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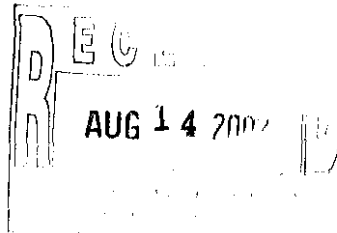
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Final Report  
Volume I

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THE ACTINIDE SOURCE-TERM WASTE TEST PROGRAM (STTP)

**Final Report**

Prepared for the DOE-Carlsbad Field Office

Summer 2001

**VOLUME I**

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NMT-11  
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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, complexing 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*.

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### 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.

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## 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 required 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<sup>2</sup> • 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., <sup>14</sup>C, <sup>85</sup>Kr, <sup>222</sup>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 nor 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 <sup>222</sup>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.,  $^{226}\text{Ra}$ ) 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  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{234}\text{U}$ ,  $^{233}\text{U}$ , and  $^{230}\text{Th}^*$  (Helton et al., 1992). At early times, the bulk of the activity comes from Pu ( $^{238}\text{Pu}$  and  $^{239}\text{Pu}$ ) and  $^{241}\text{Am}$ . However, other actinide isotopes come into play during the 10,000 year post-operational phase. The inventories of  $^{234}\text{U}$  and  $^{230}\text{Th}$  increase as  $^{238}\text{Pu}$  decays (99.95% conversion to  $^{234}\text{U}$  after 1000 years), and significant quantities of  $^{237}\text{Np}$  result from alpha-decay of  $^{241}\text{Am}$  (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  $\text{PuO}_2^+$ ) extends from  $10^{-17}$  to  $10^{-3}$  M or 14 orders of magnitude. The range for Am (as  $\text{AmCl}_2^+$ ) 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.

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### 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., ethylenediaminetetraacetic 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<sub>2</sub> 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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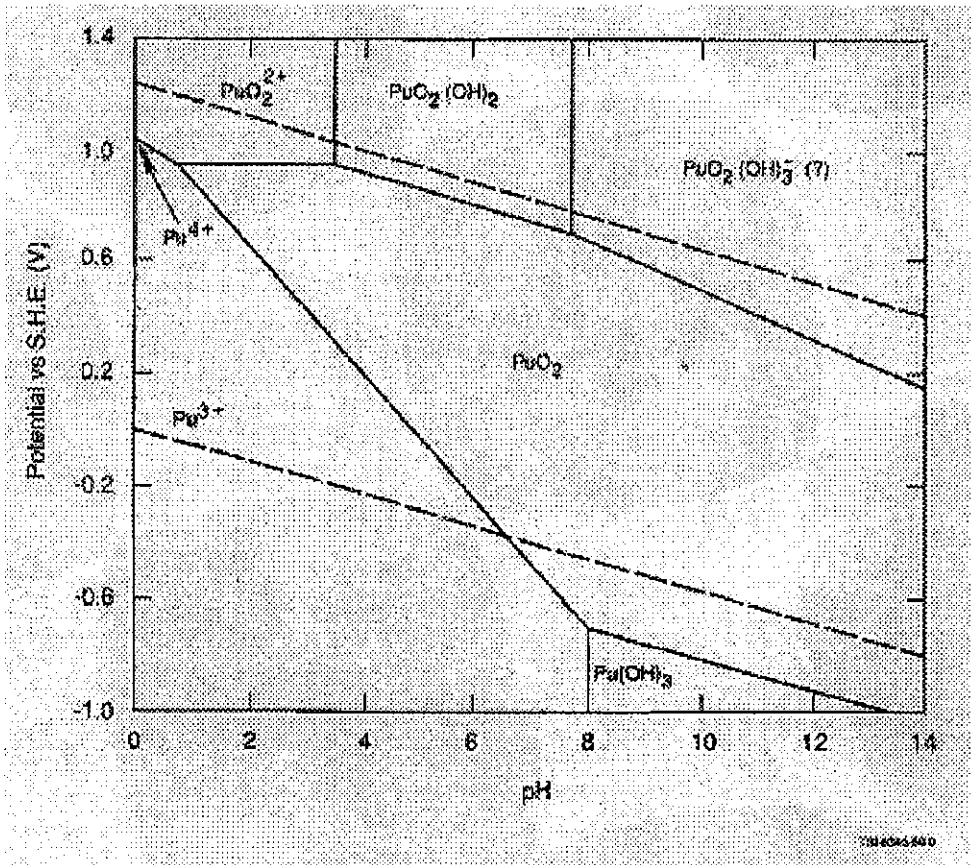


Figure 1.

Oxidation potential (Eh) vs. pH phase diagram for Pu in H<sub>2</sub>O 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<sub>2</sub> and H<sub>2</sub>, 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.

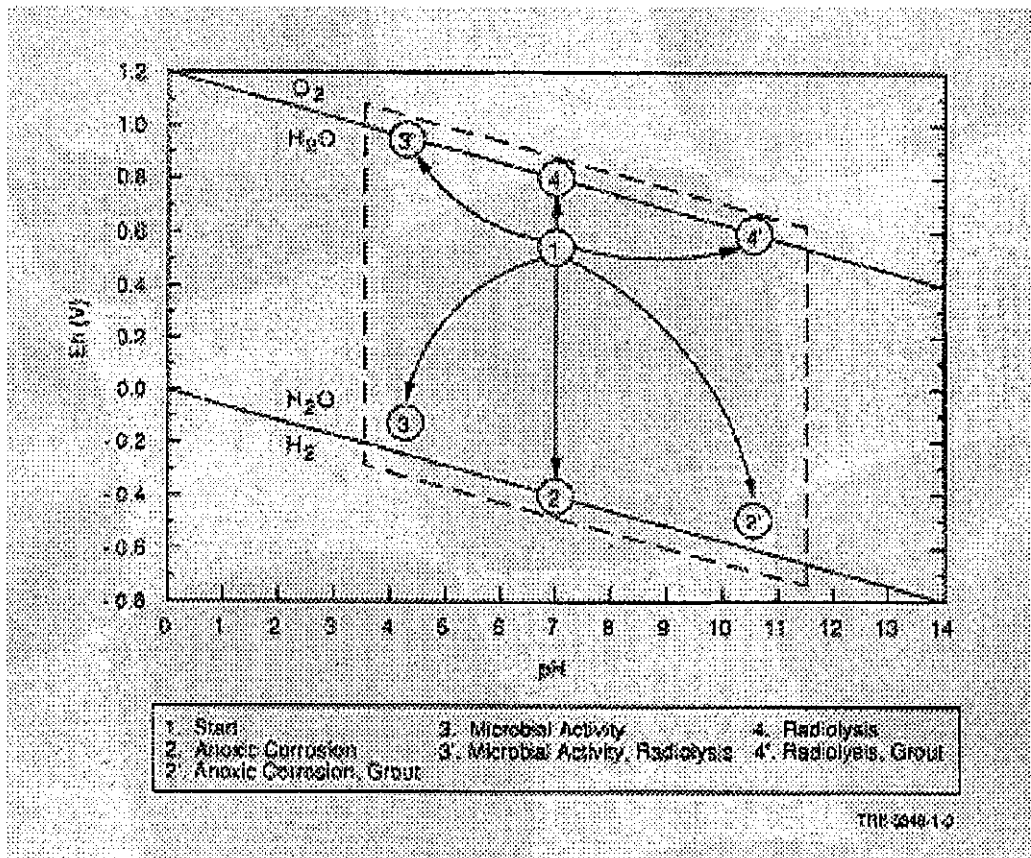


Figure 2.

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.,  $\alpha$ -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  $\text{CO}_2$  are generated by microbial activity. A high  $\text{CO}_2$  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. Sorption capacity will also vary with pH and concentrations of other ions in the brines (such as Al and Fe) that can compete with actinide ions for surface sites.
5. **The formation of 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  $\text{PuO}_2 \cdot n\text{H}_2\text{O}$  (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.

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### **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.

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### 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  $^{239}\text{Pu}$  (and, at early times, from  $^{241}\text{Am}$ ).

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 ( $\text{pK}_{\text{a}}$ s) of organic acids produced by the microbes, the basicity of the cement or grout in the waste or backfill (if any),  $\text{CO}_2$  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  $\alpha$ -hydroxycarboxylic acids (such as lactic and citric acid) while reducing nitrate ion to  $\text{N}_2$  or  $\text{NH}_3$ . Sulfate reduction can further oxidize these acids to  $\text{CO}_2$  while reducing sulfate to  $\text{H}_2\text{S}$ . Finally, methanogenesis can reduce  $\text{CO}_2$  to methane ( $\text{CH}_4$ ) in the presence of excess  $\text{H}_2$  (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  $\text{Fe}^{3+}/\text{Fe}^{2+}$ . 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 cellulose (from combustibles) may produce  $\alpha$ -hydroxycarboxylate chelating agents in significant quantity. Sulfate reduction (using  $\text{SO}_4^{2-}$  in brine) may further oxidize these compounds to  $\text{CO}_2$ . Microbial degradation of cellulose 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  $\text{CO}_2$ .

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  $\text{CO}_2$ . 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 colloidal particle is somewhat arbitrary, and we have defined the maximum size of a colloid to be 1  $\mu\text{m}$ . 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.

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### 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<sub>2</sub> pressure. The rooms may fill with CO<sub>2</sub> as cellulose ferment, and the solubility of actinides under these conditions is highly relevant because CO<sub>2</sub> 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<sub>2</sub> will determine if the lower solution pH and/or formation of actinide carbonate complexes from CO<sub>2</sub> dissolution result in higher actinide solubilities. These tests will use CO<sub>2</sub> overpressures of approximately 60 bar. Beyond this pressure, the increase of CO<sub>2</sub> fugacity with pressure becomes much more gradual, and thus the decrease in pH with increased CO<sub>2</sub> 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.

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### 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 oxidic 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:  $\text{ThO}_2$  (aq) for Pu(IV),  $\text{NpO}_2^+$  for Pu(V),  $\text{UO}_2^{2+}$  for Pu(VI), and  $\text{Nd}^{3+}$  (or  $\text{Am}^{3+}$ ) 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.

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### 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 Eh. 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  $\text{NO}_3^-$  is in turn reduced to  $\text{N}_2$  or  $\text{NH}_3$ . Denitrifying bacteria can oxidize organic acids to  $\alpha$ -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  $\text{H}_2\text{S}$  (from sulfate reduction) is present.
6. solidified aqueous inorganic process sludge, TRUCON 111/211 (L1-3)  
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 floc may also be capable of generating colloids that can serve as hosts for suspended radionuclides.
7. solidified aqueous inorganic sludge, TRUCON 111/211 with  $\text{CO}_2$  (L4-6)  
These tests will be conducted with a  $\text{CO}_2$  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  $\text{CO}_2$  in the rooms may passivate steel by forming a surface layer of siderite ( $\text{FeCO}_3$ ), 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<sub>2</sub>.
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<sup>2+</sup>) that compete with the actinides for sorption sites on the clay particles.
16. pyrochemical salt waste (TRUCON 124/224) with CO<sub>2</sub> (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

compared to determine the significance of CO<sub>2</sub> 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 <sup>241</sup>Am) increases the rate of brine radiolysis, rendering the system more oxidic, as the H<sub>2</sub> produced is relatively inert. The oxidizing products of radiolysis (such as O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, 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 oxidic 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 be 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  $\beta$  and  $\gamma$  activity in RH TRU waste will significantly impact brine chemistry because these types of radiation have a much lower linear energy transfer than  $\alpha$  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 <sup>238</sup>Pu (used as heat sources in radioisotope thermoelectric generator [RTG] systems), there is no intrinsic chemical difference between this isotope and <sup>239</sup>Pu. The indirect effects of higher alpha activity and consequently more intense radiolysis on system Eh and actinide mobilization will be explored in the <sup>241</sup>Am-enriched test vessels, and there is therefore no need to include <sup>238</sup>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.
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## 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.

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### 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  $\pm 10\%$  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  $^{241}\text{Am}$  and  $^{239}\text{Pu}$ , 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 will be smaller than all of the colloidal particles in the leachate, with the possible exception of hydrated  $\text{PuO}_2$  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.

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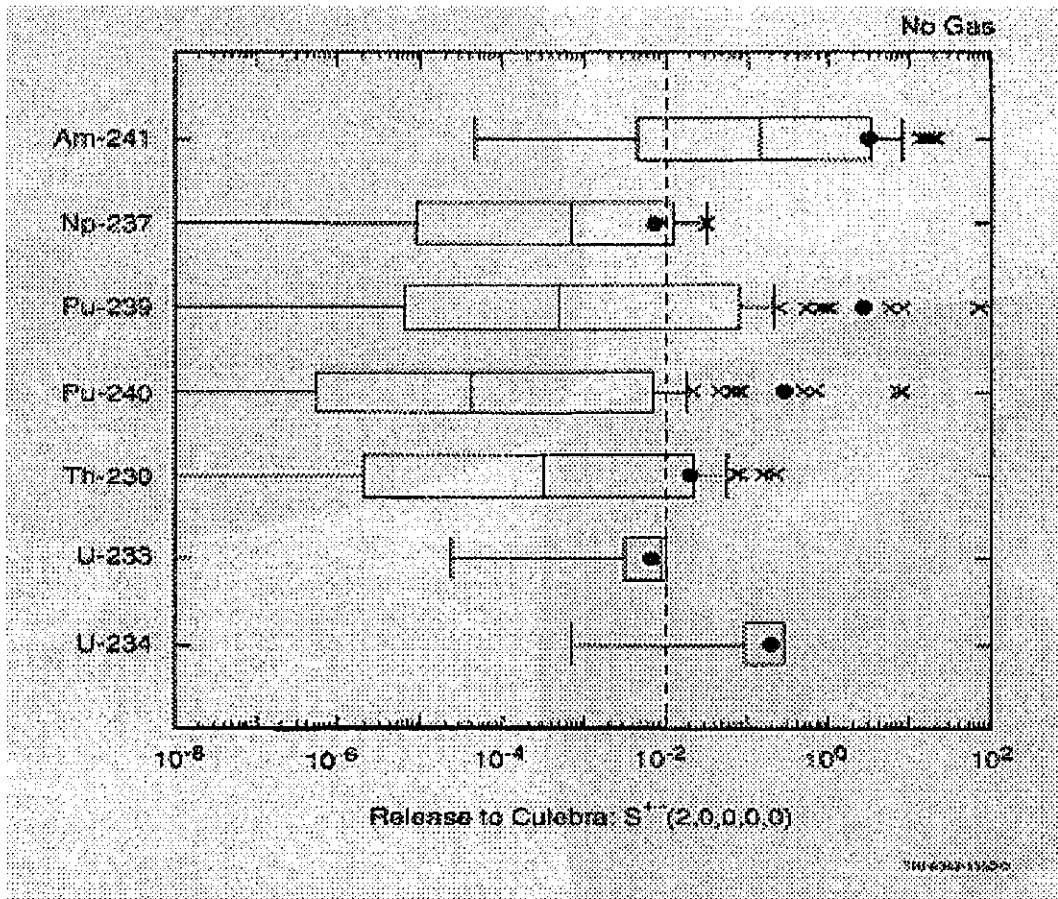
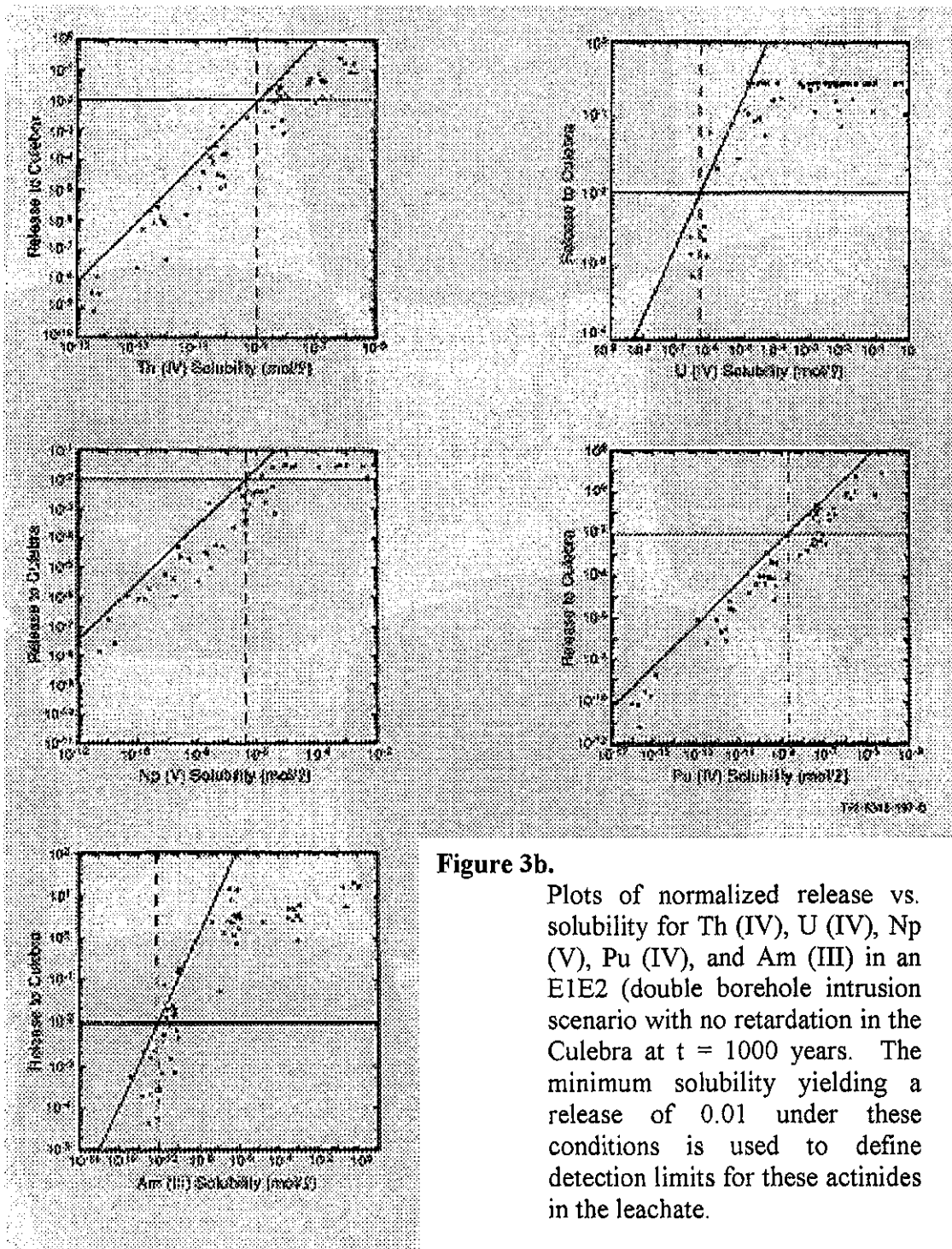


Figure 3a.

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 be used in the SSTR.



**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.

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## 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  $^{239}\text{Pu}$  (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").  $^{239}\text{Pu}$  should be the predominant plutonium isotope in the waste, though the precise value of the  $^{239}\text{Pu}/^{240}\text{Pu}$  isotope ratio is not very significant. This test program does not require any tests with  $^{238}\text{Pu}$ , 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  $^{241}\text{Am}$ -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."

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### 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  $^{239}\text{Pu}$ ) are present for conducting the tests. Total Pu and Am may be estimated from the quantity of  $^{239}\text{Pu}$  measured and  $^{239}\text{Pu}/\text{total Pu}$  and  $^{241}\text{Am}/^{239}\text{Pu}$  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.

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### 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 while 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  $^{232}\text{Th}$ ,  $^{238}\text{U}$ ,  $^{237}\text{Np}$ , and  $^{241}\text{Am}$  (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.,  $\text{ThCl}_4$ ), neptunium as  $\text{NpO}_2^+$  (e.g.,  $\text{NpO}_2\text{Cl}$ ), uranium as  $\text{UO}_2^{2+}$  (e.g.,  $\text{UO}_2\text{Cl}_2$ ), and Nd as  $\text{Nd}^{3+}$  (e.g.,  $\text{NdCl}_3$ ). 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  $^{241}\text{Am}$  in addition to the other four actinides. Test containers falling short of this level may be spiked with an americium salt such as  $\text{Am}_2(\text{SO}_4)_3$ . 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-ethylhexyl) phosphoric acid (DHP), EDTA, 2-hydroxybutyrate, 8-hydroxyquinoline, lactate, oxalate, 1,10 phenanthroline, thenoyltrifluoroacetate (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  $4\text{m}^2$  (considering both internal and external surface). The liter-scale tests require corrodant with area equal to  $(4\text{m}^2)$  (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.

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### 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.

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**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 be 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.

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**Temperature  
Monitoring  
and Control**

Temperature of the test environment should be held at 30°C with a maximum deviation of  $\pm 5^\circ\text{C}$ . 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  $2^\circ\text{C}$  will be sufficient.

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**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  $\mu\text{Ci/mL}$ .\*

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  $\text{O}_2$  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 quantities are less than those generated by radiolysis, or are insufficient to inhibit anoxic corrosion or anaerobic activity. Unfortunately, the maximum  $\text{O}_2$  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  $\text{O}_2$  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  $^{239}\text{Pu}$  (Reed et al., 1993), it is calculated that radiolysis from a solution of  $10^{-7}$  mol/L  $^{239}\text{Pu}$  in brine in a 250 L container will generate oxidizing species equivalent to 1.3 ppm  $\text{O}_2$  per year.

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\* This assumption is based on a maximum Pu and Am concentrations of  $2 \times 10^{-4}$  M in the brine, and alpha-curie contents of 0.07 Ci/g and 3.5 Ci/g for weapons-grade Pu and  $^{241}\text{Am}$ , 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<sub>2</sub> 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<sub>2</sub> ingress rate exceeding 20 ppm O<sub>2</sub> 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<sub>2</sub> ingress rate and He leak rate must be established either by calculation or by experiment using prototype containers.

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**High-  
Pressure  
Experiments**

The CO<sub>2</sub> 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 be great enough to cause them to rupture. Pressure must be held constant during sampling using an external source of CO<sub>2</sub>. 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.

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## 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  $\mu\text{m}$  filter. All dissolved species and suspended colloidal particles in the liquid sample (defined here as having an effective, diameter of less than 1  $\mu\text{m}$ ) 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  $\mu\text{m}$  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 be 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.

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## 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 ( $-\log_{10}[\text{H}^+]$ , as opposed to  $-\log_{10}\alpha\text{H}^+$ ) 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  $\text{Fe}^{+3}/\text{Fe}^{+2}$ .\*
3. **Filtration:** half of the leachate sample will be sequentially filtered to remove all suspended material. One possible series of pore sizes would be  $1\mu\text{m} \rightarrow 450\text{ nm} \rightarrow 220\text{ nm} \rightarrow 100\text{ nm} \rightarrow 50\text{ nm} \rightarrow 20\text{ nm}$ . 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  $\pm 2\%$ . In subsequent analyses, coarsely filtered leachate refers to brine that has passed a  $1\mu\text{m}$  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  $\mu\text{m}$  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 interferences) 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, thenoyltrifluoroacetate (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  $\pm 20\%$  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 ligands. 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  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , etc.) will indicate culturing a sample of coarsely filtered leachate and measuring the concentration of colony-forming units (CFUs) in the brine. This analysis will 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.



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## 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<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S, and N<sub>2</sub>, 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.

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## 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.

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**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
<i>Drum-scale tests:</i>			
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:*

L1, L2, L3	111/211	dewatered aqueous inorganic sludge	none
L4, L5, L6	111/211	dewatered inorganic sludge w/CO <sub>2</sub> *	none
L7, L8, L9	111/211	inorganic sludge, no iron	none
L10, L11, L12	111/211	sludge, no iron, <sup>241</sup> 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	124/214	pyrochemical salt waste	none
L28, L29, L30	124/214	pyrochemical salt waste w/CO <sub>2</sub> *	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, <sup>241</sup> Am spiked	none

Total: 39 liter-scale tests

- CO<sub>2</sub> = 60 bar CO<sub>2</sub> 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  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  or 39.73 kg  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$   
20.02 kg NaCl  
11.44 k-g KCl  
1.24 kg  $\text{Na}_2\text{SO}_4$   
390 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$   
332 g  $\text{CaCl}_2$   
192 g  $\text{NaHCO}_3$   
104 g NaBr  
25.0 g LiCl  
5.45 g RbCl  
3.0 g  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$   
2.6 g KI  
2.5 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   
0.25 g CsCl  
2.5 mL 12 N HCl  
 $\text{H}_2\text{O}$  deionized, to 200 L

Reagents are added to water in a plastic barrel while stirring, using an electric mixer.  $\text{MgCl}_2$  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  
M E M O R A N D U M

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.	
<i>Sediment slurry (ml)</i>	<i>Brine (ml)</i>
Laguna Quatro	100
Laguna Cinco	100
Laguna Tres South	100
Lindsey Lake	100
Surprise Springs	<u>100</u>
Total	500
<b>TOTAL</b>	<b>5000</b>

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<sub>2</sub> 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-phenylindole 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<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup>.

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 metabolic 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 <u>C</u> hemical <u>S</u> cience and <u>T</u> echnology 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	thenoyltrifluoroacetate
USQD	unreviewed safety question determination
WCRRF	Waste Characterization, Reduction, and Repackaging Facility
WIPP	Waste Isolation Pilot Plant
WDXRFS	wavelength-dispersive x-ray fluorescence spectrometry

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## 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*.

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## 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

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  $1 \times 10^{-6}$  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 extraction, 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.

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 (pH),
- oxidation-reduction potential (Eh),
- 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.

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## 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.

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### pH (pcH)

The pcH (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 pcH), 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<sup>(VI)</sup>] and precipitate neptunium [Np<sup>(V)</sup>] and plutonium [Pu<sup>(III)</sup>] in slightly basic solutions but can solubilize all actinides in concentrated basic solutions (pH >9). For the STTP, the pcH 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.

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### Eh

The Eh 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.

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### 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 pcH 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), thenoyltrifluoroacetate (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.

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#### 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.

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#### Colloidal Suspension

For the STTP, SNL has defined "colloid" as particles having characteristic size between 0.001  $\mu\text{m}$  and 1  $\mu\text{m}$ , 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 ( $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ ). 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.

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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,  $\text{CO}_2$ , and ligands.

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## 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  $^{239}\text{Pu}$  (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  $10^{-4}\text{M}$  solution if the plutonium were to dissolve completely. Plutonium concentrations as high as  $10^{-3}\text{M}$  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 oxidic  $Eh$ . (The effects of higher alpha activity and consequently more intense radiolysis on system  $Eh$  and actinide mobilization will be explored in  $^{241}\text{Am}$ -enriched test vessels (sections d "Actinides," e "Pyrochemical Salt Wastes with Added  $\text{CO}_2$ ," and e "Pyrochemical Salt Wastes with  $\text{Ca}(\text{OH})_2$  & Chelators"). The  $^{239}\text{Pu}/^{240}\text{Pu}$  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  $^{238}\text{Pu}$ , 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  $^{241}\text{Am}$  concentrations in pyrochemical salts will be an indicator for  $^{238}\text{Pu}$  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.

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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 least 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).

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### 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.

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#### 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  $^{239}\text{Pu}$  are present
- determine that  $^{241}\text{Am}$  is not present in unacceptably high concentrations
- ascertain whether  $^{238}\text{Pu}$  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  $^{239}\text{Pu}$ . Drums failing to meet this criterion will not be used for testing. The  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ , 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  $^{239}\text{Pu}$  in a waste drum is that the radionuclide assay method verify that the total  $^{239}\text{Pu}$  content in a 55-gal. drum is at least 5g or  $>5\text{g} + 200\%$ . At the 20g content level, the DQO is  $10\text{g} + 100\%$ ,  $- 50\%$ . In summary, the DQOs for radionuclide assay are:

- $5\text{g} + 200\% - 0\%$
- $10\text{g} + 200\% - 50\%$ , and
- $20\text{g} + 100\% - 75\%$ .

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  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  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  $^{239}\text{Pu}$  in homogeneous waste core samples taken from 55-gal. drums must be  $>25\text{mg}$  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  $^{239}\text{Pu}$  concentration of 25 mg per liter of waste. The DQOs for radionuclide assay of core samples taken from the semihomogeneous waste drums are:

- $25\text{ mg/L} + 100\% - 0\%$ ,
- $50\text{ mg/L} + 100\% - 50\%$ , and
- $100\text{ mg/L} \pm 50\%$

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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  $^{239}\text{Pu}$  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.

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**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.

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**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.

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**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.

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**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  $30 \pm 5^\circ\text{C}$  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.

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**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).

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**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.

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**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.

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**Leak-Tightness**

The drum-scale test containers were initially designed to meet the theoretical leak-rate criterion for brine containing activity levels of 200  $\mu\text{Ci/mL}$ . 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  $\text{O}_2$  ingress per year (5  $\mu\text{L/L/yr}$  or 0.0137  $\mu\text{L/L/day}$ ). 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  $\text{O}_2$  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  $\text{O}_2$  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.

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**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  $30 \pm 5^\circ\text{C}$  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  $\sim 1\text{L}$  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  $\sim 3\text{L}$ .

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**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).

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**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.

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**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.

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**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  $\mu\text{Ci/mL}$ . 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  $\text{O}_2$  per year (5  $\mu\text{L/L/yr}$  or 0.0137  $\mu\text{L/L/day}$ ).

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  $1 \times 10^{-9} \text{ cm}^3/\text{s}$ .

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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<sub>2</sub> 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<sub>2</sub> 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.

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### Pressurized CO<sub>2</sub> Test Containers

The STTP test matrix includes six liter-scale tests to be conducted at 60 bars with CO<sub>2</sub> gas. The pressurized CO<sub>2</sub> tests will determine if the lower pH will affect actinide concentrations or if an increase in the carbonate concentration at lower (more acid) pH will increase actinide carbonate concentration at lower (more acid) pH 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<sub>2</sub> 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 1µm 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.

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### 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.

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**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.

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**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.

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**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.

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**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  $^{241}\text{Am}$  per liter as a soluble americium salt if that concentration is not already present. The other three actinides ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ,  $^{237}\text{Np}$ ) 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  $^{241}\text{Am}$ . 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  $4\text{m}^2$ . 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<sub>2</sub>O
- 3) Acetic acid, sodium salt
- 4) Citric acid, sodium salt • 2H<sub>2</sub>O
- 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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*Continued on next page*

These minor chelators (30mg/ml) are:

- 1) Lactic acid, Na salt
- 2) 1,10 phenathroline
- 3)  $\alpha$ -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**

<i>Compound</i>	<i>Brine A (g/l)</i>	<i>Castile Brine (g/l)</i>
MgCl <sub>2</sub> •6H <sub>2</sub> O	292.10	3.86
NaCl	100.10	261.64
KCl	57.20	7.23
Na <sub>2</sub> SO <sub>4</sub>	6.20	23.70
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> •10H <sub>2</sub> O	1.95	6.00
CaCl <sub>2</sub>	1.66	1.33
NaHCO <sub>3</sub>	0.96	0.00
NaBr	0.52	1.13
LiCl	0.125	0.00
RbCl	0.027	0.00
SrCl <sub>2</sub> •6H <sub>2</sub> O	0.015	0.00
KI	0.013	0.00
FeCl <sub>2</sub> •6H <sub>2</sub> O	0.0125	0.00
CsCl	0.00125	0.00

*Continued on next page*

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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.

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## 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 *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.

---

**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.

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**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  $\text{NO}_3$  is in turn reduced to  $\text{N}_2$  or  $\text{NH}_3$ . Denitrifying bacteria can oxidize organic acids to  $\alpha$ -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.  $\text{NaNO}_3$  and  $\text{NaH}_2\text{PO}_4$  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  $\text{H}_2\text{S}$  (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  $\text{Ca}(\text{OH})_2$ , ferric sulfate, and a flocculation aid. This slurry was solidified in 55-gallon drums with various portions of Portland Cement, vermiculite, and sodium silicate.

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**Solidified  
Aqueous  
Inorganic Process  
Sludge, TRUCON  
111/211 with  $\text{CO}_2$   
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  $\text{CO}_2$ . 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,  $\text{CO}_2$  in the rooms might passivate steel by forming a surface layer of siderite ( $\text{FeCO}_3$ ), 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.

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**Solidified  
Aqueous  
Inorganic Process  
Sludge w/o Fe,  
TRUCON  
111/211 Portland  
Cement;  $^{241}\text{Am}$   
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.

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**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.

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**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.

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**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.

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**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  $\text{CaCl}_2$ ,  $\text{CaF}_2$ , Ca metal, CaO, and magnesia (MgO) from the MgO crucible. The pyrochemical salt wastes from DOR and  $\text{O}_2$  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  $\text{Ca}(\text{OH})_2$  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.

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**Pyrochemical Salt  
Wastes with  
Added  $\text{CO}_2$ ,  
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  $\text{CO}_2$  pressure at about 60 bars (~870 psig). Any basicity from the Ca compounds should be neutralized by the  $\text{CO}_2$  headspace. The bicarbonate and carbonates formed from the  $\text{CO}_2$  may increase the solubility of actinides, especially uranium.

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**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<sub>2</sub> sparging process resulted in wastes as discussed in the "Pyrochemical Salt Wastes with Added CO<sub>2</sub>" 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<sup>2+</sup>), which compete with the actinides for sorption sites on the clay particles.

**Pyrochemical  
Salt Wastes with  
Ca(OH)<sub>2</sub> &  
Chelators,  
TRUCON  
124/224  
(L34-36)**

This set of tests consists of L34 with pyrochemical salt wastes from the O<sub>2</sub> sparging process and L35 and 36 with wastes from the DOR process. All three tests have added Ca(OH)<sub>2</sub> to increase the basicity of the brine and to determine the effect of the basic solution on generated CO<sub>2</sub> 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 <sup>241</sup>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<sub>2</sub> sparging process. All three tests have added <sup>241</sup>Am, which may render the system more oxidic and provide an indication of Pu-238 effects on brine chemistry. The oxidizing products of radiolysis such as O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, or OCl<sup>-</sup> 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.

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### 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 top 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 *Eh*, gas composition is a qualitative *Eh* 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**

<i>Process</i>	<i>Gas Composition</i>
Corrosion	H <sub>2</sub> , CO <sub>2</sub>
Microbial decomposition	CO <sub>2</sub> , CO, CH <sub>4</sub> , N <sub>2</sub> , H <sub>2</sub> S, and N <sub>2</sub> O
Radiolysis	O <sub>2</sub> , H <sub>2</sub> , CO, CO <sub>2</sub>
Leakage	O <sub>2</sub> , N <sub>2</sub> , Ar, CO <sub>2</sub> (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.

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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 loop 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**

<i>Gas</i>	<i>Requirement</i>
H <sub>2</sub>	STTP
O <sub>2</sub>	STTP
CH <sub>4</sub>	STTP
CO	STTP
CO <sub>2</sub>	STTP
H <sub>2</sub> S	STTP
N <sub>2</sub>	STTP
N <sub>2</sub> O	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<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub>. N<sub>2</sub>O 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**

<i>Scheduled Frequency</i>	<i>Drum-Scale Tests</i>	<i>Unpressurized Liter-Scale Tests</i>	<i>Pressurized Liter-Scale Tests</i>
# of containers	15*	33	6
<b>Brine</b>			
<b>First Year</b>			
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
<b>Subsequent Years</b>			
	15 x 6 = 90	33 x 6 = 198	6 x 3 = 18
<b>Gas</b>			
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  $\pm 100\%$  at the 1-ppm level and  $\pm 10\%$  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.

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## 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.

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**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

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

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**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  $\pm 15\text{-}25\%$ .

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**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  $\pm 10\%$  or less.

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**Table 5. DQO Levels for STTP Activities**

<i>Technical Requirements</i>	<i>Method/Instrument</i>	<i>DQO Level</i>
Headspace gas analyses	Gas chromatography	II
Brine leachate filtration	Amicon centrifuge	II
Alpha activity measurements	Liquid scintillation counting	II
Total elemental analyses	WDXRFS	II
pcH	pcH meter, UV/VIS spec.	II, III
<i>EH</i>	<i>EH</i> 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**

<i>STTP Activity</i>	<i>Target Limit of Quantitation<sup>a</sup></i>	<i>Target Limit of Detection<sup>a</sup></i>	<i>Target Precision</i>
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
Eh			ND <sup>b</sup>
ICP-MS for actinides (a)		10 <sup>-10</sup> M	± 100%
(b)		10 <sup>-9</sup> 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 <sup>b</sup>
Colloid characterization			ND <sup>b</sup>
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%

<sup>a</sup> 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.

<sup>b</sup>Not Determined.

**Table 7. DQOs for STTP Preparatory Activities**

<i>Activity</i>	<i>DQO</i>
RTR for TRUCON verification	Results must be certifiable
PAN; SGS; GRT for <sup>238</sup> Pu and <sup>241</sup> Am in waste drums	<b>For Drum-Scale Test Containers:</b> @ 5-g level + 200%, - 0% @ 10-g level + 200%, - 50% @ 20-g level + 200%, - 75% <b>For Liter-Scale Test Containers</b> @ 25 mg/L + 100%, - 0% @ 50 mg/L + 100%, - 50% @ 100 mg/L + 50%, - 50%
PAN; SGS; GRT for <sup>238</sup> Pu and <sup>241</sup> 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

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### 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., 2000xxxxxx) 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.

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## 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.

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### 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  $30 \pm 5^\circ\text{C}$ .

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### 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.

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### 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<sub>2</sub> may change the pH. 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.

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### 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<sub>2</sub> Test Containers."

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#### 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.

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## 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.

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### 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.

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**Precision**

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

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

where, RPD = relative percent difference  
C<sub>1</sub> = analytical results from the first sample  
C<sub>2</sub> = analytical results from the second sample, and  
C<sub>1</sub> = 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:

$$RSD = \frac{\sigma}{\bar{y}} \times 100$$

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<sub>i</sub> = measured value of the i<sup>th</sup> measurement and  
n = number of replicates.

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**Accuracy**

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

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

where, C<sub>m</sub> = measured concentration level against calibration standard and  
C<sub>srm</sub> = true or certified concentration of the analyte(s) in the sample.

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

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

where, S = measured concentration in spiked aliquot,  
U = measured concentration in unspiked aliquot, and  
C<sub>ac</sub> = actual concentration of spike added.

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**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:

$$\%C = \frac{V}{n} \times 100$$

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.

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**Method  
Detection  
Limit (MDL)**

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

$$MDL = t(n-1, 1-\alpha = .99) \times \sigma$$

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,  
 $\sigma$  = standard deviation of replicate measurements.

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## Safety

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

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### 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.

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### 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<sub>2</sub>. 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.

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### 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.

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<b>Transportation of Waste Drums to and from LANL Facilities</b>	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.
<b>Transportation from WCRRF to the CMR Building</b>	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.
<b>Wing 9 Design Activities</b>	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.
<b>Analytical Instrumentation (Gloveboxes)</b>	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.
<b>Chemical Analyses</b>	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 <i>"MST-5 Training and Qualification Plan,"</i> MST5-GEN-QAP2-003, latest revision.

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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.

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## 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.

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### 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 pH in brine leachate,
- measurement of Eh 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,

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- 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 1.0 $\mu$ m**

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 1.2 $\mu$ m 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<sub>2</sub> Test Containers."

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### Filtration to Less than 20 nm

Following the removal of the large particles and suspended solids to 1.0  $\mu\text{m}$ , 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 0.22 $\mu\text{m}$  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.

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### Determination of Actinide Alpha Activity

Total high-specific-activity, alpha-active actinide radioisotopes such as  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ , 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.

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### Rough Concentration Measurement (X-Ray Fluorescence Spectrometry)

The concentration of relatively low specific activity actinides, for example, thorium as  $^{232}\text{Th}$ , uranium as  $^{238}\text{U}$ , and neptunium as  $^{237}\text{Np}$ , 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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### **pH Measurements**

The 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* (p*C*H) 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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### **Eh Measurements**

The measurement of *Eh* in a nearly saturated brine solution is expected to have complexities similar to those for the measurement of p*C*H. The experience gained from the determination of p*C*H can be transferred to the measurement of *Eh*. Specialized *Eh* 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 *Eh* electrodes in Brine A solution were conducted as part of the methods development for this measurement.

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### **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 1 $\mu$ m. Results from preliminary filtration experiments indicate that filtration to 10nm (0.01 $\mu$ m 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.

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#### **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<sup>-10</sup>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<sup>-10</sup>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.

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### **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.

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### **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 <sup>241</sup>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.

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### **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.

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### **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.

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### 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.

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### 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, isotachopheresis, 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  $\pm 20\%$ . On-going experiments indicate that a target of 20 to 100 ppm may be more realistic.

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### 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  $E_h$  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.

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### 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.

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#### 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.

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#### 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.

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## 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.

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### 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.

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### 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.

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### 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."

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**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.

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**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.

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**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.

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**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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*Continued on next page*

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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.

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

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### 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.

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**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

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#### 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

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## 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

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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

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January  
1992

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

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**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

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**May 15, 1992**      Final proposals for Contact-Handled Transuranic Waste Source-Term Program due to WPSO and WPIO (Joe Lippis and Arlen Hunt)

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**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

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**October 8, 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

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**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



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**December 9, 1993** DOE appoints George Dials, Manager of Carlsbad area office

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**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 "except EA"
- 

**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

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**January 23, 1995**

STTP environmental assessment approved - no significant impact documented

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**January 20, 1995**

LANL receives authorization to initiate STTP from CAO (Dick Lark)

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<b>February 1995</b>	Shipment of waste to Waste Characterization, Reduction, and Repackaging Facility
	<ul style="list-style-type: none"><li>• TA-54 Inventory (02-01-95)</li><li>• CMR Building (02-03-95)</li><li>• TA-55 Inventory (02-15-95)</li></ul>
<hr/>	
<b>March 23, 1995</b>	<ul style="list-style-type: none"><li>• Commenced core drilling</li><li>• Completed loading of liter-scale test containers</li><li>• Added brine to liter-scale test containers</li><li>• Transported LS test containers to CMR</li><li>• Added Inoculum to liter-scale test containers</li></ul>
<hr/>	
<b>March 29, 1995</b>	Commenced liter-scale tests
<hr/>	
<b>May 9, 1995</b>	<ul style="list-style-type: none"><li>• Commenced characterization of heterogeneous waste for drum-scale tests</li><li>• Completed loading of drum-scale tests</li><li>• Transferred drum-scale tests to CMR</li><li>• Added Inoculum to drum-scale tests</li></ul>
<hr/>	
<b>May 10, 1995</b>	Commenced drum-scale tests
<hr/>	
<b>May 26, 1995</b>	Completed first data package of liter-scale tests
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<b>June 19, 1995</b>	Completed first data package of drum-scale tests
<hr/>	
<b>November 2, 1995</b>	Plan for the utilization and interpretation of Actinide Source-Term Waste Test Program data issued by Sandia National Laboratories
<hr/>	
<b>Remainder of 1995</b>	Conducted sampling and analysis of brine and headspace gas for all test containers
<hr/>	
<b>April 1996</b>	<ul style="list-style-type: none"><li>• Completed first year of STTP sampling and analysis activities</li><li>• Received revised Technical Requirements Document from SNL</li><li>• Continued sampling and analysis</li></ul>

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- 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
- 
- 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
-

### 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 CO<sub>2</sub>
- 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.
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**III. (c) Projected Chronological Chemical Conditions in the WIPP Repository for 500 Years**

Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2150	150	<p><b>IV. WIPP Creep Closure Period</b></p> <ol style="list-style-type: none"> <li>1. Administrative controls cease.</li> <li>2. Early panels 70% closed from creep closure.</li> <li>3. Late panels &gt;50% closed from creep closure.</li> <li>4. Compaction of non-cemented drums on going.</li> <li>5. MgO sacks crushed open.</li> <li>6. Salado Brine seepage continues.</li> <li>7. Repository remains dry.</li> <li>8. Porosity disequilibrium exists between disposal rooms and panels.</li> <li>9. Permeability decreases because of deformability of rock salt and compacted waste and other materials.</li> </ol>	<ol style="list-style-type: none"> <li>1. MgO reacts with brine seepage by four mechanisms.</li> <li>2. Corrosion rate of mild steel drum levels off.</li> <li>3. Oxygen is depleted by corrosion of metals.</li> <li>4. Headspace gas is primarily N<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, and VOCs.</li> <li>5. CO<sub>2</sub> reacts with Mg(OH)<sub>2</sub> to form MgCO<sub>3</sub> • 3H<sub>2</sub>O and Mg Oxychloride nodules.</li> <li>6. CO<sub>2</sub> reacts with MgO to form physico chemical weak mono and bidentate complexes.</li> <li>7. Salado Brine salts continue to precipitate/ crystallize and accumulate as hardened mass.</li> <li>8. Water acts as catalyst to form MgCO<sub>3</sub> • H<sub>2</sub>O.</li> <li>9. Microbial activity is limited and Produces CO<sub>2</sub> and CH<sub>4</sub></li> <li>10. Radiolysis processes are limited and produce limited H<sub>2</sub> and CO<sub>2</sub>.</li> <li>11. Alpha activity degradation of organics produces H<sub>2</sub> and CO<sub>2</sub>.</li> <li>12. No solubility of actinides occurring.</li> <li>13. Repository pressure increases but void volume is small.</li> <li>14. Anhydrite interloads provides diffusion path for H<sub>2</sub></li> <li>15. Effect of swelling of MgO reactions noticeable        MgO → Mg(OH)<sub>2</sub> → MgCO<sub>3</sub> • 3H<sub>2</sub>O.</li> <li>16. Overall degradation from all processes is slow.</li> <li>17. Less than 12.0% of MgO has reacted with brine @ in-leakage rate of 4 m<sup>3</sup>/disposal room/yr. for 50 years</li> </ol>

Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2600	500	(V.) WIPP Solidification Period (W/O Brine Intrusion)	<ol style="list-style-type: none"> <li>1. MgO – brine reaction continues to maintain dry repository</li> <li>2. Mild steel drums continue to corrode non-uniformly</li> <li>3. H<sub>2</sub> with N<sub>2</sub> is prevalent gas H<sub>2</sub>&gt;N<sub>2</sub>&gt;N<sub>2</sub>O&gt;CH<sub>4</sub></li> <li>4. CO<sub>2</sub> absorbed by Mg(OH)<sub>2</sub></li> <li>5. Salado Brine salt solidifies</li> <li>6. Water continues to be catalyst information of MgCO<sub>3</sub> • 3H<sub>2</sub>O</li> <li>7. Microbial activity increases slowly in dry condition; produces CO<sub>2</sub></li> <li>8. Radiolysis increases slowly in dry conditions</li> <li>6. Alpha degradation produces CO<sub>2</sub></li> <li>7. Chemical degradation is slow</li> <li>8. No solubility of actinides</li> <li>12. Cementitious material is degrading producing CO<sub>2</sub></li> <li>13. Basicity of repository is increased</li> <li>14. Anhydrite interbeds continue to provide diffusion path for H<sub>2</sub></li> <li>9. Repository pressure due to all gases increases because of small void space</li> <li>16. Swelling of MgO → MgCO<sub>3</sub> • 3H<sub>2</sub>O decreases void space</li> <li>17. Iron corrosion begins to impact available void space</li> <li>18. Less than 15% of MgO reacted with brine</li> <li>19. <sup>241</sup>Am has gone through one half-life and reduced source term</li> <li>20. Particle size of waste form remains large</li> <li>21. No colloids will form in this high ionic strength condition</li> <li>22. Shear strength of compacted waste is high</li> </ol>



Date	Elapsed Time (Yr.)	Repository Condition	Chemical Condition/Processes
2600	500	<b>(V<sub>a</sub>) WIPP Solidification Period</b>	<b>(W/Brine Intrusion)</b>
		<ol style="list-style-type: none"> <li>1. Dynamic creep closure complete</li> <li>2. Non-cemented drums compacted</li> <li>3. Cemented drums encased</li> <li>4. MgO is dispersed</li> <li>5. Porosity is at equilibrium</li> <li>6. Permeability is minimal</li> <li>7. Tortuosity retards intra-repository communication</li> <li>8. Human intrusion scenario results in brine intrusion into repository from Castile</li> </ol>	<ol style="list-style-type: none"> <li>1. Brine diffuses into available void volume</li> <li>2. Infused brine reacts with MgO resulting in greater swelling and decreased porosity and permeability</li> <li>3. Castile Brine infusion yields Mg(OH)<sub>2</sub> and salt</li> <li>4. Radiolysis becomes active in producing H<sub>2</sub> and CO<sub>2</sub> over hundreds of years</li> <li>5. Microbial activity increases and accelerates degradation of cementitious solids yielding more basic system (kinetics of hundreds of years)</li> <li>10. Only part of repository will be inundated and release of pressure will be localized</li> <li>11. Corrosion of mild steel drums will accelerate</li> <li>12. Chemical degradation will be accelerated</li> <li>13. <sup>241</sup>Am has gone through one half-life</li> <li>14. Actinides that solubilize will precipitate and be adsorbed on Mg(OH)<sub>2</sub></li> <li>15. Void space will be essentially nonexistent</li> </ol>

## 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<sup>1</sup>*

- 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<sup>3</sup>
- Excavated volume of one panel = 46,097 cm<sup>3</sup>
- Number of drums in one panel = 86,000
- Design volume of waste in repository – 1.76 × 10<sup>5</sup> m<sup>3</sup>
- Volume of one drum = 0.21 m<sup>3</sup>
- Mass of Fe in containers - 2.61 × 10<sup>7</sup> kg
- Density of Salado Brine - 1.23 gm/cm<sup>3</sup>
- Weight of MgO to be added to repository<sup>2</sup> = 85,600 tons where 1 ton = 2000 pounds
- Weight of MgO to be added to 1 panel<sup>3</sup> = 8560 tons
- Brine inflow rate into Salado Disposal Rooms - 4 m<sup>3</sup>/room/yr. for first 50 years (maximum)
- Brine inflow rate into Salado Disposal Rooms after 50 years = <0. 1 m<sup>3</sup>/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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<sup>1</sup>Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992, SAND92-0700.

<sup>2</sup>R. Vann Bynum, et.al., Implementation of Chemical Controls Through a Backfill System for the Waste Isolation Pilot Plant (WIPP).

<sup>3</sup>Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992, SAND92-0700.



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## 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 (SVvBs) 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.

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### 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.<sup>4</sup>

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### 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<sub>2</sub>, CO<sub>2</sub>, 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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<sup>4</sup>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 antibacterial and would inhibit the activity of facultative anaerobes.<sup>5, 6</sup> 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.

<sup>5</sup>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).

<sup>6</sup>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.

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#### 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.

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#### 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 4m<sup>3</sup> per disposal room per year for 50 years and < 0.1 m<sup>3</sup> per year thereafter. Assuming the 4m<sup>3</sup> per year per disposal room for 50 years, the calculated quantity of brine in the repository after 50 years would be:

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

For 50 years:

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

This is equivalent to:

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

The composition of Salado Brine (Brine A) has been reported by Martin Molecke.<sup>7,8</sup>

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

<sup>8</sup> 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<sub>2</sub>, 33% NaCl, 19% KCl, and 2% Na<sub>2</sub>SO<sub>4</sub>. 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 4m<sup>3</sup>/disposal room/year for 50 years, the quantity of crystallized salt would be (11,200 m<sup>3</sup>)(0.305) = 3416 m<sup>3</sup> of crystallized salt.

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**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/cm<sup>3</sup>, which agrees with the theoretical density 3.58 gm./cm<sup>3</sup>. 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  $1.93 \times 10^9$  mole in the repository.

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

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## 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<sub>2</sub> 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

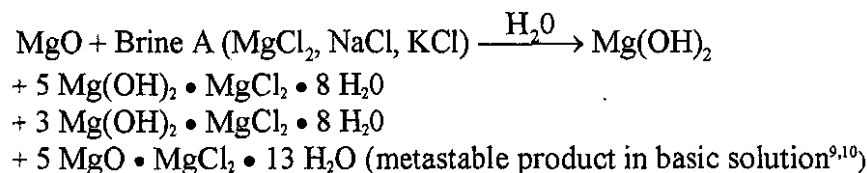
Reaction of MgO with moisture in the WIPP void volumes from vapor pressure of water at 30°C above available brine or water retained in brine A/MgO reaction products.

These four contact processes will result in different reaction products and reaction kinetics and will influence the capability of reacting with available CO<sub>2</sub> to form MgCO<sub>3</sub>, leading to MgCO<sub>3</sub> • 3H<sub>2</sub>O.

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#### *Reaction Process 1*

Reaction Process 1 will yield the following reactions and products:



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<sup>9</sup>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).

<sup>10</sup>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  $Mg(OH)_2$ .  $MgCO_3 \cdot 3H_2O$  (nesquehonite) will form upon exposure to moisture saturated atmospheres.<sup>11</sup> LANL has conducted a test by dripping brine into an excess of  $MgO$  powder and observed similar results.

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#### *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  $CO_2$ .

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#### *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  $CO_2$ .

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#### *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  $30^\circ C$  ( $86^\circ F$ ) would be high enough to penetrate the solid reaction products resulting from Processes 1, 2, and 3.

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<sup>11</sup>D. M. deCastellar, A. Traveria, J. M. Tura, and F. C. Lorente, "Nesquehonite ( $MgCO_3 \cdot 3H_2O$ ) 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.

**Headspace  
Gas**

The headspace gas in the repository during the WIPP closure period would be principally air depleted in O<sub>2</sub> and newly-generated H<sub>2</sub>, evolved VOCs, and some CH<sub>4</sub>. 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.<sup>12,13</sup> The rates of CO<sub>2</sub> production would be considerably lower with MgO addition than the projected rates without MgO.<sup>12,13</sup> 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<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> from alpha bombardment of carbonaceous materials producing H<sub>2</sub> and CO<sub>2</sub>,<sup>14</sup> alpha bombardment of high nitrate concentrations producing N<sub>2</sub>O,<sup>15</sup> low concentrations of CH<sub>4</sub> from alpha degradation of organic materials,<sup>16</sup> and via bacterial (microbial) methanogenesis.<sup>17</sup>

The production of CO<sub>2</sub> via methanogenesis could result from three classes of methanogenic carbonaceous substrates that are metabolized by anaerobic microbes. The generation of CH<sub>4</sub> from the carbon sources is maximized by conversion of CO<sub>2</sub> to CH<sub>4</sub> by reaction with H<sub>2</sub>. With MgO present in the repository, the ambient concentration of CO<sub>2</sub> will be reduced to very low levels and methanogenic CH<sub>4</sub> generation would also be reduced.

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<sup>12</sup> Douglas Caldwell, et. al., "Rates of CO<sub>2</sub> Production From Microbial Degradation of Transuranic Wastes Under Simulated Geologic Isolation Conditions," SAND 87-7170, January (1988).

<sup>13</sup> 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).

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

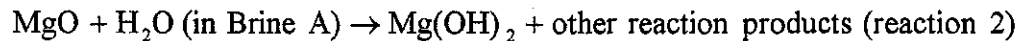
<sup>15</sup> Lisa Pansoy-Hjelvik, Memorandum to Robert Villarreal, "Denitrification of N<sub>2</sub>O Production," March 18, (1997).

<sup>16</sup> Eugene Mroz, personal communication, preliminary results from Gas Generation/Matrix Depletion Experiment, March (1997).

<sup>17</sup> 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<sup>3</sup> 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:



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

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

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

Assuming  $1.12 \times 10^{10}$  cm<sup>3</sup> of brine contains 69.5 % water, the available water is  $7.78 \times 10^9$  cm<sup>3</sup>. In reaction 2, one mole of MgO (MW = 40.30) reacts with one mole of H<sub>2</sub>O (MW = 18) to form one mole of Mg(OH)<sub>2</sub> (MW = 58.30). The ratio of the mass of H<sub>2</sub>O to MgO is  $18/40.30 = 0.45$ , and this relative mass would be theoretically reacted to form Mg(OH)<sub>2</sub>. 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.<sup>18</sup> This hydrated Mg(OH)<sub>2</sub> 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.<sup>19</sup>

Assuming the available water for reaction with MgO is  $7.78 \times 10^9$  cm<sup>3</sup> 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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<sup>18</sup> 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).

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

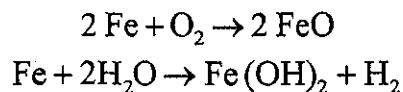


### WIPP Solidification Period (W/O Brine Intrusion)

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<sup>3</sup>/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<sub>2</sub> as follows:



The mass of Fe in the mild steel drums is reported as  $2.61 \times 10^7$  Kg.<sup>(4)</sup>

If all the Fe in the repository were converted to Fe(OH)<sub>2</sub>, the increase in volume of Fe to Fe(OH)<sub>2</sub> will be from  $3.32 \times 10^3$  M<sup>3</sup> to  $1.22 \times 10^4$  M<sup>3</sup> 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)<sub>2</sub>.

The gas composition in the porosity of the disposal rooms would be expected to be primarily H<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>. All CO<sub>2</sub> generated by microbial and radiolytic processes would be totally reacted by the Mg(OH)<sub>2</sub>.

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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 sored 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  $MgO \rightarrow Mg(OH)_2 \rightarrow MgCO_3 \rightarrow MgCO_3 \cdot 3H_2O$ .

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.

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### 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.<sup>20, 21</sup> 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.<sup>(20, 21)</sup> 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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<sup>20</sup>Robert Villarreal and Mark Phillips, "Test Plan for the Actinide Source-term Waste Test Program, "CLS I -STP SOP5-012/0, May (1993).

<sup>21</sup>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<sub>2</sub> 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<sub>2</sub> in the repository over time at low levels (<10<sup>-3</sup> atmospheres) (Vann Bynum et al., 1997). High partial pressures of CO<sub>2</sub> could potentially cause waters in the repository to attain low pH 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<sub>2</sub> Partial pressures in WIPP after closure. In particular, the Panel is concerned that CO<sub>2</sub> 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<sub>2</sub>.

This paper, will discuss the mechanisms and kinetics by which CO<sub>2</sub> could react with MgO or its hydrated forms. The discussion of mechanisms will be based on phase diagrams formulated for the MgO-H<sub>2</sub>O-CO<sub>2</sub> 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.

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#### 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 OOH B

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.

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**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.

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

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**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.

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### **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<sub>2</sub>O and CO<sub>2</sub>, 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 likely involve a Castille brine. Because these brine compositions are quite distinct, they may have different impacts on MgO/H<sub>2</sub>O/CO<sub>2</sub> reaction efficiencies.

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### **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.

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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  $\text{Mg}(\text{OH})_2$  (brucite) and  $\text{MgO}\text{-CO}_2\text{-H}_2\text{O}$  phases such as nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ), hydromagnesite ( $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ) and dypingite ( $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ). When the Salado brine is used in the experiments, the phases formed are a function of the partial pressure of  $\text{CO}_2$ . At low  $\text{CO}_2$  partial pressures, phases common to Sorel cement are formed. These are hydrated magnesium hydroxychlorides with compositions such as  $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  and  $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ .

At higher partial pressures of  $\text{CO}_2$ , 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  $\text{CO}_2$  that are above atmospheric, a useful phase diagram is one for the  $\text{MgO}\text{-H}_2\text{O}\text{-CO}_2$  system in which the variables are the  $\text{Log}(f\text{H}_2\text{O})$  and  $\text{Log}(f\text{CO}_2)$ . This phase diagram is also appropriate for the vapor phase contact mode.

Figure 1 shows the phase equilibria in the system  $\text{MgO}\text{-CO}_2\text{-H}_2\text{O}$  as a function of  $\text{Log}(f\text{H}_2\text{O})$  and  $\text{Log}(f\text{CO}_2)$  at 25 °C and 1 bar. This figure indicates that so long as periclase ( $\text{MgO}$ ) remains present and equilibrium is maintained the partial pressures of both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  should remain very low in the repository. Reaction of periclase with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in this environment produces brucite and magnesite. Once the periclase has been consumed the brucite and magnesite will begin to react with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to produce hydromagnesite. The  $\text{Log}(f\text{CO}_2)$  and  $\text{Log}(f\text{H}_2\text{O})$  increase as this reaction progresses. Eventually, the  $\text{Log}(f\text{CO}_2)$  will be buffered at approximately  $10^{-4.6}$  and the  $\text{Log}(f\text{H}_2\text{O})$  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  $\text{CO}_2$  with brucite to produce hydromagnesite will continue with the equilibrium fugacity of  $\text{CO}_2$  near  $10^{-4.6}$ . Once the brucite is consumed, the fugacity of  $\text{CO}_2$  can increase and reaction of hydromagnesite with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can proceed to produce nesquehonite. The fugacity of  $\text{CO}_2$  at equilibrium during this reaction is highly dependent on the fugacity of  $\text{H}_2\text{O}$ , but it should be below 1 bar. Thus high  $\text{CO}_2$  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.

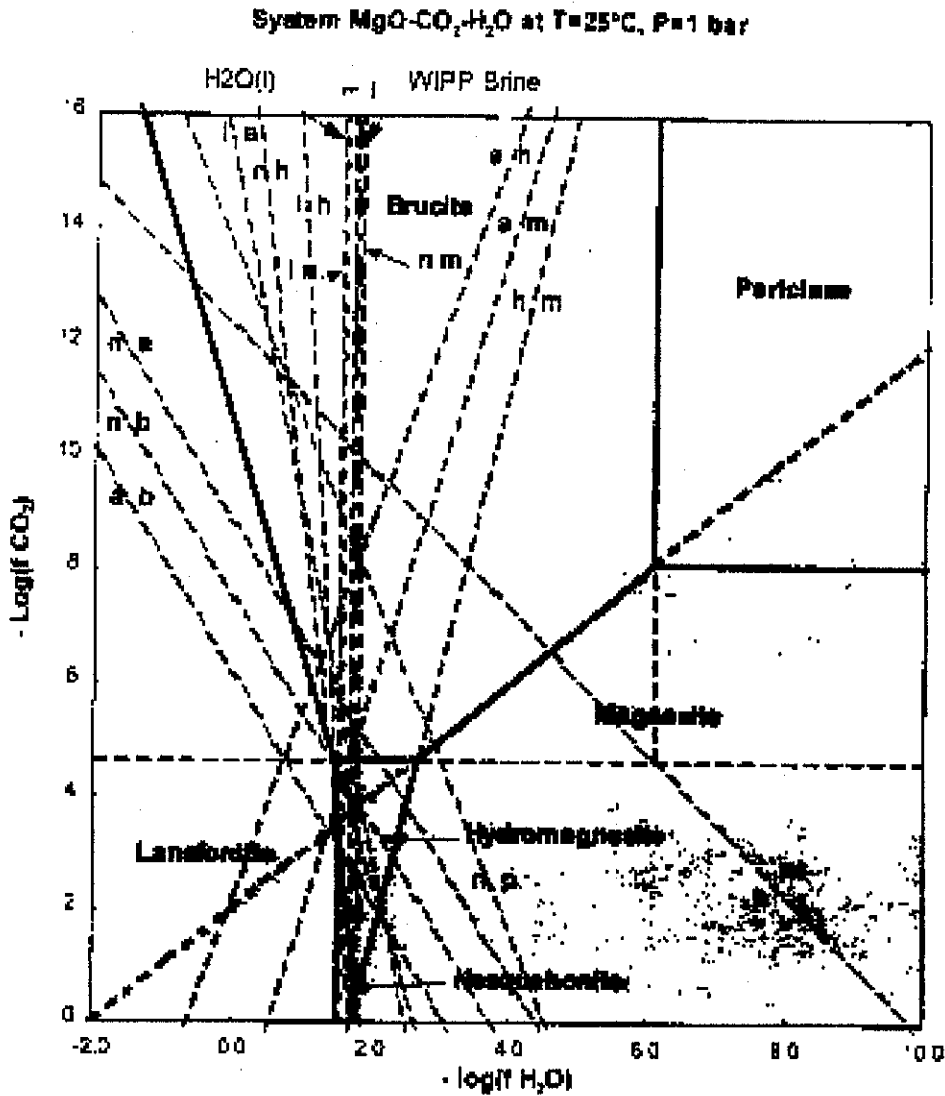


Figure 1. Data for phases in the system MgO-CO<sub>2</sub>-H<sub>2</sub>O

	Formula	Symbol	Delta G <sub>r</sub>	Reference
H <sub>2</sub> O (g)	H <sub>2</sub> O		-54525	supcrt92
CO <sub>2</sub> (g)	CO <sub>2</sub>		-94254	supcrt92
Artinite	Mg <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O	a	-609472.03	Langmuir 97
Brucite	Mg(OH) <sub>2</sub>	b	-198921.17	Langmuir 97
Hydromagnesite	Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	h	-1396991.3	Langmuir 97
Lansfordite	MgCO <sub>3</sub> ·5H <sub>2</sub> O	l	-525581.72	Langmuir 97
Magnesite	MgCO <sub>3</sub>	m	-241381.33	Langmuir 97
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O	n	-412379.09	Langmuir 97
Periclase	MgO	p	-136086	supcrt92



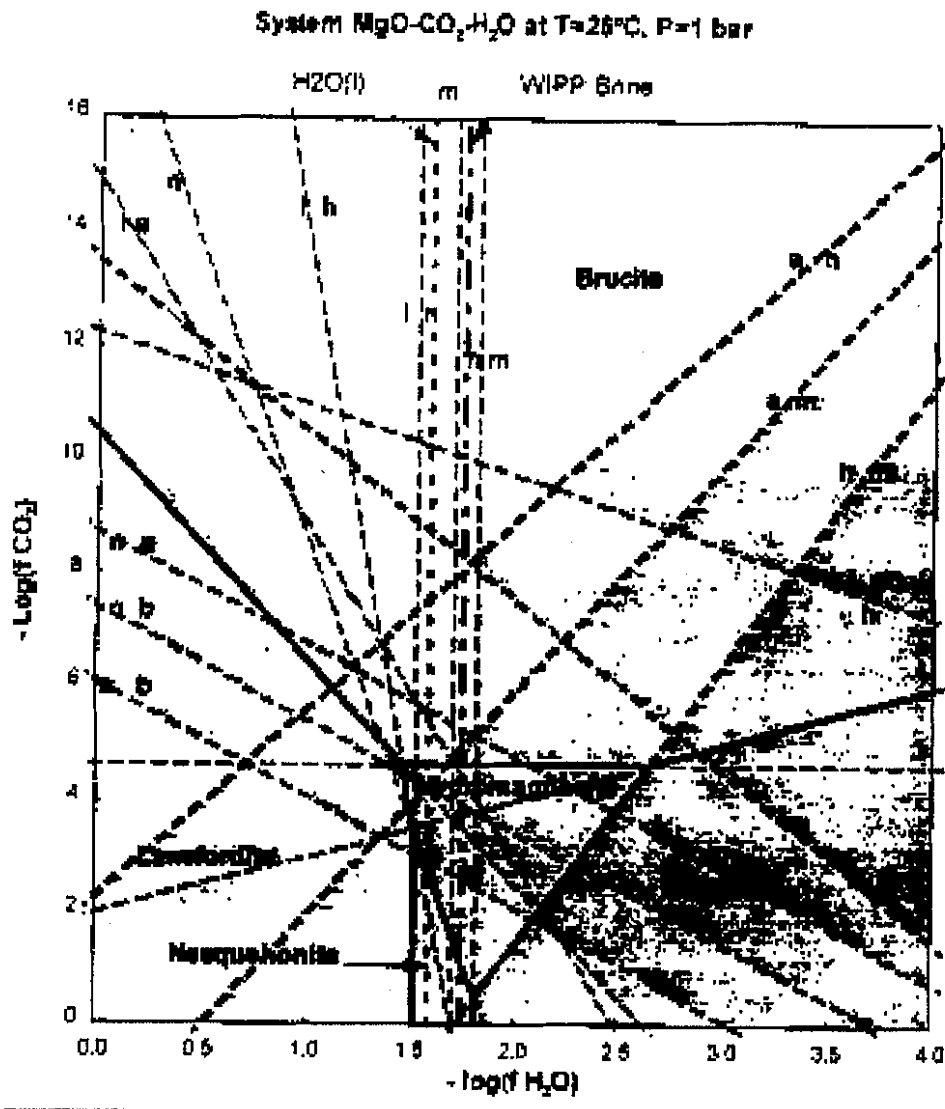


Figure 2. Mass of CO<sub>2</sub> and H<sub>2</sub>O consumed by formation of phase from MgO

	Phase Formula Weight	gH <sub>2</sub> O/g MgO	g CO <sub>2</sub> /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<sub>2</sub> produced by the degradation of organic components emplaced in the repository and maintain the partial pressure of CO<sub>2</sub> at acceptably low levels. However, the Peer Review Panel has questioned whether all the MgO to be emplaced will be accessible to CO<sub>2</sub>. 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<sub>2</sub> into the interior of the pellets. Hypothetically, several different types of reaction rims could form depending on the MgO/H<sub>2</sub>O/CO<sub>2</sub> contact mode. Each of these rims could have a somewhat different impact on CO<sub>2</sub> 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<sub>2</sub> diffusion into the pellets because this mode only involves the addition of H<sub>2</sub>O and CO<sub>2</sub> to the pellets. Literature data suggest that the conversion of MgO to Mg(OH)<sub>2</sub> involves a four step dissolution/reprecipitation process (Smithson and Bakhshi, 1969) as follows:

- (1) "Initially water vapor is chemisorbed 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)<sub>2</sub>."
- (3) "The Mg(OH)<sub>2</sub> subsequently dissolves into the water layer."
- (4) "As the water layer becomes saturated with Mg(OH)<sub>2</sub>, 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)<sub>2</sub> 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<sub>2</sub> 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.

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### 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<sub>2</sub> 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<sub>2</sub>).". 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<sub>2</sub> has access to the interior of the pellet as the hydration and carbonation reactions proceed inside the pellet.
  - (2) The diffusion rate of CO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> fixation during saturated brine interactions.
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## Conclusions

In order to bound the effectiveness of MgO in buffering the partial pressure of CO<sub>2</sub> 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<sub>2</sub>O/CO<sub>2</sub> 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)<sub>2</sub> 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.

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**STTP Chronological Events:  
References**

## References

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