Sandia National Laboratories
Waste Isolation Pilot Plant (WIPP)
Test Plan, TP 00-06

Experimental Work to Develop a Model for Cement/Brine Interactions at the WIPP Site

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3.0 REVISION HISTORY

This is the first revision of this test plan (TP). Changes to TP 00-06, other than those defined as editorial changes per Nuclear Waste Management Program (NWMP) procedure NP 20-1, "Test Plans," shall be reviewed and approved by the same level of responsibility of persons that performed the original review and approval. All TP 00-06 revisions will follow the same distribution as the original document.

4.0 DEFINITION OF ABBREVIATIONS AND ACRONYMS

ACI   American Concrete Institute

API   American Petroleum Institute

ASTM   American Society for Testing and Materials

CAH   Calcium aluminum hydrate

CAS   Calcium aluminum sulfate

CSH   Calcium silicate hydrate

CCA   Compliance Certification Application

DAS   Data acquisition system

DOE   Department of Energy

EBSD   Electron backscatter diffraction

ICP-OES   Inductively-coupled plasma optical emission spectrometery

ICP-MS   Inductively-coupled plasma mass spectrometery

GC-MS   Gas chromatograph mass spectrometry

JCPDS-ICDD   Joint Committee on Powder Diffraction Standards – International Center
               for Diffraction Data

M&TE   Measuring and Test Equipment

MOC   Management and Operations Contractor

MSH   Magnesium Silicate Hydrate

NIST   National Institute of Standards and Technology

NAS	National Academy of Sciences
NBS	National Bureau of Standards
NP	Nuclear Waste Management Program Quality Assurance Procedure
NWMP	Nuclear Waste Management Program
OPC	Ordinary portland cement
P&A	Plugging and abandonment
PA	Performance assessment
PNNL	Pacific Northwest National Laboratories
RWP	Radiological Work Permit
SEM	Scanning electron microscope
SNL	Sandia National Laboratories
SP	Activity Specific Procedure
TP	Test Plan
USI	Ultrasonic well-logging instrument
WID	[Westinghouse] Waste Isolation Division
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction

5.0   PURPOSE AND SCOPE

Upon reviewing the technical and scientific data gathered by Sandia National Laboratories (SNL) for the Waste Isolation Pilot Plant (WIPP) site characterization study, a National Academy of Sciences (NAS) review panel concluded that the only credible scenarios resulting in significant releases from the site involve human intrusion. Oil and gas deposits are common in the rock units underlying the repository formation (the Salado Formation), and currently active oil and gas wells are present within hundreds of meters of the site boundary (WIPP Compliance Certification Application (CCA), Appendix DEL). Inadvertent and intermittent drilling for resources was assumed to be the most severe human intrusion scenario. Estimates based on current and previous Delaware Basin drilling rates suggest that, over the next 10,000 years, 46.8 boreholes/km^2 will be drilled to a depth great enough to intersect the WIPP repository (CCA, Appendix DEL, Section 7.4).

Oil wells drilled within the Delaware Basin are plugged using several different plug configurations. These plug configurations are discussed in detail in the CCA, Appendix MASS, Section 16. The three most prevalent types of plug configurations are:

1) A two-plug configuration, with one plug at the top of the Salado, between the brine-bearing Rustler units and the stratigraphic level of the repository, and the other at the base of the evaporite sequence, below the Castile. The plugs are on average 40 m long, and are located at casing step-downs.

2) A three-plug configuration, that includes the two-plug configuration described in (1), plus a third plug in the Salado, either above or below the repository level. The plugs beneath the repository level are of particular importance, as they would serve to isolate the repository from brine pockets in the Castile.

3) A single-plug, extending through much or all of the evaporite section.

In the CCA, failure of borehole plugs was assumed to be a function of two processes—corrosion of the steel casing and degradation of the cementitious materials in the concrete comprising the plugs. Factors affecting the rate of plug failure include depth of emplacement and the length of the plug. Plugs emplaced above the Salado were assumed to fail in less than 200 years due to rapid casing corrosion under the oxidizing conditions present in the shallow subsurface. The resulting lack of radial confinement and radial infiltration of reactive brines into the concrete plug would then lead to fracturing, spalling and failure.

Concrete plugs extending through the entire evaporite sequence were assumed to behave as confined systems. Alteration products produced by brine/cement reactions build up in the plug, resulting in decreased porosity and permeability. Plug failure was not predicted to occur within time spans relevant to the repository.

Shorter concrete plugs emplaced at depths below the repository horizon were treated as open systems. At these depths, casing corrosion—assumed to be occurring as oxidation to goethite (α–FeOOH), with an accompanying generation of H_2 gas—was assumed to be inhibited by buildup of hydrogen gas. The porosity and permeability of the concrete plugs was assumed to remain constant until a "critical volume" of brine—assumed from work by Berner (1990) to be 100 pore volumes—passed through the plug. At that point, cementitious components would be degraded significantly by leaching and dissolution, and unconstrained microfracturing and physical failure would occur. Failure was estimated to occur very slowly, with plugs maintaining integrity for 5,000 to 50,000 years – the breadth of the range indicating the large uncertainties in the model. While the lower part of the range was ½ the regulatory period (10,000 years), the bulk of the range was much larger. On the basis of these calculations, units beneath the Castile were screened out as sources of brine for repository influx.

Since boreholes provide the only credible conduits for brine access to the repository, accurate estimates of borehole plug failure rates, especially for plugs below the repository, are critical to performance assessment (PA) modeling of releases at the WIPP site. The estimates of plug failure rates in the CCA are based upon experimental work done using cements and groundwaters that are not specific to the WIPP site. The Castile and Salado brines are considerably more complex than the electrolyte that Berner (1990) used in his experiments. Cement degradation may be slower than predicted, if precipitated minerals inhibit cement/brine reactions (Krumhansl, 1993). Carbonate-rich Castile brines may be especially effective at promoting calcite precipitation and sealing cement porosity. Alternatively, cement plug degradation may be faster than predicted in the CCA, if the "critical volume" estimate, based upon

work with dilute solutions (Berner, 1990), is smaller for the complex, high ionic strength Castile and Salado brines. Formation formation of expansive alteration products (Atkinson and Hearne, 1990; Havlica and Sahu, 1992; Xie and Beaudoin, 1992) might also shorten plug lifetimes, by causing spalling of partially reacted or unreacted material from the end of the plug, or by splitting the casing, allowing radial inflow of brine.

SNL proposes to develop a more rigorous model for borehole plug failure at the WIPP site. Two approaches will be used. The first is collection of casing and concrete samples from boreholes at the WIPP site during plugging and abandonment (P&A). Current schedules for borehole P&A at the WIPP site are described in Richardson and Crawley (1999). The samples collected during P&A will establish casing corrosion and cement degradation products and mechanisms relevant to WIPP conditions, and test plug failure assumptions in the CCA. Casing and cement sampling during borehole P&A is described in detail in a separate test plan—TP 00-02, "Collection and Analysis of Downhole Cement and Steel Samples During Borehole Plugging and Abandonment."

The second approach, which is described in this test plan, will be an experimental program to determine cement alteration reactions and mechanisms in Salado and Castile brines, and to develop a thermodynamically-based model for borehole plug degradation under conditions relevant to the WIPP. Using this model, more accurate cement plug failure rates will be determined for performance assessment (PA) analysis. This is the second revision of this test plan, and, as well as describing planned experimental work, describes and references work that has already been carried out.

The work performed under this test plan is largely intended to confirm conceptual models used in WIPP certification and recertification. Development of a new borehole plug degradation model supports assumptions of plug failure rates in radionuclide release scenarios, and will affect several parameters used in PA calculations. Evaluating the effects of cement on repository chemistry could impact estimates of actinide solubilities in WIPP brines, influencing predicted radionuclide releases in repository failure scenarios.

5.1   General Scope of the Experimental Work

A robust, versatile model for cement/brine reactions, able to incorporate effects of changing brine and solid compositions with continued reaction, and of variations in initial compositions, will incorporate equilibrium thermodynamic speciation modeling, kinetic effects due to both reaction kinetics and diffusion, and the effects of changing porosity/permeability or cement accessibility. The basic information required for the equilibrium thermodynamic model includes Pitzer binary interaction coefficients for the solution species present, and thermodynamic data (e.g. formation constants) for the solid phases present. Pitzer parameters for major components in WIPP brines have been determined, but good data do not exist for Si and Al at high pH values, such as those expected in concrete pore waters. These two components are important when considering the solubility of cement phases, which include calcium silicate hydrate (CSH), calcium aluminate hydrate (CAH), and calcium aluminum sulfate (CAS).

The first step of the experimental program will be to carry out solubility experiments with simple Si and Al phases — amorphous silica, crystalline silica, and gibbsite $(Al(OH)_3)$— in single and multi-component electrolytes covering a range of concentrations. From these data, Pitzer interaction parameters will be determined.

The second round of experiments will be aimed at determining the mineral phases present under WIPP conditions. In these batch experiments, crushed or powdered cement and cement coupons will be aged in synthetic WIPP brines, and the cement alteration phases that form will be identified. If thermodynamic data are unavailable for some phases, thermodynamic parameters may be measured experimentally using solubility experiments, or data for mineral analogs may be used. The mode of alteration will also be documented.

The third round of experiments will involve use of cement cores. Brine will be pumped through (synthetically) fractured and unfractured cement cores, and chemical changes in both the effluent brine and the cement will be measured. Changes in the cement porosity, permeability, and texture will be monitored. As opposed to the batch systems, the cement will constantly be exposed to fresh brine. These experiments will yield information on the mode of cement failure under flow-through conditions; local expansion and fracturing would result in more rapid and extensive degradation than diffusion-limited alteration. Successful modeling of the brine effluent composition will be a measure of the thermodynamic model performance.

5.2   Previous Work

It is beyond the scope of this document to review the huge body of literature on the degradation of cement in various environments. However, a review of previous studies examining cement degradation in WIPP-related brines, and previous thermodynamic modeling, is appropriate.

Previous cement studies involving WIPP-related materials are summarized in Krumhansl (1995). Several studies document degradation of the concrete waste shaft liner due to interactions with Mg-rich brine at the Rustler-Salado Contact (Lambert et al., 1992; Wakely et al., 1992). The liner is composed of ASTM Type V (sulfate-resistant) cement that was mixed with fresh water. Microscopy and X-ray diffraction studies determined that the degraded liner showed surficial spalling and extensive microfracturing and contained brucite, gypsum, magnesium hydroxychloride hydrate, and locally calcium aluminum chloride. Wakely et al. (1994), and Poole et al. (1994) performed experimental work to explain the observed shaft liner degradation and to examine the chemical stability of concrete developed for the repository panel closures. Batch experiments were carried out using cement wafers aged in Mg-sulfate rich brine. After several months to a year, most specimens had developed surface coatings of precipitated minerals, and showed alteration of the underlying cement. Formation of a Mg-rich silicate phase was predicted, but not observed, and the authors postulated that the alteration process was driven by precipitation of brucite on the cement surface, lowering the activity of OH^- in solution. This caused dissolution of $Ca(OH)_2$ and ultimately, of CSH gel, in the cement matrix. The mineralogy of the alteration assemblage was very sensitive to the brine composition, and included phases not observed in altered cement samples collected from the shaft liner.

Krumhansl and Lambert (1992) and Krumhansl (1993) examined the degradation of salt-saturated cement at elevated temperatures, by a Mg-sulfate-rich brine formulated to represent a composite of Rustler groundwaters, and by synthetic Salado brine. They used batch systems with cement coupons or prisms, aged at temperatures of 100ºC to 250ºC to speed reactions. Surface coatings of brucite and calcium sulfate phases (anhydrite, gypsum, or bassanite, depending upon temperature) were observed. These phases, as well as Mg and Mg-Al hydroxychlorides, were also observed in the altered cement matrix. In contrast to the experimental work done by Wakely et al. (1994) and Poole et al. (1994), Ca was quantitatively replaced in CSH with Mg to form magnesium silicate hydrate (MSH). The mineralogy and texture of the surface coatings varied with brine composition and temperature, and that these coating properties had a strong influence the continued conversion of CSH to MSH in the cement matrix.

Krumhansl (1995) examined possible failure rates for cement shaft liners in the Culebra and Salado, and panel seals within the repository. He developed a thermodynamic model to examine cement stability in Culebra and Salado brines. Because of the lack of available thermodynamic data for actual cement phases, he used thermodynamic data for mineral analogs of cement and alteration phases. In addition, because of the unavailability of data for a Pitzer activity coefficient model, Krumhansl could only estimate the activities of species in solution. He concluded that dominant phases present in ordinary Portland cement (OPC) are unstable in all of the WIPP brines examined in the study. Krumhansl also estimated cement degradation rates in synthetic Culebra and Salado brines, using two different models. The first, the "shrinking core model," estimated the rate at which the alteration front would move into the cement, by assuming that diffusion of Ca and hydroxide out of the cement is the rate-limiting step. The second model was based upon mass balance arguments; cement degradation was assumed to be a function of the rate at which Mg could be delivered to the cement surface, and hence to be controlled by brine availability and inflow rates. Shaft liners (50 cm thick) were found to fail in hundreds to thousands of years, depending upon model assumptions; the 12-meter-thick panel seals were not significantly degraded over thousands of years. Krumhansl also evaluated the effect of microfracturing induced by expansive alteration products, and concluded that it could potentially increase failure rates by orders of magnitude. He concluded that accurate modeling of cement degradation rates at the WIPP was not possible with available models, due to several factors: 1) the lack of material-specific properties, such as thermodynamic data, on WIPP-relevant cement and alteration phases, requiring the use of mineral analog data and simplifying assumptions; 2) inability to incorporate the effects of microfracturing and mineral precipitation on brine accessibility to cement beneath the altered rim; 3) the lack of kinetic information for alteration reactions, and the potential formation of metastable phases; and 4), the lack of site-specific information, such as brine distribution and availability.

Bonen (1996) examined 9-year-old cement (Type H, salt saturated) from the WIPP repository, and found little evidence for alteration, other than minor carbonation along the salt/cement contact. He also examined 20-year-old cement grout (initial composition unknown) from a nearby potash mine. The grout, which had been in contact with Mg-rich formation waters, showed widespread alteration, with precipitation of brucite and conversion of CSH to MSH. In laboratory studies, Bonen examined the reactivity of American Petroleum Institute (API) Type H (equivalent of ACI type 2) salt-saturated cement with Mg-sulfate-rich brines similar in composition to those from the base of the Rustler Formation. The

cement showed massive alteration, with precipitation of brucite and gypsum coatings and conversion of CSH to MSH.

To summarize, previous experimental work has consisted largely of characterization of liner samples collected from the waste handling shaft, and laboratory studies to determine the stability of liner cement or proposed panel seal cement in brines similar to that found in the Rustler or Salado Formations. No work has been done to examine cement interactions with sulfate-rich Castile brine. Only Krumhansl (1995) attempted to predict failure rates for cement materials, and he recognized that only crude modeling was possible with the available data.

5.3   Modeling cement degradation

A great deal of thermodynamic data are available on cement and alteration phases, and thermodynamic models for cement degradation in dilute solutions have been formulated.   The information needed to expand those existing models to cover WIPP conditions can be summarized as follows:

1. Parameters for a Pitzer model for the activities of aqueous species in the brines. Pitzer parameters for the dominant species present in WIPP brines are summarized in Harvie et al. (1984) and Pitzer (1987). Some solubility data and Pitzer interaction coefficients are available for Si and Al in concentrated electrolytes at low to intermediate pH and in some cases, at high pH (Marshall, 1980; Chen and Marshall, 1982; Gasteiger, et al., 1992; Palmer and Wesolowski, 1992; Wesolowski, 1992; Wesolowski and Palmer, 1992, 1994; Felmy et al., 1994a,b; Azaroual et al., 1997; Richter et al., 2000).   However, a complete data set of the necessary Pitzer parameters is not available for Si and Al at pH values and brine compositions relevant to the WIPP or to cement pore fluids (pH 9-13).

2. Identification of the initial hydrated cement phases, cement alteration phases, and alteration pathways. The phases that are present in hydrated cement are well known, and can be calculated modally from the initial composition of the cement blend (Atkins et al., 1992a; Macphee et al., 1989). These phases are listed in Table 1. Degradation of both salt-free and salt-saturated cement in different electrolytes has been widely studied (Atkinson and Hearne, 1990; Bonen, 1992; Bonen and Cohen, 1992; Havlica and Sahu, 1992; Krumhansl 1993, 1995; Krumhansl and Lambert, 1992; Lambert et al., 1992; Wakely et al., 1992, 1994; Poole et al., 1994; ; Neall, 1994, 1996; Bonen, 1996; Pfingsten and Shiotsuki, 1998), and possible alteration phases that are likely to form have been identified, and have also been listed in Table 1. Although several studies have been done with synthetic WIPP brines, the actual alteration phases that form will have to be determined experimentally, for several reasons.   In previous studies, the results varied from study to study, and were in some cases inconsistent. In addition, no experiments have been run with simulated Castile brine, one of the most WIPP-relevant brines with respect to borehole plug degradation. Also, the alteration phases that form are dependent upon the initial composition of the cement. Most alteration studies have been done with American Cement Institute (ACI) Type 1 portland cement or API Type H oilfield cement mixed with fresh water, in some cases with NaCl added to make it salt-saturated. In the Delaware Basin, oilfield cements may be mixed with "formation fluids" or with locally mined "salt", that may contain

Table 1. Phases Likely to Occur in Fresh and Altered Cement

Initial Cement Phases (assuming 100% hydration)

Calcium Silicate Hydrate (CSH)	$xCaO \cdot SiO_2 \cdot yH_2O$
($0.8 \leq x \leq 1.8$, generally 1.4–1.8 for Portland cements)	
Calcium aluminum ferrite hydrate	$3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 6H_2O$
("hydrogarnet")	
Calcium aluminum silicate hydrate	$2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$
Calcium aluminate monosulfate	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$
Ettringite (high sulfate)	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
Gibbsite	$Al(OH)_3$
Gypsum	$CaSO_4 \cdot 2H_2O$
Hydrotalcite	$4MgO \cdot Al_2O_3 \cdot 10H_2O$
Portlandite	$Ca(OH)_2$

Secondary (alteration) Phases

Brucite	$Mg(OH)_2$
Calcite	$CaCO_3$
Calcium aluminum chloride hydrate (I)	$3CaO \cdot Al_2O_3 \cdot CaCl_2 * 12\,H_2O$
CSH (depleted in Ca)	
Gypsum	$CaSO_4 \cdot 2H_2O$
Ettringite (high sulfate)	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
Magnesite	$MgCO_3$
Magnesium silicate hydrate	$xMgO \cdot SiO_2 \cdot yH_2O$
Magnesium hydroxychloride	$Mg_3(OH)_5Cl * 4\,H_2O$
Magnesium sulfate hydrate	$Mg_6O_5SO_4 * 8\,H_2O$

significant amounts of K, Mg, or SO_4^{-2}. These species will significantly affect the initial mineralogical composition of the cement and of the alteration phases that form as it degrades.

3. Once the important phases have been identified, thermodynamic data must be compiled, and an equilibrium thermodynamic model will be generated. Thermodynamic data are available for cement phases, alteration phases, and naturally-occurring mineral analogs (Goto et al., 1979; Gartner and Jennings, 1987; Glasser et al., 1987; Atkinson et al, 1989; Atkins et al., 1991a, 1991b, 1992b; Damidot and Glasser, 1992, 1993; Taylor, 1992; Xie and Beaudoin, 1992). Where possible, data for the actual cement phases will be used, as mineral analogs are commonly more crystalline than the cement phases, and are not compositionally identical. Finally, the model will be compared to existing thermodynamic models for cement degradation (Berner, 1987, 1988; Atkins et al., 1992a; Bennett, et al., 1992; Neall, 1994, 1996; Krumhansl, 1995; Pfingsten and Shiotsuki, 1998).

4. A complete equilibrium thermodynamic model for brine/cement interactions is still insufficient for describing cement plug degradation, as it is not an equilibrium process. Reaction kinetics may inhibit

formation of specific phases; coatings may form on cement/brine interfaces or precipitated phases may reduce porosity and permeability, inhibiting further reaction; or expansive alteration phases may fracture the cement, resulting in spalling of partially reacted cement from the end of the core and reducing the amount of brine access necessary for plug failure. In addition to developing the thermodynamic model, column experiments with cement cores will be performed to evaluate the impact of these non-equilibrium processes. Finally, a more comprehensive degradation model, incorporating these non-equilibrium processes, will be implemented with EQ3/6 (Wolery, 1992; Wolery and Daveler, 1992) using a mixing tank approach (Berner, 1987, 1988, 1990; Neall, 1994, 1996). Reactive transport simulations will be conducted using activity coefficients calculated from EQ3/6. It is expected that the activity coefficients for a given brine composition will remain more or less constant along a flow path. Version 7.2a of EQ3/6 is currently qualified for WIPP use.

6.0   EXPERIMENTAL PROCESS DESCRIPTION

6.1   Planning Overall Strategy and Process

Developing the cement degradation model will be done in several steps. First, Pitzer parameters applicable to Si and Al in WIPP brines will be determined. Simultaneously, completely hydrated cement wafers and crushed or powdered cement will be exposed to synthetic Culebra and Salado brines to determine the alteration phases that form in those solutions. Once the important cement phases and alteration phases have been identified, a survey will be made of the thermodynamic data available for those phases and for mineral analogs. This information will be used to develop an equilibrium thermodynamic model for cement alteration. In addition, column experiments will be performed using cement cores. Brines will be pumped through whole and synthetically fractured cement cores, and geometric effects on cement alteration (e.g., the formation of low-porosity mineral coatings or changes in matrix porosity due to plugging of existing porosity or expansion and fracturing) will be observed and documented. Finally, a comprehensive model, incorporating both the equilibrium model and the empirically measured disequilibrium effects, will be developed.

6.1.1 Brines

Two synthetic brines, representative of those occurring in the Salado and the Castile formations at the WIPP, will be used in this study. These brines are GW brine, and ERDA-6 brine, respectively, and will be prepared using the recipes given in Table 2, and following the procedures described in NWMP Technical Operating Procedure (TOP) TOP-544, "Preparing Synthetic Brines for Chemical Retardation and Transport Experiments."

Table 2. Composition of synthetic Salado and Castile Brines

Compound	Salado generic weep (GW) brine[1] (g/L)	Castile (ERDA-6) brine[2] (g/L)
$MgCl_2 \cdot 6\,H_2O$	207.05	3.86
NaCl	179.61	261.64
KCl	34.84	7.23
Na_2SO_4	25.23	23.7
$Na_2B_4O_7 \cdot 10H_2O$	15.06	6.00
$CaCl_2 \cdot 2H_2O$	2.03	1.76
NaBr	2.74	1.13
LiCl	0.186	–
Component	**M, GW brine**	**M, ERDA-6 brine**
Na	3.536	4.854
K	0.467	0.097
Li	0.004	–
Ca	0.014	0.012
Mg	1.018	0.019
Cl	5.609	4.636
Br	0.027	0.011
SO_4	0.178	0.167
B_4O_7	0.039	0.016

[1] Zhang et al., 1999

[2] Villareal et al, 1999

6.1.2 Cement types used

In order to determine the type of cement used in the oilfield for borehole plugging operations, borehole plugging logs for wells in the Delaware Basin were examined. The results for 52 boreholes are summarized in Table 3. Type C sulfate-resistant cement is the most common type specified. Type H cement is also used—it is sulfate resistant and is chemically similar to Type C, but cures more slowly because it is coarsely ground. It is mostly used in deeper holes (>7000 ft) where higher temperatures accelerate curing and a slow-hardening cement is required. The borehole plugs were poured "neat"—without aggregate, and additives to accelerate or retard curing were rarely used (in three instances, 2% $CaCl_2$ was used as an accelerant, and in one instance, 2% KCl).

Schlumberger/Dowell, an oilfield service company, was also contacted. They confirmed that "neat" Type C cement is the most common type used for borehole plugs, and that aggregate is not used under normal circumstances. The cement is mixed at the surface, adding water equivalent to 44% of the dry weight of the cement. Only 27% water is necessary for complete hydration—the excess is added to thin the cement for pumping purposes. If the plug is to be emplaced in an evaporite section, the cement must be salt-saturated. To accomplish this, an amount of dry NaCl, equal to 37 wt% of the water added, is added to the mix.

Because Type C cement is commonly used at WIPP-relevant depths, and because there is little difference, other that initial grain size, between Type C and Type H cement, only Type C cement is being

**Table 3. Summary of borehole plug cement types,
extracted from 52 borehole plugging logs.**

Cement type used	Number of boreholes
Type C	21
Type H	5
Type C and Type H	2
Not specified in log	24

used in the borehole plug degradation experiments described in this test plan. Both salt-free and salt-saturated cement are being used in powdered cement, cement wafer, and cement core experiments.

The cement used to mix cementitious waste forms is commonly ordinary Portland cement (OPC). Type C cement, because it is sulfate-resistant, is a poor analog for OPC. Thus, in order to evaluate the effects of cement on repository chemistry, salt-free OPC is also being used in the experiments with powdered cement and cement wafers.

Approximately 25 kg of both Type C cement and OPC were obtained from Lone Star Industries, Inc., a cement company that supplies oilfield service companies in the Delaware Basin. These materials are being used in the experimental work performed under this test plan.

In the oilfield, cement is mixed on the surface, using whatever water is available, and then pumped into the boreholes. The conditions for mixing cementitious waste forms vary widely, but air exposure during mixing is likely. Thus, no effort was made to exclude CO_2 when the cements were prepared, and all cement types are expected to contain some calcium carbonate. The cements were mixed in the proportions described above for oilfield use, and sealed into one liter rectangular plastic containers to cure for two weeks. It is recognized that cement does not fully hydrate in two weeks—full hydration can take decades or even centuries. However, accelerating the hydration process by autoclaving would affect the crystallinity and mineralogy of the hydration products, and is not desirable. After two weeks, the hardened cement "bricks" were removed from the containers, and different fractions of each were crushed to <100 mesh (150 μm), cut into 25mm square by 3mm thick wafers, and cored to produce 1" diameter by 2-3" long cement cores. All materials were stored in sealed plastic bottles or bags until use.

6.1.3 Atmospheric conditions

Within the repository, CO_2 fugacities will be controlled by the presence of brucite and a magnesium carbonate mineral, probably hydromagnesite. This corresponds to a P_{CO_2} of $10^{-5.5}$, or about 3 ppm. In the presence of cement, calcite/portlandite are the expected controlling phases (Novak, 1997) and will limit the P_{CO_2} to even lower values. Significant calcite will initially be present in the systems

because the cements will be mixed under atmospheric P_{CO2}, simulating oilfield conditions for mixing cement for borehole plugs, and conditions for solidifying cementitious waste forms. Rather than attempting to maintain such low CO_2 fugacities in a glovebox, samples will be kept sealed, and higher levels of CO_2 will be excluded as much as possible from the experimental setup. If diffusion of CO_2 into the systems is minimized, then the presence of calcite and portlandite will maintain the desired P_{CO_2}. Diffusion of CO_2 into the systems will only affect the P_{CO_2} if it occurs more rapidly than carbonate can precipitate, or if the amount diffusing in overwhelms the amount of portlandite available. For these reasons, all brines will be sparged with Ar or N_2 (industrial grade, >99.99% pure) prior to use to render them carbonate-free, and all experiments will be carried out in inert atmosphere in a glove box to minimize carbonation reactions. To ensure that the atmosphere in the glovebox is carbonate-free, Ar or N_2 will be slowly bled into the chamber to maintain a positive pressure with respect to the external atmosphere. In addition, a small pump will recirculate the atmosphere in the glove box through a bubbler (0.1 M NaOH + 0.05 M $BaCl_2$) at a rate of ~2 liters/minute to remove CO_2. The solution in the bubbler scavenges CO_2 from the glovebox atmosphere by precipitation of barium carbonate ($BaCO_3$), and will be replaced on a monthly cycle. The atmosphere in the glove box will be sampled and analyzed by gas chromatography–mass spectrometry (GC-MS) on a regular basis to monitor the amount of CO_2 present.

Some experiments may be run under higher P_{CO2} conditions—probably atmospheric—in order to evaluate the changes in pH and alteration product mineralogy as the portlandite is consumed through precipitation of calcite.

6.1.4 Measuring Si and Al Pitzer parameters

Pitzer binary interaction coefficients for the major ions in WIPP brines—H^+, Na^+, Mg^{2+}, Ca^{2+}, OH^-, Cl^-, SO_4^{2-}, and CO_3^{2-}—are known for most conditions of medium and high pH. However, interaction coefficients between Si and Al and some of these ions (Mg^{2+}, Ca^{2+}, and SO_4^{2-}) are not known, especially at high pH. Experimental work to determine some interaction parameters for silica is currently being carried out at by Andrew Felmy at Pacific Northwest National Laboratories (PNNL). The silica system is complex at high pH because multiple aqueous chain and ring silica polymers may form. Al–containing systems are less complex, as only monomeric and dimeric Al species are stable in solution. We will use batch experiments to examine Al solubilities and identify the solid phases present at equilibrium. In collaboration with Felmy, we will interpret pH-solubility curves to determine Pitzer parameters.

It is anticipated that the concentrations of both Si and Al in solution will be pH-dependent, as the silicon phase in solution is a weak acid (H_4SiO_4), which will progressively deprotonate and polymerize with increasing pH, and aluminum will be present as monomeric and dimeric aqueous hydroxide species. Thus, solubilities will be measured over a pH range starting at 7 and extending to higher values. The upper pH limit will vary with the salt used and the electrolyte concentration—care must be taken to avoid precipitation of such large volumes of hydroxide that the electrolyte concentration is affected. Initial experiments will be run with crystalline $Al(OH)_3$ (gibbsite); solids present at equilibrium will be determined by XRD. Solubilities will be measured over a range of ionic strengths, typically in 4-6 steps, from 0.1 M to saturation for the salt involved. For example, the suite of $MgCl_2$ concentrations to be used

to determine Pitzer interaction parameters for Al and Mg will be 0.1, 0.2, 0.5, 1.0, 2.0, and 3.7M, where 3.7M is saturation for the salt involved.

The solubility experiments will be run in polyethylene or polycarbonate Oak Ridge style screw-cap centrifuge tubes, with 0.1 to 0.5 gram of gibbsite in each tube, and 25-30 ml of electrolyte. The system pH will be adjusted with NaOH, and will be checked and readjusted as necessary over the first few weeks of the experiment. Samples will be aged in temperature-regulated orbital-mixing water baths. Two sets of samples will be run for each electrolyte concentration. One will be aged at 25ºC, and will approach equilibrium from an undersaturated state. The other set will be aged at 50ºC and allowed to re-equilibrate at 25ºC. Thus, it will approach equilibrium from an oversaturated state. Samples of the electrolyte will be collected at the end of the experiment, and analyzed to determine the Al concentration and to check if hydroxide precipitation has significantly affected the concentration of the binary electrolyte. To be acceptable, the electrolyte concentration must be within 5% of the nominal value. Coincidence of the two data sets will provide evidence for equilibrium.

Although electrolytes will be degassed by sparging with N_2 to remove CO_2, the samples will not be aged in a glove box. Other than keeping the samples tightly closed, no effort will be made to keep out CO_2. This is because the carbonate concentration, even up to one-tenth molar quantities, has little effect on Al solubility (Felmy, personal communication).

The concentration of Al in solution will be measured using several methods, including inductively-coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer Optima 3300, colorimetric methods, using a Cary 300 UV-visible spectrophotometer, and possibly ICP-mass spectrometry (ICP-MS). The solids present will be identified by X-ray Diffraction (XRD).

6.1.5 Cement-brine equilibration experiments

Cement brine equilibration experiments are being run with both powdered cement and cement wafers, and are summarized in Table 4. Experiments with powdered cement include 1) equilibration rate experiments, to determine how long systems will have to be mixed in order to see significant generation of cement alteration products; 2) long-term equilibration experiments, to generate enough alteration products for identification and analysis; and 3) leaching experiments, to evaluate the effect of introducing fresh brine on alteration product mineralogy and cement degradation. The cement wafer experiments will evaluate the effects of disequilibrium processes (mineral precipitation, fracturing due to expansive mineral growth, etc.) on cement degradation. In all of these experiments, both OPC and API Type C cement are being used.

6.1.5.1   REACTION RATE EXPERIMENT

The goal of this experiment was to determine, in a general sense, the rate of reaction between the powdered cement and brine. This information was used to plan longer-term cement/brine equilibration experiments, in order to guarantee that sufficient reaction products formed for analysis.

Table 4. Experimental matrix for cement/brine equilibration experiments

Reaction rate experiment		
Brines (2)	**Cements (3)**	**Cement/brine ratios (2)**
GW	OPC	1g/110ml
ERDA-6	Salt-free Type C	5g/110ml
	Salt-sat. Type C	

Total number of systems: 12, each sampled 10 times over a period of 3.5 months.

Conditions: Systems agitated. Containers sealed and stored in a N_2-purged glovebox.

Long-term cement/brine equilibration experiment		
Brines (2)	**Cements (3)**	**Cement/brine ratios (6)**
GW	OPC	0.1g/30ml
ERDA-6	Salt-free Type C	0.2g/30ml
	Salt-sat. Type C	0.5g/30ml
		1.0g/30ml
		2.0g/30ml
		5.0g/30ml

Total number of systems: 36 (first experiment), sampled after 3.5 months. 24(second experiment).

Conditions: Systems agitated. Containers sealed and stored in a N_2-purged glovebox. A second set has been initiated using only OPC and salt-free Type C cement.

Cement leaching experiment		
Brines (2)	**Cements (3)**	**Cement/brine ratios (1)**
GW	OPC	1g/30ml
ERDA-6	Salt-free Type C	
	Salt-sat. Type C	

Total number of systems: 36 (6 per cement/brine combination).

Conditions: Systems agitated. Containers sealed and stored in a N_2-purged glovebox.

Cement wafer experiment		
Brines (2)	**Cements (3)**	**Cement/brine ratios (1)**
GW	OPC	1 wafer(~3g) /250ml
ERDA-6	Salt-free Type C	
	Salt-sat. Type C	

Total number of systems: 60 (10 per cement/brine combination). Sampled every 1-2 months

Conditions: Systems not agitated. Containers sealed and stored in a N_2-purged glovebox.

In this experiment, powdered cement was aged in GW and ERDA-6 brines, and brine pH and composition was monitored over several months to monitor reaction progress. Three types of cement were used—salt-free and salt-saturated Type C cement, and OPC cement. Experiments were run in 250 ml polypropylene bottles, using cement/brine ratios of 1g/110 ml and 5g/110 ml. Brines were degassed prior to use, and samples were stored as described in section *6.1.2* above, to control the P_{CO_2}.

During aging, the bottles were agitated constantly on a rotary mixing platform. Brine samples were collected at intervals for 3.5 months, and analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES). Results of this experiment are presented in the July, 2002 Technical Baseline Reports to the DOE (RI130). To summarize, brine chemistry changed rapidly initially, and then more slowly over the entire sampling period, indicating that equilibrium was not reached. A longer-term rate experiment will be initiated.

6.1.5.2 LONG-TERM EQUILIBRATION EXPERIMENTS

In these experiments, cement-brine systems of varying cement/brine ratio will be aged for extended periods of time (the reaction rate experiment was designed to provide guidance on the length of time necessary), and then sampled. Brine compositions and reaction product mineralogy will be analyzed by pH meter, ICP-OES, and ICP-MS, and the solids will be identified by SEM and XRD. The purpose of this experiment is two-fold. First, identification of the alteration products produced by brine/cement reactions is necessary for development of the thermodynamic model. Second, each pair of brine compositions and corresponding alteration minerals will provide a data point for validation of the thermodynamic model.

In the first phase of these experiments, reported in the July, 2002 Technical Baseline Reports to the DOE (RI130), three cements were used—OPC and both salt-saturated and salt-free Type C. As there was no discernable difference in brine composition or alteration products between the salt-saturated and salt-free Type C cement systems, in the second set of experiments, only OPC and salt-free Type C cement were used.

These experiments are being carried out in polycarbonate and polypropylene screw-cap Oak Ridge-style centrifuge tubes (40-50ml), using 30 ml of brine, and 0.1 to 5 grams of powdered cement. The amount of cement in the system affects the brine composition (especially the pH and the Mg^{2+}, Ca^{2+}, and SO_4^{2-} contents), and thus influences the reaction products that form. The systems are prepared with degassed brine, sealed tightly, and aged in a nitrogen-sparged glovebox, as described in section 6.1.2. They are constantly agitated on hematology mixers or rotary mixers. The initial experiment was sampled after 3.5 months—a new experiment has been started, and will be sampled after 6 months. Both brine and solid samples are collected at sampling. The brine samples are filtered through 0.2μm syringe filters, and are then acidified to 1% HNO_3 to prevent precipitation. The remaining material is vacuum filtered through 0.2μm membrane filters to separate the solids, which are lightly washed with deionized water to remove the last of the brine. Care is taken to limit the deionized water contact time, to minimize dissolution of gypsum, portlandite and other cement phases.

Following collection, brine compositions are measured by pH meter, ICP-OES, and ICP-MS, and the solids identified by SEM and XRD. The results of the initial experiment, reported in the July, 2002 Technical Baseline Reports to the DOE (RI130), indicate that other than gypsum and portlandite, well-crystallized alteration phases are restricted to the systems containing smaller amounts of cement. Systems with more cement have higher pH values, which may stabilize CSH and MSH relative to crystalline materials. It is not clear whether longer aging times will affect this.

6.1.5.3   CEMENT LEACHING EXPERIMENT

In the cement leaching experiments, powdered cement/brine systems will be aged for extended periods of time, and then the brine will be centrifuged off and replaced. Several samples will be run simultaneously, and at each step, one of the samples will be sacrificed to analyze the solids. This experiment is intended to measure the volume of brine necessary to completely leach components out of the cement, and serves two purposes. The first is to provide electrolyte/solid data pairs to validate the thermodynamic model. The second is to provide information for a simpler borehole plug degradation model based on mass balances, similar to that used in the CCA. The CCA model assumes that 100 pore volumes of brine will leach sufficient components out of the cement to cause complete failure of the plug. This was based on reactions between cement and low ionic strength waters (Berner, 1990). A similar model, based on interactions with actual WIPP brines, might be more readily instituted than a thermodynamic model. For instance, the results collected from the cement wafer experiment (section 6.1.5.1) during the first several months suggest that one criterion of cement plug failure might be complete replacement of CSH with MSH, which causes shrinkage and fracturing in the wafer. Alternatively, in Berner's (1990) experiments, failure was described as crumbling of the cement, after nearly everything but silica had been leached out. If analysis of the solids in the cement leaching experiment indicates that all Ca has been replaced by Mg, or that only silica remains after exposure to a given volume of brine, then a mass balance model, involving predicted brine flow rates, can be developed.

Six systems, each containing 1g powdered cement and 30ml degassed brine, have been prepared for each cement/brine combination. The samples will be aged in a glove box as described in section 6.1.2, and will be constantly agitated. Every 6 months, each sample will be centrifuged and the brine will be decanted off and collected for analysis. The solids in one sample will be retained for analysis. Fresh brine will be added to the remaining samples, which will be returned to the glove box to re-equilibrate.

6.1.5.4   CEMENT WAFER EXPERIMENT

In the cement wafer experiment, thin wafers of cement are being aged in brine for extended periods of time. In the experiments with cement powders, the goal was to react the cement and brine as quickly and completely as possible, in order to reach equilibrium or steady state conditions. The wafer experiments examine the effects of non-equilibrium processes—the formation of mineral coatings, diffusion-limited reactions, the formation of expansive alteration phases (e.g., ettringite)—on the rate of cement reaction, and on the alteration products that form.

Salt-saturated Type C cement, salt-free Type C cement, and OPC were used. The wafers are 25 mm square by 3 mm thick and weigh about 3 grams. Each is aged in 250 ml of degassed brine (GW or ERDA-6) in a sealed polycarbonate wide-mouth bottle, stored in a N_2-sparged glove-box. Both brines and wafers are being sampled periodically (monthly/bimonthly) to observe the mineral coatings that form, and the possible effects these may have on the alteration mineral assemblage that forms in the underlying cement. It is possible that formation of low-porosity mineral coatings will significantly deplete cement pore waters in some aqueous species, resulting in formation of different alteration products than those observed in the crushed cement systems.

The results of SEM analyses of samples collected over the first 5 months of the experiment are discussed in the July, 2002 Technical Baseline Reports to the DOE (RI130).

6.1.6 Column experiments with cement

Cured salt-free Type H cement was dry-cored using a 1" diamond core drill, and cores 2"–3" long were recovered. These will be used in core-column flow experiments, in which fresh brine will be pumped through the cores. The brine will not be degassed; rather, the GW brine will be mixed with the appropriate carbonate concentration for equilibrium with brucite/hydromagnesite, and the ERDA-6 brine will contain the same carbonate content as was measured in field samples. The brines will be sealed in a Hastalloy C accumulator to prevent degassing. An ISCO model 500D syringe pump will pump deionized water into the accumulator, pushing a piston which forces the brine through the core. The core will be encased in an ISCO RCH-type (radial confining pressure) core holder, with a Viton rubber core sleeve. The pump, accumulator, and core sleeve are capable of maintaining a pressure of greater than 2500 psi. Initially, the pumping pressure will be low, and the confining pressure a few hundred psi (just enough to seal the core sleeve against the core), but as minerals precipitate at the cement/brine interface and in the cement pore space, the pumping pressure and the confining pressure will be raised. A differential of 200 psi will be maintained between the pumping pressure and the confining pressure, to avoid leakage around the core. If the confining pressure reaches 2000 psi, the experiment will be terminated.

The core effluent will be collected using a fraction collector, and analyzed for pH, major elements, Si, and Al. Following the termination of the experiment, the core will be removed from the core holder and sliced in half. One half of the core will be impregnated with epoxy and characterized texturally and petrographically by optical microscopy and SEM imaging. Material from the other half will be crushed and analyzed by XRD to determine the alteration phases present, or digested and chemically analyzed to determine the chemical changes associated with alteration.

In addition to pumping brine through intact cores, the cores will be sliced to simulate a fracture, and the brine pumped through the fracture. In this case, the fracture surface is continuously exposed to fresh brine, and cement and brine components can diffuse into and out of the cement matrix, accelerating the rate of degradation.

6.2   Sample Control

Samples created routinely in the laboratory will be handled following the procedures described in NP 13-1 "Sample Control." They will be labeled with a unique sample number, as described and recorded in the scientific notebook. Any necessary handling and storage requirements will be stated in the scientific notebooks. Failure to meet those requirements will result in the data being disqualified and the experiment repeated; this will be documented and the appropriate action taken, as described in NP 13-1 "Sample Control."

No samples will be collected at the WIPP site for this project. Should offsite sample transfer be necessary, it will be accomplished following the procedures outlined in NP 13-1 "Sample Control," and SP 13-1 "Chain-of-Custody".

6.3   Data Control

A calibration program will be implemented for the work described in this test plan in accordance with NP 12-1, "Control of Measuring and Test Equipment." This M&TE calibration program will meet the requirements in NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of our standards to nationally recognized standards such as those from the National Institute of Standards and Technology (NIST); (4) maintaining calibration records. In addition, NP 13-1 and SP 13-1 identify requirements and appropriate forms for documenting and tracking sample possession.

6.3.1 Data Quality Control

Data collection procedures are specific to individual instruments. For details of the data acquisition for a particular instrument, see the specific SP or Users Manual for that instrument. A list of the relevant SPs is provided in Section 7.0. If no SP exists, or the analysis procedure listed in the SP is modified, the new procedure will be recorded in the scientific notebook. Any data acquired by a data acquisition system (DAS) will be attached directly to the scientific notebook or compiled in separate loose leaf binders with identifying labels to allow cross reference to the appropriate Scientific Notebook. If the instrument allows data to be recorded electronically, copies of the data disks will be submitted to the NWMP Records Center. For instruments that do not have direct data printout, the instrument readings will be recorded directly into the scientific notebook. Current versions of the DAS software will be included in the SNL WIPP Baseline Software List, if appropriate.

Quality control of the Scientific Notebooks will be established by procedures described in NP 20-2 "Scientific Notebooks." Methods for justification, evaluation, approval, and documentation of deviation from test standards and establishment of special prepared test procedures will be documented in the scientific notebooks. General procedures, goals and quality assurance controls for TP 00-06 are described below. Procedures including use of replicates, spikes, split samples, control charts, blanks and reagent controls will be determined during the development of experimental techniques as described in Section 5.1 above and documented in the scientific notebooks.

6.3.2 Data Acquisition Plan

The approach for collecting data varies for each instrument being used. Equipment data printouts will be attached directly to the scientific notebook or submitted to the SNL WIPP Record Center. For instruments that do not have direct data printout (balances, pH meters), the instrument reading will be directly recorded in the scientific notebook. The numerical data will be transferred from data printouts and scientific notebooks to Microsoft Excel (Office 97 version) spreadsheets. Data transfer and reduction shall be performed in such a way to ensure that data transfer is accurate, that no information is lost in the transfer, and that the input is completely recoverable. Data transfer and reduction shall be controlled to permit independent reproducibility by another qualified individual. A copy of each spreadsheet will be taped into the scientific notebook, and a second person will compare the data recorded in the notebook and that on the spreadsheet to verify that no transcription errors have occurred during technical and/or QA review of the notebook. This verification will be documented in the notebook when it is "signed off" by the reviewer.

6.3.3 Data Identification and Use

All calculations performed as part of the activities of TP 00-06 will be documented in a scientific notebook. The notebook will be technically reviewed periodically by a second person, who will note concurrence by co-signing the examined material. If a discrepancy is found, that discrepancy and its resolution will be documented in the notebook. In addition, there will be periodic quality assurance reviews of the notebook to ensure that the requirements of NP 20-2 "Scientific Notebooks" are addressed.

Data generated under this TP will be used to evaluate the casing corrosion and cement alteration models used in the CCA, and to develop a more robust borehole plug degradation model for conditions at the WIPP site.

6.4   Equipment

A variety of measuring and analytical equipment will be used for the work described in this test plan. This equipment includes that listed below, as well as equipment not yet identified. A complete, up-to-date, equipment list, including serial numbers, will be maintained in the scientific notebook. Scientific notebooks will be used to record all laboratory work activity.

Measuring and analytical equipment to be used for this project include:

6.4.1 Weighing Equipment.

Several balances are present in the facility and may be used for this project. These include a Mettler AT-261 five-decimal place electronic balance, an ANC three-decimal place balance, and top loading balances and scales with maximum ranges of 2 to 150 kilograms. Balance calibration checks will

be performed routinely using NIST-traceable weight sets, which are calibrated by the SNL Calibration Laboratory every 3 years. These weight sets include, but are not limited to, the following:

- *Troemner Calibration weight set*, ASTM Class 1, Serial number 22803, 1 mg – 100 g, calibration expires 12/16/02.

- *Troemner Calibration weight*, NBS-Class 1, Serial number 42795, 100 g, calibration expires 11/19/02.

- *Troemner Calibration weight*, NBS-Class 1, Serial number 42797, 100 g, calibration expires 11/19/02.

- *Troemner Calibration weight*, NBS-Class 1, Serial number 42799, 100 g, currently being re calibrated.

- *Troemner Calibration weight*, NBS-Class 1, Serial number 42800, 100 g, currently being recalibrated.

- *Troemner Calibration weight*, ASTM-Class 1, Serial number 47824, 200 g, calibration expires 11/19/02.

- *Troemner Calibration weight*, ASTM-Class 1, Serial number 55335, 1000 g, calibration expires 11/19/02.

- *Troemner Calibration weight*, ASTM-Class 2, Serial number I-12, 10 kg, calibration expires 12/17/02.

Balance accuracy and precision will be checked daily or prior to use (whichever is less frequent), using the calibration weight sets listed above. Calibration checks will be recorded in a scientific notebook.

6.4.2 Liquid Measuring Equipment

Standard Laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times. In addition, several adjustable Eppendorf pipettes are available for use in the laboratory. The calibration of pipettes will be checked routinely against a calibrated balance, and will be recorded in the scientific notebook.

6.4.3 Other Analytical Equipment

- *Glass and digital thermometers* – Solution and oven temperatures will be measured using either: 1) NIST-traceable liquid-in-glass or digital thermometers, calibrated on an annual or biannual schedule as determined by the calibration service provider; or 2) thermometers which have been calibration-checked against the NIST-traceable thermometers described above. Such calibration checks will be recorded in the scientific notebook.

- *pH Meters and Autotitrators* – solution pH may be measured using pH meters and/or autotitrators. The range for all pH meters is 0.00 to 14.00. Electrodes will be calibrated before each use or daily (whichever is less frequent) with pH 4, 7, and 10 buffers manufactured by Fisher Scientific with unique lot numbers and expiration dates; traceable to the National Institute of Standards and Technology (NIST). The accuracy of the buffers is

±0.01 pH units; buffer values will be adjusted for laboratory temperatures as per buffer instruction sheets if necessary. Calibration checks will be recorded in the scientific notebook.

- *Equipment for Chemical Analysis* – Several instruments may be used to chemically characterize crushed or digested samples of cement or brines. These include a Perkin Elmer Optima 3300 DV Inductively-Coupled Plasma Optical Emission Spectrometer (ICP); a Cary 300 UV-Visible Spectrophotometer; and a UIC, Inc. Carbon Analyzer, consisting of an acidification module, a furnace module, and a CO_2 coulometer. These instruments will be user-calibrated according to the manufacturers specifications each time they are used and the calibration documented in the scientific notebook. Other instruments may be used as required.

- *Equipment for Petrographic, and Textural Characterization* – Several instruments will be used for physical characterization of the cement samples. The mineralogy and texture may be characterized using either an Olympus BX60 Polarizing Microscope or a JEOL JSM 5900LV scanning electron microscope. Bulk sample mineralogy will be determined using a Bruker AXS D-8 Advance X-Ray Diffractometer.

NMWP Activity/project-Specific Procedures may be written for these instruments if necessary. Until that time, detailed procedure descriptions will be documented in laboratory notebooks.

6.5   Location and Personnel

All experimental work related to TP 00-06 will be performed at the SNL Carlsbad Operations laboratory facility located in Carlsbad, NM. Sandia Personnel, including but not limited to Charles Bryan, Yifeng Wang, and Huizhen Gao will carry out the work. Users of identified equipment have received appropriate training by virtue of advanced technical degrees and years of laboratory experience.

7.0   NUCLEAR WASTE MANAGEMENT QUALITY ASSURANCE PROGRAM PROCEDURES (NPS), AND NWMP ACTIVITY SPECIFIC PROCEDURES (SPS)

The following project documents cover the work described in this Test Plan.

NP 2-1 – *Qualification and Training.* Rev 5, effective date 10/28/02.

NP 4-1 – *Procurement.* Rev 4, effective date 03/01/02.

NP 6-1 – *Document Review Process.* Rev 3, effective date 02/15/02.

NP 9-1 – *Analyses.* Rev 4, effective date 08/29/01.

NP 12-1 – *Control Of Measuring And Test Equipment.* Rev. 3, effective date 11/06/02.

NP 13-1 – *Sample Control.* Rev 1, effective date 04/14/99.

NP 16-1 – *Corrective Action*. Rev 2, effective date 11/23/99

NP 17-1 – *Records*. Rev. 2, effective date 05/14/01.

NP 19-1 – *Software Requirements*. Rev 9, effective date 06/12/02

NP 20-2 – *Scientific Notebooks*. Rev 1, effective date 04/26/99.

SP 1-1 – *QA Grading*. Rev. 3, effective date 03/01/02.

SP 12-1 – *Use of Laboratory Balances and Scales*. Rev. 0, effective date 08/08/00.

SP 12-2 – *Use and Maintenance of the UIC, Inc. Model CM5014 CO_2 Coulometer, CM5130 Acidification Module and CM5120 Furnace Apparatus*. Rev 0, effective date 12/05/00.

SP 13-1 – *Chain of Custody*. Rev. 2, effective date 06/13/00.

TOP 544 – *Preparing Synthetic Brines for Chemical Retardation and Transport Experiments*. Rev 0, effective date 01/05/96.

Any revisions in the above technical work documents that occur during the course of this project will be implemented, and do not require modification of this test plan. Current versions of the documents listed above are maintained at the following SNL NWMP web site:

> http://www.nwmp.sandia.gov/onlinedocuments

In addition, procedures for use of the ICP, SEM, XRD, and UV-Vis spectrophotometer will be recorded in the scientific notebooks until such time as SP's are written for these instruments. Cement mixing and sample preparation procedures, which may vary from sample to sample as work scope evolves, will be detailed in Scientific Notebooks, in accordance with NP 20-2.

8.0   RECORDS, REPORTS, AND AUDITS

All records providing evidence of quality, including but not necessarily limited to personnel qualification and training forms, lists of M&TE and software, electronic data, technical procedures, laboratory notebooks, calibration records and certificates, and reports, will be QA records. These records will be maintained in accordance with NP 17-1, "Records." To the maximum extent possible, the format of the enclosed WIPP Records Package will be used to organize QA records. All records will be accurate, complete, identifiable, and legible, and will be inspected to ensure they satisfy these requirements prior to submittal to the SNL/WIPP Records Center. Two copies of all QA records will be submitted.

Documents will be prepared for review and approval in accordance with NP 6-1, "Document Review Process." NP 6-1 requires that the author(s) and reviewer(s): (1) use the DRC Form NP 6-1-1,

(see Appendix A in NP 6-1) in some, but not all, cases; (2) resolve all of the comments; (3) return this form with all signatures to the SNL/WIPP Records Center.

9.0   TRAINING

All personnel involved in the experiments described in TP 00-06 will be trained and qualified for their assigned work. This requirement will be implemented through NP 2-1 Qualification and Training. Evidence of training to assigned NPs, SPs, TOPs, TP 00-06, ES&H procedures, and any other required training will be documented through Form NP 2-1-1 *Qualification and Training Form*. Annual Refresher QA training will ensure on-site personnel are trained to the SNL/WIPP QA Program.

10.0   HEALTH AND SAFETY

All of the health and safety requirements relevant to the work described in TP 00-06 and the procedures that will be used to satisfy these requirements are described in a SNL ES&H standard operating procedure (SOP-C001, "Activities in the SNL/Carlsbad Laboratory Facility"). This document describes the hazards associated with these experiments and the procedures to deal with those hazards, including all the training requirements for personnel involved in conducting the experiments. In addition, a Radiological Work Permit (RWP-1617) and Radiological Work License (RWL 6000-16, "Use of the XRD Unit Located in the Carlsbad Laboratory Facility") covers activities involving use of the X-Ray Diffractometer. Additional SPs and RWPs may be mandated by SNL corporate ES&H requirements and their issuance will not require revision of this Test Plan.

11.0   PERMITTING/LICENSING

RWL and RWP documents are in place for use of the X-ray diffractometer in the Carlsbad Laboratory Facility. There are no other special licenses or permit requirements for the work described in TP 00-06.

12.0   REFERENCES

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