39	18000-17000	<1	130-190↑	7.0	8.19
DS-04	bentonite	90-20	5000-5000	15	110-180↑	7.4	9.11
DS-05	bentonite	46-20	4800-4800	8	650-800↑	7.3	9.38
DS-06	bentonite	150-145	17000-16000	5	230-370↑	7.1	10.78
DS-07	chelators	38-35	5000-5000	20	260-330↑	7.4	11.6
DS-08	chelators	800-800	5000-48000	26	360-540↑	7.2	14.94
DS-09	chelators	500-530	17000-17000	6	475-600↑	7.3	16.25
DS-10*	NO_3^-/PO_4^{-3}	680-10↓↓	4900-4900	12	380-590↑	7.5	16.44
DS-11*	NO_3^-/PO_4^{-3}	440-5↓↓	4700-4800	4	200-300↑	7.5	16.45
DS-12*	NO_3^-/PO_4^{-3}	600-550	17000-17000	2	200-600↑↑	6.5	16.7
DS-13	metals	10-<5	5000-5000	16	40-70↑	6.0	12.74
DS-14	metals	60-15	5000-4900	5	45-88↑	6.8	8.19
DS-15	metals	234-<5↓↓	17000-16000	1	70-137↑	7.8	16.22

* Added 159 gm of nitrate equivalent to 763 ppm

XXII. Effect of Brine Type on Fe after Phosphate Addition

The addition of sodium dihydrogen phosphate (258 gm or ~ 2060 ppm) to the three drum scale tests with chelators (DS-07, 08, and 09) was very successful in reducing the actinides by 90% by precipitation as insoluble phosphates. The precipitation was successful in all tests despite the high stability constant chelators such as citrate and oxalate. However, when the soluble Fe concentration was followed during the same period, a rather curious result was obtained in that the Fe concentration in the brine was not reduced in the tests with Brine A but was significantly reduced (>97%) in the test with Castile Brine (DS-09). There was essentially no difference in the waste for these tests and the pcH was about the same for all three tests. The major difference was the higher concentration of Mg in the Brine A and the higher concentration of sulfate in Castile Brine. The lack of Mg in the Castile Brine test in D09 is what is considered to be the reason that Fe precipitated in this test. This result supports the conclusion that Mg usurped much of the strong chelators by the common ion effect leaving the Fe in the test with less Mg to combine with phosphate and be precipitated. The high ionic strength of Brine A with a high concentration of Mg seems to have had a significant influence in minimizing the effect of soluble chelators on Fe relative to phosphate. This could be a significant finding for mitigating the solubilizing effect of chelators in the presence of high concentrations of soluble Mg in Brine A and Castile Brine in contact with MgO. The concentration of Fe before and after addition of phosphate in the three drum-scale tests is shown below.

Table 32. Impact of Phosphate Addition to Fe in D07, D08 and D09 Tests

	DS-07	**DS-08**	**DS-09**
Date	**Fe, ppm**	**Fe, ppm**	**Fe, ppm**
11-30-98	118	160	218
02-01-99	206	318	352
	Phosphate Added	**Phosphate Added**	
07-22-99	198	-	-
07-22-99	199	-	-
07-29-99	207	-	-
08-09-99	158	176	-
08-09-99	184	-	-
08-25-99	-	-	195
			Phosphate Added
09-20-99	-	55	**5**
10-18-99	138	122	**3**

Table 33. pcH Change after Addition of Phosphate

	PcH Before Addition	PcH After Addition
DS-07	7.5	5.2
DS-08	7.3	7.0
DS-09	7.3	7.4

Ca and Mg concentrations were not affected by phosphate addition.

* 258 gm of $NaH_2PO_4 \cdot H_2O$ is equivalent to ~ 2060 mg/liter or 2060 ppm in the drum-scale brine

XXIII. Phosphate Addition to drum-Scale tests with Chelators; Application to Sulfate

The drum-scale tests with added chelators were at least 2 to 3 orders of magnitude greater in concentration of all soluble actinides and Nd relative to other drum-scale tests. Drum-scale tests DS-7, 8, and 9 were loaded with combustible wastes (TRU CON code 116/216) with DS-7, and 8 containing Brine A and DS-9 containing Castile Brine. Each drum contained Th-232 (4.77g), Np-237 (4.97g), U-238 (4.97g) and 6.42 g of $NdCl_3$. Each drum contained ~ 5.3 liters of microbial inoculum that consisted of 1.06 liters of cake brine and sediment mixture (20%), 1.59 liters of muck-pile solution mixture (30%), and 2.65 liters of G-Seep brine from the Salado Formation (50%).

Based on experience established by assessing the impact of phosphates added to samples of brine from both liter-scale and drum-scale tests, it became obvious that phosphate was effective in reducing the concentration of actinides in STTP brine. However, this experience did not extend to drum-scale tests with added chelators. At the beginning of the STTP, phosphate in the form of $NaH_2PO_4 \cdot H_2O$ had been added to DS-10, 11, and 12 at a concentration of 258 g of $NaH_2PO_4 \cdot H_2O$ per drum or about 1.38 gm/liter based on a brine volume of about 49.4 gal/drum. This represented a concentration of 1.87 mole of $NaH_2PO_4 \cdot H_2O$ per drum or 0.0378 mole/liter. The phosphate concentration was about 0.0378 x 0.6882 = 0.0260 molar solution of phosphate. This is about 1.38 x 0.6882 = 0.95 gm of PO_4^{3-} added per liter or 950 mg/liter which is equivalent to 950 ppm. This concentration of phosphate appeared to be very effective for precipitating and reducing the concentration of actinides in DS 10, DS 11, and DS 12 and a decision was made to add phosphate to DS 7, 8, and 9 to establish the effectiveness of reducing actinide concentrations in the brine of these drums with added chelators.

The identity and concentrations of chelators added to DS-7, 8, and 9 given below.

Table 34. Identity and Concentration of Chelators Added to Drum-Scale Tests

Chelator	DS-07	DS-08	DS-09
Oxalic Acid, Na Salt $\cdot H_2O$	217 ppm	217 ppm	217 ppm
Sodium acetate	210 ppm	210 ppm	210 ppm
Trisodium Citrate $\cdot H_2O$	233 ppm	233 ppm	233 ppm
Acetamide	151 ppm	151 ppm	151 ppm
Ammonium thiocyanate	222 ppm	222 ppm	222 ppm

The concentration of phosphate as sodium orthophosphate or sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) added to each of the tests in DS-7, 8, and 9 was 3 gm per liter or ~ 567.75 gm/drum. This would represent 4.11 mole of $NaH_2PO_4 \cdot H_2O$ or 2.83 mole of phosphate per drum or a solution that is 0.0217 molar in phosphate . Addition of 3 gm of $NaH_2PO_4 \cdot H_2O$ per liter will give a concentration of ~ 2060 mg/liter or 2060 ppm of phosphate. After addition of the phosphate solution, each drum was rotated to mix the phosphate into the brine in the drum.

Effectiveness of the addition of phosphate to the drums with chelators is given below for DS-7, 8, and 9.

Table 35. Reduction in Nd and Actinide Concentrations, DS-07

Element	Average Conc. Before Adding Phosphate (ppb)	Lowest Conc. After Adding Phosphate (ppb)	Reduction Factor	% Reduction
Nd	3,807	40.0	95.6	99.0
Th	10,986	368	29,9	96.7
Np	19,100	1,050	18.2	94.5
U	18,162	721	25.2	96.0
Pu	1,546	32.0	48.3	97.9
Am	7	0.4	17.5	94.3

Table 36. Reduction in Nd and Actinide Concentrations, DS-08

Element	Average Concentration		Reduction Factor	% Reduction
	Before Adding Phosphate (ppb)	After Adding Phosphate (ppb)		
Nd	4,493	206	21.8	95.4
Th	13,338	5,488	2.44	59.2
Np	14,547	2,988	4.87	79.5
U	13,188	894	14.8	93.2
Pu	3,019	506	5.97	83.2
Am	34.9	2.77	12.6	92.1

Table 37. Reduction in Nd and Actinide Concentrations, DS-09

Element	Average Concentration		Reduction Factor	% Reduction
	Before Adding Phosphate (ppb)	After Adding Phosphate (ppb)		
Nd	3,520	388	10.4	90.4
Th	7,880	865.5	9.10	89.0
Np	16,900	1,841	9.20	89.1
U	16,300	826.5	19.7	94.9
Pu	2,180	371.5	5.86	82.9
Am	16.53	2.7	6.12	83.7

The stability constants of the added chelators to the STTP drum-scale tests DS07, 08, and 09 are dependent on the pcH and ionic strength of the solutions. The pcH of the brine solutions before and after addition of phosphate is given in the following data.

Table 38. Impact of Phosphate Addition to pcH of DS-07, 08, and 09

Liter-scale	**Brine**	**PcH Before Addition**	**PcH After Addition**
DS-07	Brine A	7.4-7.5	5.0-5.5
DS-08	Brine A	7.2-7.3	6.8-8.1
DS-09	Castile	7.2-7.4	7.4

The chelators added were very successful in solubilizing all actinides and Nd in three tests. Citrate and oxalate were expected to have the greatest effect in solubilizing the actinides as both have stability constants greater than the hydroxide radical in neutral to basic pHs. The concentration of those two chelators was 233 ppm and 217 ppm, respectively. We added phosphate at a concentration that was ~10 times the concentration of the citrate (2060 ppm vs 233 ppm) to try to precipitate the chelated actinides as insoluble phosphates. The reduction of all actinides and Nd averaged about 90% so the phosphate was successful in the metathesis of insoluble actinide phosphates with the soluble chelated species. Interestingly, the Fe, Ca, and Mg were not significantly affected by the addition of phosphate to the Brine A experiments DS-07 and DS-08 but the Fe was significantly reduced in DS-09, the Castile Brine experiment. This data supports the observation that high Mg content increases the ionic strength of Brine A experiments and reduce the effectiveness of chelators in solubilizing actinides in the presence of other chelators with similar stability constants.

Sulfate forms strong complexes in acid solution with tetravalent Pu as demonstrated by potentiometric and spectrophotometric changes. Sulfate does not have high stability constants as phosphate but in the absence of other complexing agents can have a significant effect in stabilizing Pu in the Pu (IV) state. However, the chemistry of Pu and sulfate in a basic media has not been extensively studied. In the absence of other organic and inorganic anions and complexing agents, sulfate has a stabilizing effect for maintaining Pu in the Pu (IV) oxidation state and could have had a major role in allowing Pu (IV) to be oxidized in the sulfate-deficient pertinent liter-scale tests with Direct Oxide Reduction salts.

XXIV. A Comparison of Actinide Concentrations; Rotation vs. Quiescent Mode

The STTP liter-scale and drum-scale tests were all rotated weekly during the 4-5 year test period to assure thorough mixing of the waste with the brine. The process of rotation was integrated into the STTP operation as a compromise that would allow more rapid steady-state conditions for actinides in the comminuted STTP wastes because a test time frame pertinent to the repository would not be practical. The condition in the repository would be more of a quasi-static or quiescent state because movement of brine would be initiated by massive salt creep that would occur relatively slowly compared to the time of the STTP tests. Sampling of STTP tests was conducted about 32 hours after rotation to allow precipitates and large suspensions to settle prior to sampling. On occasion, the needle from the sampling syringe would draw a settled material from the bottom of the test container screen that would eventually be filtered out in the filtering processes. The rotation process for all test containers continued until spring of 1999 (March, April timeframe) and the test containers were allowed to set without rotation for the remainder of the experiments. A comparison was made of the samples taken as part of the final rotation and a sample taken after the test containers set for 1 to 2 years in a quiescent mode after the final rotation had been conducted. The analytical results were compared to determine if there were any test containers that showed unusually large changes in concentration, especially high increases during the quiescent period. Abnormal decreases in activity were also noted to determine whether there was a significant difference between the rotation and quiescent modes of operation. The ICP-MS used for the final analysis of the quiescent mode samples was a newer instrument with greater sensitivity than the analyses made during the rotation mode of operation. It was expected that actinide concentrations would decrease during the quiescent mode because less leaching of the waste would be effected during the quiescent period and small particulate could be adsorbed/absorbed by aged precipitates.

Portland Cement Test Results

The results of the Portland Cement tests were generally a comparison of very low levels of actinide concentrations. The comparison of actinide concentration during rotation and quiescent periods of operation showed in general that there was not a significant increase or decrease in concentration except for pressurized liter-scale test, LS-6 with Castile Brine. For LS-6, U increased during the quiescent mode from 3675 ppb to 7900 ppb and Pu decreased from 319 ppb to 4.2 ppb. The increase in U concentration can be explained because about 60 bar of CO_2 pressure was maintained on this test and U could certainly be solubilized as carbonates during the test period. The greater impact on the Castile Brine test is typical of other STTP test results. The large decrease of Pu from 319 ppb to 4.2 was rather surprising and no explanation is given for this change in concentration.

Envirostone Test Results

The actinide concentrations of the Envirostone tests varied more than the Portland Cement tests, especially the U and Pu results. Liter-scale tests LS-16 and LS-18 were examples of large increases in the concentration of Np, U, and Pu. LS-16 was unique in that it was on a definite upward trend of Pu and Np concentrations while U was on a significant downward trend. The increase of concentrations for Np (213 to 1000 ppb), U (182 to1800 ppb) and Pu (1187 to3000 ppb) is considered to be significant for a quiescent mode experiment and no explanation could be established for this difference in concentration. LS-16 was one of the only STTP tests that had a significant upward trend of Pu concentrations at the end of the test period. Likewise, LS-18 showed significant increases in concentration for Th (<0.10 to 7.9 ppb), Np (79 to 560 ppb), U (9519 to 29000 ppb) and Pu (2.7 to 18 ppb). No explanation could be established for the unusual increases in actinide concentrations for this test container. Most other Envirostone tests did not show significant increases in concentration.

Pyrochemical Salt Waste Test Results

The Pyrochemical Salt waste tests contained the highest levels of actinides and were expected to have some of the largest differences in concentrations of actinides between the samples taken during rotation and the samples taken after a lengthy quiescent mode. This expectation was not realized because most of the results did not show significant differences in actinide concentrations. Some of the large differences were noted in the following test containers.

LS-25	Pu increased from 39.8 to 250 ppb.
LS-29	(Pressurized) Pu increased from 6865 to 14000 ppb.
LS-30	U decreased from 2787 to 300 ppb.
LS-34	Pu increased from 13.5 to 87 ppb.
LS-36	Pu decreased from 1439 to 420 ppb.
LS-37	Pu significantly increased from 194 to 5500 ppb.

No explanation for the changes in actinide concentrations was attempted.

Drum-Scale Test Results

The drum-scale tests generally contained very low levels of soluble actinides except for DS-07, 08 and 09, which had added chelators. The levels of activity in these test drums were reduced by addition of sodium dihydrogen phosphate late in the test. The concentrations of actinides in the drum-scale tests conducted during the rotation phase were generally a little higher than the sample analyzed after the quiescent mode, as expected. The examples of tests with significant differences are summarized as follows.

DS-09 All actinides decreased significantly
- Nd (293 to 0.28 ppb)
- Th (794 to 2.0 ppb)
- Np (1615 to 5.4 ppb)
- U (728 to 4.7 ppb)
- Pu (328 to 140 ppb)
- Am (2.4 to 0.5 ppb)

DS-12 All actinides increased significantly
- Nd (<2.0 to 190 ppb)
- Th (<1.2 to 1000 ppb)
- Np (<0.8 to 1200 ppb)
- U (4.6 to 450 ppb)
- Pu (<1.3 to 220 ppb)
- Am (<0.4 to 1.1 ppb)

The differences in the above two test containers are so significant that a confusion of these two samples must be considered. There is no other explanation for the large differences in concentration of the two sets of data.

Overall Assessment of Comparison of Samples with and without Rotation

The environment in the WIPP repository is projected to be fairly static or quiescent for most of the lifetime of the repository. If brine is present in sufficient quantities to immerse the waste, the only perturbation to the brine in the Disposal Room environment would be due to massive salt creep closure movement which is projected to be relatively slow during the 20 to 200 year closure timeframe. A more vigorous brine perturbation could occur on a one-time basis due to human intrusion or geologic upheaval. Given the conditions that are projected for the repository, the concentration of actinides in actual non-comminuted wastes assumed to be immersed in quiescent brine would be at considerably lower levers than found in the STTP tests. For the STTP, the comparison of samples taken during the rotational phase was not significantly different from the sample set taken after one to two years in a quiescent mode.

Analytical Results of Final Sampling of STTP Test Containers in a Quiescent Mode

The analytical data obtained for the final set of samples taken after the liter-scale and drum-scale test containers remained in a static mode for up to 2 years at 30°C is presented. The results were obtained on an ICP-MS that was newer and had a greater sensitivity for actinides than the ICP-MS used for the earlier samples taken during the rotational phase of the STTP. The newer ICP-MS was located in a different laboratory at TA-48 and the final samples were transported to that laboratory for analyses. A comparison follows for the final samples taken during the test phase when the test containers were rotated and analyzed by the ICP-MS in the CMR building and the final samples analyzed at TA-48. The greater sensitivity and lower detection limit of the new TA-48 ICP-MS is most evident in the Am-241 results. The comparison of the two sample sets for Portland Cement, Envirostone, Pyrochemical Salts and Drum-Scale Heterogeneous wastes follows.

Table 39. Final Sampling of STTP Liter-scale Test Containers (Reportable results ppb)

ID	Date	Nd-146	Th-232	Np-237	U-238	Pu-239	Am-241
LS-02	4/10/01	0.10	0.10	0.14	1.3	0.78	<0.0024
LS-03	4/13/01	0.062	0.25	0.22	14	1.7	<0.00063
LS-04	5/11/01	<0.28	3.767	1.4	6500	6.3	0.30
LS-05	5/11/01	<0.057	0.56	0.13	380	1.8	0.07
LS-06	4/21/01	<0.28	1.4	0.51	7900	4.2	0.29
LS-07	4/10/01	<0.057	0.40	130	15	1.0	<0.0011
LS-08	4/10/01	<0.057	<0.14	0.16	0.79	1.3	<0.0024
LS-09	4/27/01	<0.057	0.079	0.24	4.9	0.72	0.057
LS-10	2/7/01	<0.057	0.69	93	13	20	0.24
LS-11	2/7/01	0.10	0.16	0.15	5.1	1.2	<0.0024
LS-12	2/1/01	0.062	0.17	0.11	0.82	<0.78	<0.0024
LS-13	1/25/01	2.9	3.1	2.4	270	5.2	0.14
LS-14	1/19/01	13	2.2	0.95	320	6.8	0.27
LS-15	4/27/01	22	7.8	88	3500	17	0.30
LS-16	12/20/00	170	190	1000	1800	3000	3.9
LS-17	2/15/01	4.7	0.38	50	1000	1.5	0.063
LS-18	1/10/01	<1.1	7.9	560	29000	18	1.4
LS-22	4/10/01	1.1	0.39	2.1	1000	0.88	0.090
LS-23	3/14/01	6.1	0.64	250	770	2.6	0.89
LS-24	4/13/01	0.50	1.4	0.57	330	0.81	0.069
LS-25	4/10/01	<0.28	2.0	120	6.4	250	0.63
LS-26	1/25/01	<4.2	<14	9.1	<6.3	2400	12
LS-28	5/11/01	<52	430	580	410	86000	160
LS-29	6/6/01	30	130	9300	8200	14000	35
LS-30	6/6/01	0.77	29	100	300	710	0.69
LS-33	2/1/01	<0.084	<0.28	11	4.6	140	0.37
LS-34	4/10/01	<0.057	0.51	13	21	87	0.20
LS-35	3/14/01	0.43	36	630	34	83	0.83
LS-36	11/30/00	<0.42	16	4.4	0.85	420	3.4
LS-37	12/6/00	<8.4	0.47	15	0.93	5500	8.6
LS-38	12/20/00	<0.042	0.084	0.22	0.037	15	0.022
LS-39	11/15/00	<0.84	2.5	3.5	31	970	2.7

Table 40. Final Sampling of STTP Drum-Scale Test Containers (Reportable results ppb)

ID	Date	Nd-146	Th-232	Np-237	U-238	Pu-239	Am-241
DS-01	6/6/01	2.4	6.4	32	29	1.2	0.020
DS-02	6/6/01	0.82	2.7	23	180	0.81	0.020
DS-03	6/6/01	0.67	1.4	5.7	110	0.77	0.011
DS-04	6/6/01	0.10	1.2	2.3	13	0.29	0.008
DS-05	6/6/01	0.20	1.3	1.0	15	1.1	0.014
DS-06	6/6/01	0.21	1.3	17	39	1.3	0.015
DS-07	6/6/01	14	290	480	300	19	0.67
DS-08	6/6/01	78	5000	2400	760	210	1.6
DS-09	6/6/01	<0.28	2.0	5.4	4.7	140	0.50
DS-10	6/6/01	0.064	2.3	11	20	0.56	0.016
DS-11	6/6/01	0.091	1.3	6.0	51	0.25	0.026
DS-12	6/6/01	190	1000	1200	450	220	1.1
DS-13	6/6/01	<0.055	3.1	4.2	4.1	1.3	0.020
DS-14	6/6/01	28	1.3	11	6.1	0.84	0.022
DS-15	6/6/01	49	1.6	2.2	2.9	1.1	0.093

Table 41. Portland Cement Test Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-02	12/14/98	<2.0	<1.2	<0.9	1.2	<1.3	<0.4	10.3
	4/10/01	0.10	0.10	0.14	14	0.78	<0.0024	
LS-03	2/22/99	<2.0	<1.2	<0.9	9.6	0.60	<0.4	12.9
	4/13/01	0.06	0.25	0.22	14	1.7	<0.00063	
LS-04	9/21/98	<0.5	6.3	15.9	8507.0	255	0.70	7.3
	5/11/01	<0.28	3.8	1.4	6500	6.3	0.30	
LS-05	9/21/98	<0.5	0.6	1.7	479.0	13.9	<0.1	7.4
	5/11/01	<0.06	0.56	0.13	380	1.8	0.07	
LS-06	9/21/98	2.7	3.0	11.4	3675.0	319.0	0.90	7.6
	4/21/01	<0.28	1.4	0.51	7900	4.2	0.29	
LS-07	3/15/91	5.6	1.5	254.0	12.7	4.1	0.80	8.8
	4/10/01	<0.06	0.04	130	15	1.0	<0.0011	
LS-08	3/15/91	4.8	0.90	0.90	1.4	11.3	1.0	9.3
	4/10/01	<0.06	<0.14	0.16	0.79	1.3	<0.0024	
LS-09	3/15/99	4.3	0.90	0.80	3.2	3.6	1.0	13.0
	4/27/01	<0.06	0.80	0.24	4.9	0.72	0.057	
LS-10	3/15/99	5.9	3.2	32.5	11.9	21.5	1.9	8.7
	2/7/01	<0.06	0.69	93	13	20	0.24	
LS-11	3/15/99	3.9	1.0	0.60	1.1	6.4	0.7	9.7
	2/7/01	0.10	0.16	0.15	5.1	1.2	<0.0024	
LS-12	3/15/99	3.3	0.70	0.60	0.80	3.1	0.7	13.0
	2/1/01	0.06	0.17	0.11	0.82	<0.78	<0.0024	

* The first date for each test container is the final sample taken during the test phase with rotation. Analysis completed in the CMR building.
The second date is the sample taken after the quiescent mode. Analysis completed at TA-48 with newer ICP-MS.

Table 42. Envirostone Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-13	3/1/99	<2.0	<1.2	<0.9	1295.0	26.0	<0.4	7.1
	1/25/01	2.9	3.1	2.4	270	5.2	0.14	
LS-14	4/5/99	16.5	19.2	3.6	1651.0	62.0	1.4	7.1
	1/19/01	13	2.2	0.95	320	6.8	0.27	
LS-15	4/5/99	22.1	6.4	59.8	1052.0	22	1.3	7.6
	4/27/01	22	7.8	88	3500	17	0.30	
LS-16	2/22/99	51.2	282.0	213.0	182.0	1187.0	3.0	7.5
	12/20/01	170	190	1000	1800	3000	3.9	
LS-17	2/22/99	<2.0	<1.2	1.6	269.0	1.5	0.4	7.8
	2/15/01	4.7	0.38	50	1000	1.5	0.063	
LS-18	3/8/99	1.4	<0.10	79.0	9519.0	2.7	0.3	7.8
	1/10/01	<1.1	7.9	560	29000	18	1.4	
LS-22	2/22/99	2.5	<1.2	<0.9	619.0	2.4	<0.4	7.2
	4/10/01	1.1	0.39	2.1	1000	0.88	0.090	
LS-23	3/01/99	<2.0	<1.2	<0.9	261.0	8.2	<0.4	7.5
	3/14/01	6.1	0.64	250	77	2.6	0.89	
LS-24	2/22/99	<2.0	<1.2	3.5	267.0	2.0	<0.4	7.8
	4/13/01	0.50	1.4	0.57	330	0.81	0.069	

Table 43. Pyrochemical Salt Test Results Actinide Concentrations after Final Rotation vs. Brine Quiescent State for 1-2 Years (all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-25	10/18/99	4.4	2.4	154	5.1	39.8	0.5	8.1
	4/10/01	<0.28	2.0	120	6.4	250	0.63	
LS-26	10/18/99	2.6	0.5	1.7	0.8	3287.0	9.9	8.1
	1/25/01	<4.2	<14	9.1	<6.3	2400	12	
LS-28	5/17/99	49.3	519.0	744.0	668.0	188463	347	5.1
	5/11/01	<52	430	580	410	86000	160	
LS-29	9/21/98	6.9	377	8179.0	9513.0	6865.0	36.6	4.7
	6/6/01	30	130	9300	8200	14000	35	
LS-30	9/21/98	6.0	32.9	135.0	2787.0	1011.0	2.8	6.6
	6/6/01	0.77	29	100	300	7.0	0.69	
LS-33	3/8/99	1.5	0.4	5.5	0.7	135.0	0.8	9.6
	2/1/01	<0.08	<0.28	11	4.6	140	0.37	
LS-34	3/8/99	1.6	11.1	152.0	74.0	13.5	0.60	8.8
	4/10/01	<0.06	0.51	13	21	87	0.20	
LS-35	3/8/99	1.0	62.0	1260.0	53.0	86.0	0.90	8.3
	3/14/01	0.43	36	630	34	83	0.83	
LS-36	3/8/99	1.4	53.0	16.5	4.4	1439.0	6.7	11.4
	11/30/01	<0.42	16	4.4	0.85	420	3.4	
LS-37	3/15/99	3.2	0.6	0.6	0.5	194.0	1.2	7.8
	12/6/01	<8.4	0.47	15	0.93	5500	8.6	
LS-38	3/15/99	4.2	0.6	0.9	0.9	16.8	0.8	8.0
	12/20/01	<0.04	0.08	0.22	0.04	15	0.022	
LS-39	3/15/99	4.1	0.8	5.9	31.1	1994.0	17.6	9.5
	11/15/01	<0.84	2.5	3.5	31	970	2.7	

Table 44. Drum-Scale Test Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
DS-01	2/1/99	6.5	10.6	44.0	45.0	1.8	0.6	7.7
	6/6/01	2.4	6.4	32	29	1.2	0.020	
DS-02	2/1/99	5.4	16.7	51.0	227.0	2.6	0.7	7.7
	6/6/01	0.82	2.7	23	180	0.81	0.020	
DS-03	2/1/99	1.5	0.8	0.9	142.0	0.6	0.5	6.9
	6/6/01	0.67	1.4	5.7	110	0.77	0.011	
DS-04	2/1/99	0.5	0.5	0.6	20.2	1.0	0.3	7.4
	6/6/01	0.10	1.2	2.3	13	0.29	0.008	
DS-05	2/1/99	<0.4	0.5	1.1	32.2	1.1	0.3	7.2
	6/6/01	0.20	1.3	1.0	15	1.1	0.014	
DS-06	2/1/99	<0.4	0.2	1.6	11.5	0.3	0.4	7.2
	6/6/01	0.21	1.3	17	39	1.3	0.015	
DS-07	10/1/99	39.8	368.0	1052.0	721.0	32.0	0.4	5.0
	6/6/01	14	290	480	300	19	0.67	
DS-08	10/18/99	197.0	6400.0	3508.0	980.0	538.0	2.6	6.8
	6/6/01	78	5000	2400	760	210	1.6	
DS-09	10/18/99	293.0	794.0	1615.0	728.0	328.0	2.4	7.4
	6/6/01	0.28	2.0	5.4	4.7	140	0.50	
DS-10	2/8/99	<2.0	23.7	312.0	131.0	24.9	<0.4	7.5
	6/6/01	0.06	2.3	11	20	0.56	0.016	
DS-11	2/8/99	<2.0	<1.2	1.6	25.2	1.2	<0.4	7.4
	6/6/01	0.091	1.3	6.0	51	0.25	0.026	
DS-12	2/8/99	<2.0	<1.2	<0.8	4.6	<1.3	<0.4	6.3
	6/6/01	190	1000	1200	450	220	1.1	
DS-13	2/8/99	55	<1.2	0.7	1.1	1.6	<0.3	6.0
	6/6/01	<0.06	3.1	4.2	4.1	1.3	0.02	
DS-14	2/8/99	18	<1.2	25.3	375.0	<1.3	<0.3	6.7
	6/6/01	28	1.3	11	6.1	0.84	0.022	
DS-15	2/8/99	<2.0	<1.3	44.7	404	<1.3	<0.4	7.7
	6/6/01	49	1.6	2.2	2.9	1.1	0.093	

XXV. Oxidation-Reduction (Eh) of STTP Samples

The measurement of the Eh or oxidation-reduction potential in STTP brines was accomplished by observing the response of a Pt electrode/Ag/AgCl reference electrode that had been calibrated in the high ionic strength brine solutions. Each measurement was completed after allowing the redox electrodes to achieve equilibrium in the solution as evidenced by an electrode readout drift of $\leq$ 1 mV/min. A measurement that resulted in a readout that failed to attain the $\leq$ 1 mV/min stability within 10 minutes was considered to not be in equilibrium. The measurement system was checked against a Fe^{2+}/Fe^{3+} ammonium sulfate solution in 1M H_2SO_4. The goal of the measurement of Eh is to establish the oxidation-reduction potential in a very complex and high ionic strength brine solution that actually expresses the thermodynamic red-ox state of the solution. To accomplish this measurement in the STTP solutions required a recognition that a large number of factors could yield results that are not representative of the thermodynamic properties of the solution such as variable exchange currents, non-electroactive redox couples in actual samples, mixed potentials, electrode poisoning, non-equilibrium of couples in non-ideal solutions, different gas compositions in the headspace of samples, and establishing Eh measurements in samples with a host of different cations, anions, and radiolytic levels. It would be presumptuous to assert that a comparison of the redox conditions in different test containers can be made. With some degree of confidence, one could say that a specific test container is changing in time from measurement to measurement in a specific direction. To establish whether a specific test container has established a specific oxidation-reduction environment requires that an arbitrary Eh value be selected to indicate whether a solution is oxidizing or reducing and to what extent the solution exhibits these properties.

An assessment of all the Eh measurements made of STTP samples resulted in a conclusion that only one test showed significant oxidizing Eh values, liter-scale No. 26. Interestingly, LS-26 was the test container that had the highest and most persistent concentration of Pu (VI). A graphic display of the Eh measurements made on select test containers and LS-26 is shown as follows.

Table 45. Select STTP Eh Results

Container ID	Content	Description	Most Recent Eh (mV)	Date	Redox
LS-03	Portland cement		-30.6	02-Jul-98	Reducing
LS-05	Portland cement	CO_2 pressure	-38.8	07-Aug-97	Reducing
LS-12	Portland cement	^{241}Am added	7.5	22-Jul-98	Reducing
LS-14	Envirostone	Organic added	11.2	09-Jul-98	Reducing
LS-15	Envirostone	Organic added	-10.9	09-Jul-98	Reducing
LS-26	Pyrochem. salt	DOR	441.4	09-Jul-98	Oxidizing
LS-27	Pyrochem. salt	DOR	220.6	09-Jul-98	Neutral
LS-36	Pyrochem. salt	DOR	190.7	15-Jul-98	Neutral
DS-04	Drum scale	Combustible	46.2	28-Jul-98	Reducing
DS-14	Drum scale	Metal	-89.8	17-Jun-98	Reducing

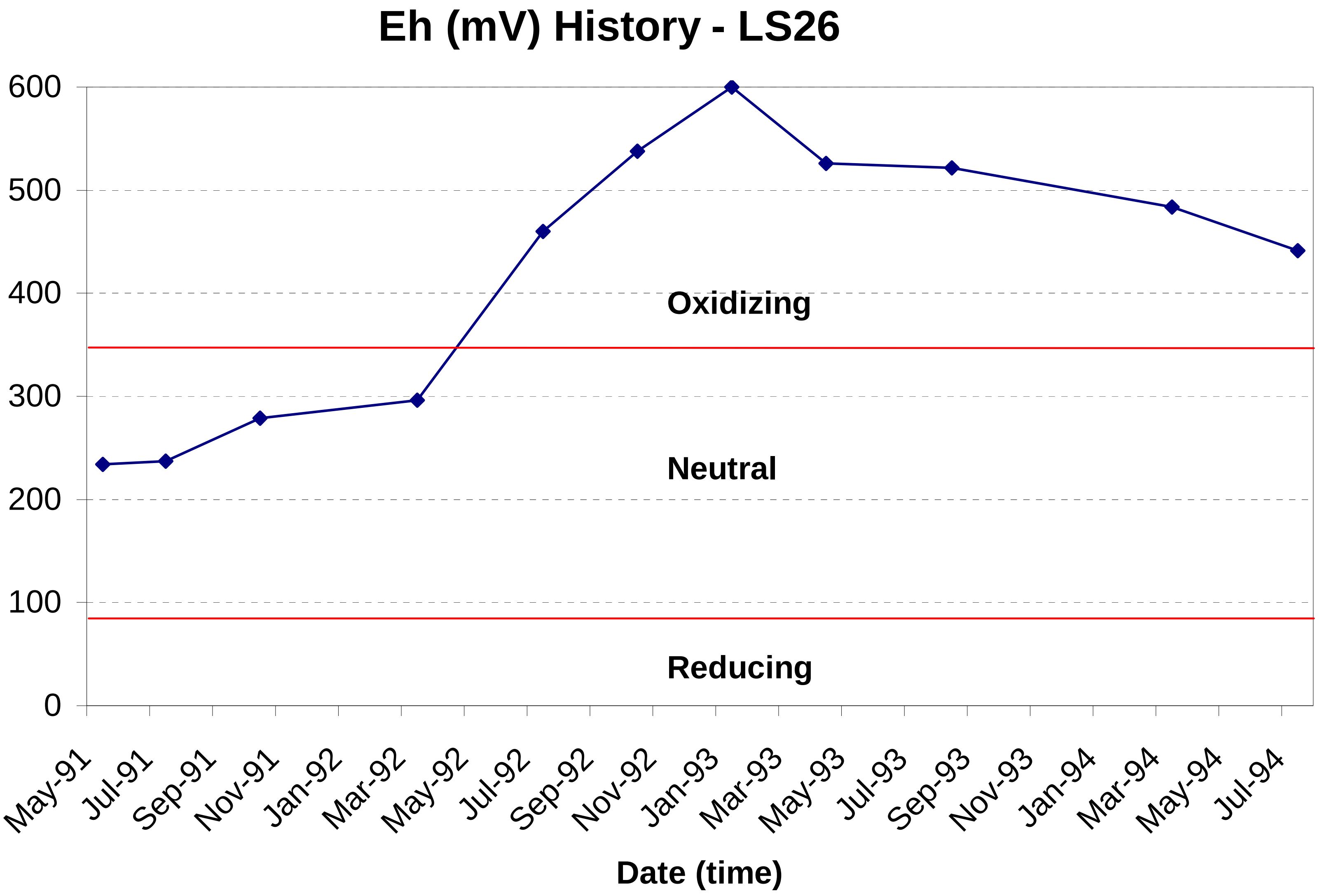
Eh: vs Ag/AgCl reference electrode
Red/Ox criteria:
Reducing is arbitrarily selected to be within 250 mV of the lowest measured value, -164.3 mV
Oxidizing is arbitrarily selected to be within 250 mV of the highest value, 600 mV

Table 46. LS-26 Eh History

Date	Eh (mV)
05-May-95	234.2 (Neutral)
13-Jul-95	237.2 (Neutral)
25-Oct-95	278.9 (Neutral)
14-Mar-96	296.3 (Neutral)
02-Jul-96	460 (Oxidizing)
02-Oct-96	538 (Oxidizing)
29-Jan-97	600 (Oxidizing)
30-Apr-97	525.8 (Oxidizing)
20-Aug-97	521.6 (Oxidizing)
01-Apr-98	483.3 (Oxidizing)
09-Jul-98	441.4 (Oxidizing)

Liter-scale test container L-26 had Pu (VI) and LS-27 and L-36 had Pu (V).

Figure 12.


Eh (mV) History - LS26
600
500
400
300
200
100
0
Eh (mV)
Oxidizing
Neutral
Reducing
May-91
Jul-91
Sep-91
Nov-91
Jan-92
Mar-92
May-92
Jul-92
Sep-92
Nov-92
Jan-93
Mar-93
May-93
Jul-93
Sep-93
Nov-93
Jan-94
Mar-94
May-94
Jul-94
Date (time)