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Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis

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February 2003

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
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Abstract

CH2M HILL Hanford Group, Inc. is identifying and developing supplemental process technologies to accelerate the Hanford tank waste cleanup mission. Bulk vitrification, containerized grout, and steam reforming are three technologies under consideration for treatment of the radioactive saltcake wastes in 68 single-shell tanks. To support development and testing of these technologies, Pacific Northwest National Laboratory (PNNL) was tasked with developing a cold dissolved saltcake simulant formulation to be representative of an actual saltcake waste stream, preparing a 25-L batch of the simulant, and analyzing the composition of the batch to ensure conformance to formulation targets.

Lacking a defined composition for dissolved actual saltcake waste, PNNL used available tank waste composition information and an equilibrium chemistry model (Environmental Simulation Program [ESP™]) to predict the concentrations of analytes in solution. Observations of insoluble solids in initial laboratory preparations for the model-predicted formulation prompted reductions in the concentration of phosphate and silicon in the final simulant formulation. The analytical results for the 25-L simulant batch agree within the expected measurement accuracy (~10%) of the target concentrations and are highly consistent for replicate measurements, with a few minor exceptions. The instrumental analyses indicate that the batch of solution adequately reflects the as-formulated simulant composition.

In parallel with the simulant development effort, a nominal 5-M (molar) sodium actual waste solution was prepared at the Hanford Site from a limited number of tank waste samples. Because this actual waste solution was also to be used for testing the supplemental treatment technologies, the modeled simulant formulation was predicated on the composite of waste samples used to prepare it. Subsequently, the actual waste solution was filtered and pretreated to remove radioactive cesium at PNNL and then analyzed using the same instrumentation and procedures applied to the simulant samples. The overall agreement of measured simulant and actual waste solution compositions is better than ±10% for the most concentrated species including sodium, nitrate, hydroxide, carbonate, and nitrite. While the magnitude of the relative difference in the simulant and actual waste composition is large (>20% difference) for a few analytes (aluminum, chromium, fluoride, potassium, and total organic carbon), the absolute differences in concentration are in general not appreciable. Our evaluation is that these differences in simulant and actual waste solutions should have a negligible impact on bulk vitrification and containerized grout process testing, while the impact of the low aluminum concentration on steam reforming is yet to be determined.

Executive Summary

CH2M HILL Hanford Group, Inc. (CH2M HILL) is identifying and developing supplemental process technologies to accelerate the Hanford tank waste cleanup mission. Bulk vitrification, containerized grout, and steam reforming are three technologies under consideration for treatment of the radioactive saltcake wastes. To support development and testing of supplemental technologies, Pacific Northwest National Laboratory (PNNL) was tasked with developing a cold dissolved saltcake simulant formulation to represent an actual saltcake waste stream. Additionally, PNNL procured 25 L of the cold saltcake solution and analyzed samples to ascertain its conformance to formulation targets. The results are reported in this document. The measured simulant composition is also compared with an actual waste solution from which the simulant formulation was modeled.

During the execution of the simulant development task described here, an actual saltcake waste composite was prepared from numerous saltcake waste samples (from Hanford 241 S and U tank farms) and “retrieved” (dissolved in water) at the Hanford 222-S Laboratory to produce an actual saltcake waste solution nominally 5 M (molar) in sodium (Callaway 2002). Subsequently, this actual waste solution was delivered to the Radiochemical Processing Laboratory at PNNL to be filtered and to remove ^{137}Cs (cesium) by ion exchange and for analysis of the final solution composition.(a) To provide consistency between the actual waste and cold simulant solutions to be used in supplemental technology process tests, PNNL attempted to match the cold simulant solution composition to that of the actual waste solution. However, because the actual waste solution analyses were not available on the schedule required for cold simulant definition, the cold simulant composition was derived from a sample-based estimate of the actual waste composition.

The actual waste solution was prepared from the sample composite by adding water until the concentration of sodium in the resulting liquid in contact with solids was ~5 M (Callaway 2002). To match the cold simulant composition to the actual waste solution before analytical results were available, we predicted the composition using the following calculation scheme. First, we calculated the composition of the saltcake composite as a weighted average of the compositions of all the samples, weighting each composition by the mass of the sample that went into the composite. The sample compositions were taken from the Hanford Tank Waste Information Network Systems (TWINS) database. The calculated composite composition was used as an input to the Environmental Simulation Program (ESP™)(b) solution thermodynamic model, which predicted the phase distributions of the analytes and thereby the composition of the liquid.

(a) As described in a letter report by BM Rapko and TG Levitskaia, *Removal of ^{137}Cs from Dissolved Hanford Tank Saltcake by Treatment with IE-911.* TWS 03.030, February 2003, Pacific Northwest National Laboratory, Richland, WA. A final PNNL report describing the pretreatment process and containing the analytical results for the actual saltcake waste solution is expected in April 2003.

(b) ESP is a trademark of OLI Systems, Inc., Morris Plains, New Jersey.

The amount of water in the ESP input was varied until the program predicted a dissolved sodium concentration of 5 M in the liquid. The predicted liquid composition at that level of dilution was used as the cold simulant composition with the exceptions noted below.

The estimated composition of the composite of samples used to produce the actual waste solution was compared with the estimated composition for a blend of all the waste that could be retrieved by water dissolution from 68 Hanford single-shell tanks that are considered to contain predominantly saltcake waste. The compositions of the all-saltcake-tank blend and the more limited composite of samples were found to be comparable, indicating that the model simulant is likely representative of retrieved Hanford saltcake wastes.

The dissolved saltcake simulant formulation contains 5.0 M of Na, other metals (cations), inorganic anions, and organic components. The other metals, from most to least concentrated on a molar concentration basis, are aluminum, potassium, chromium, and nonradioactive cesium. The inorganic anions are dominated by nitrate followed by hydroxide, carbonate, nitrite, sulfate, phosphate, chloride, and fluoride. Organic constituents contributing to total organic carbon (TOC) are highly soluble acetate salts and lesser soluble oxalate salts.

The dissolved saltcake solution simulant formulation does not contain species predicted in very low concentrations (<0.001 M) except cesium. Exclusion of these minor constituents is not expected to have a significant impact on bulk vitrification and containerized grout processes. The concentrations of the key constituents (>0.001 M) match those obtained from the model predictions for the sample of dissolved actual waste composite described above with two notable exceptions. First, in deference to the great excess of silicon containing formers that would be added to bulk vitrification glass and containerized grout formulations, the relatively small quantity of silicon expected in the actual waste sample (~0.008 M Si) is omitted. Secondly, the simulant formulation includes 20% less phosphate than the model predicted solubility limit. Laboratory preparation of a cold simulant batch containing the full amount of phosphate resulted in a small amount of precipitate. Using Raman spectroscopy to analyze the solids, it appears that primarily the sodium fluoride-phosphate double salt [$Na_7F(PO_4)_2{\bullet}19H_2O$], and, to a lesser extent sodium oxalate, precipitated. The phosphate concentration was reduced to minimize the potential formation of the double salt.

Samples from a 25-L batch of cold dissolved saltcake solution prepared by NOAH Technologies Corporation (NOAH) according to the PNNL prescribed formulation were analyzed at PNNL to satisfy project quality assurance program requirements. To measure the concentrations of all analytes in the simulant solution, a suite of five of instrumental analyses was completed: inductively coupled plasma atomic emission spectrometry for metals; ion chromatography for inorganic anions (and oxalate); ion chromatography for organic acids (and fluoride); hydroxide titration; and hot persulfate method carbon analysis for total inorganic carbon (TIC, including carbonate) and TOC. The analyses comply with the Hanford Analytical Quality Assurance Requirements Document (HASQARD) and the relevant elements of American Society of

Mechanical Engineers (ASME) NQA-1 (Nuclear Quality Assurance) program. An independent analytical laboratory completed a second set of information-only composition analyses on a sample of the simulant as well.

For the majority of analytes, the analytical results for the simulant batch agree within the expected analytical measurement accuracy (~10%) of the target values and are highly consistent for replicate measurements. The discrepancy in the measured and target concentrations of TOC contributors (oxalate and acetate) is greater than 10% and the uncertainty in the results for these analytes is also greater than for most other species. While the uncertainty in the actual concentration of these individual species is high, direct-measurements of the TOC made at PNNL and the independent laboratory are within 1% and 7% of the target, respectively. The instrumental analyses indicate that the 25-L batch of solution adequately reflects the as-formulated simulant composition. Additionally, the formulation appears stable against precipitation at room temperature more than a month after preparation.

Using the same analytical procedures and instrumentation, the cold simulant solution composition measurements also agree significantly with those of the actual dissolved saltcake waste solution discussed above. For the majority of analytes in the two solutions, the measured concentrations agree to within ±10%, including the analytes with the highest molar concentrations (sodium, nitrate, hydroxide, carbonate, and nitrite). The most significant discrepancies (>20% difference) between the cold simulant liquid and the actual dissolved composite waste liquid are in the aluminum, chromium, fluoride, potassium, and TOC concentrations. The simulant is more concentrated than the actual waste in fluoride, potassium, and TOC, but less concentrated in aluminum and chromium.

Of these, the largest relative and absolute error was in the measured aluminum concentrations. The simulant solution at 0.058-M aluminum was only about one-fourth as concentrated as the actual waste solution (0.21 M). The discrepancy in these results may be traced to model input assumptions regarding the phase and associated solubility of aluminum. The form of aluminum in the waste solids was unknown, and the standard form of gibbsite, aluminum hydroxide, was assumed to dominate. It is quite possible that the aluminum hydroxide in the core composite was a more soluble crystalline form than the gibbsite phase used by the ESP model to estimate the simulant composition.

While model predictions may have contributed to discrepancies for a few analytes, the overall agreement of simulant and actual waste solutions is quite good, especially for the most concentrated species. Other factors, including alkali metal concentration changes in the actual waste solution due to ion-exchange processing and differences in dilution of simulant and actual waste solutions, help explain the less significant differences in the majority of species. A reported Na concentration for the actual waste solution (5.10 M) is ~2% higher than the 5.0-M Na target, whereas the simulant measurement (4.75 M Na) is ~5% lower than formulated. The

~7% difference in Na concentration in the two solutions is attributed to the effects of water dilution.

While the magnitude of the relative difference in the simulant and actual waste composition is large for a few analytes, the absolute differences in concentration are, in general, not appreciable. Our evaluation is that these differences should have a negligible impact on bulk vitrification and containerized grout supplemental treatment process testing. The impact of the low aluminum concentration on the steam-reforming product, which, like the other supplemental technologies, is prepared with an excess of aluminum-containing compounds, is yet to be determined.

Acknowledgments

The authors would like to thank other individuals who have contributed to the success of this project. Many Hanford Site staff provided significant technical expertise related to waste chemistry and the supplemental technology processes for which the dissolved saltcake simulant was developed. Dan Herting of Fluor Hanford and Mike Johnson of CH2M HILL reviewed and provided insightful comments on the simulant formulation early on. Several PNNL staff were consulted for their expertise in waste process technologies and waste forms including Larry Bagaasen and Jeff Serne for grout, John Vienna and John Tixier for vitrification, and Pete McGrail for steam reforming. Brian Rapko graciously provided actual waste data for comparison to the simulant composition and technical review of this report. We thank Sheila Bennett for her valuable editorial support on a tight schedule. We also appreciate the effort of Kerry Cullerton for her help in procuring a batch of simulant from NOAH Technologies Corporation and Kelly Sellers, Chief Chemist at NOAH, for his responsiveness and insights to simulant batch preparation.

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1.0 Introduction

CH2M HILL Hanford Group, Inc. (CH2M HILL) is identifying and developing supplemental process technologies to accelerate the tank waste cleanup mission. A range of technologies is being evaluated to allow disposal of Hanford waste types, including transuranic wastes and low-activity saltcake wastes. Bulk vitrification, containerized grout, and steam reforming are three technologies under consideration for treatment of the radioactive saltcake wastes. To develop and test these technologies, both actual and nonradioactive (cold) simulated waste samples are needed. In support of CH2M HILL's effort to develop supplemental technologies, Pacific Northwest National Laboratory (PNNL) was tasked with developing a cold dissolved saltcake solution simulant formulation to be representative of an actual waste stream expected to be ~5 molar (M) in sodium (Na).[a] Additionally, PNNL procured a 25-L batch of the simulant and analyzed samples of the batch for comparison to formulation targets.

In parallel with the simulant development effort, about 5 L of nominally 5-M Na actual waste solution was being prepared at Hanford (Callaway 2002). The analytical results of this actual waste solution composition were not available at the time a simulant recipe was needed to meet project schedules. Therefore, it was necessary to estimate the dissolved saltcake simulant formulation independently using available saltcake waste composition information and a solution thermodynamic equilibrium model. By matching the simulant composition to that predicted for an actual waste composite, the supplemental treatment process vendors should be able to tune their formulations and processes using readily available simulant. They can thereby maximize the use of the limited amount of actual waste sample for the critical performance tests and demonstrations.

The Hanford Tank Waste Information Network System (TWINS) database, in May 2002, indicated that 68 single-shell tanks (SSTs) contained 50,000 gallons or more of saltcake waste. Wastes in these tanks are considered candidates for treatment by supplemental technologies (Gasper et al. 2002). The composition of dissolved saltcake waste that a supplemental treatment process such as bulk vitrification, containerized grout, or steam reforming would receive during operation could vary significantly. Factors affecting the waste composition include the contents of the source waste tank(s), the extent to which a given tank has been retrieved (i.e., varied composition during retrieval due to "selective dissolution" and waste heterogeneity in tanks), and the extent of waste blending or mixing in a process feed tank (e.g., a double-shell tank). Three main approaches were considered for defining the composition of a dissolved saltcake simulant:

(a) At the time the dissolved saltcake simulant was developed, bulk vitrification and containerized grout technology vendors were thought to be the primary recipients of this simulant. Therefore, the requirements and potential impacts of the simulant formulation on these two technologies were considered prominently during development. In as much as the simulant is representative of an actual saltcake waste stream, it should also be suitable for steam reforming process testing.

- Assuming a blend of the readily retrieved waste from all 68 saltcake waste SSTs
- Assuming a blend of the readily retrieved waste from the smallest subset of saltcake waste tanks containing 50% of the total sodium inventory (21 SSTs)
- Assuming a blend of a limited number of waste tank samples (e.g., the samples used in an actual waste composite).

The total blend of the saltcake waste inventory represents a nominal or typical waste composition. In practice, it is unlikely that a treatment process will receive a waste blended to this extreme. It is more likely that the process feed will be a blend of waste from one or a limited number of tanks. Therefore, a simulant formulation based on a more limited number of waste tank samples is also representative. This is especially true if the species concentrations for the limited waste blend are not grossly different than the nominal composition expected from the all-tank blend.

The approach selected was to match the simulant composition to that expected from the dissolution of a composite of actual saltcake waste samples that was prepared at the 222-S Laboratory (Callaway 2002). The nominally 5-M Na actual waste solution was derived from numerous samples from Hanford tanks 241-S-101, S-109, S-110, S-111, U-106, and U-109. The solution prepared from the composite was transferred to PNNL for filtration and Cs removal in preparation for eventual delivery to bulk vitrification and containerized grout vendors for testing. Preliminary analytical results for this decontaminated (pretreated) actual waste solution are now available for comparison to the target simulant formulation and the equivalent analytical measurements for samples of the 25-L simulant batch.

The PNNL estimates of the composition of the liquid produced by dissolving the actual saltcake waste composite are discussed in Section 2, and the basis for the cold simulant recipe is given. The simulant composition, derived from the waste composite, was found not to be significantly different from the estimated composition for the nominal all-tank blend. Section 3 gives the final simulant formulation and preparation procedure. This section also includes observations made during the preparation of small simulant batches in the laboratory, which led to slight modifications of the simulant recipe. The results of instrumental analyses completed on samples of the 25-L simulant batch are given in Section 4, where related quality assurance (QA) topics also are discussed. Section 5 briefly compares the measured analyte concentrations of the pretreated actual waste and simulant solutions. A few apparent differences in the actual waste and simulant are discussed. Section 6 contains the cited references. Additional documentation is included as an appendix.

2.0 Basis of Simulant Composition

PNNL considered several different approaches to defining a "cold" simulant for retrieved saltcake waste. The initial approach involved estimating the concentrations of species that would be retrieved, together with sodium, by water—dissolving the inventories of sodium salts in the 68 SSTs defined as saltcake tanks and considering different blends of these retrieved saltcake liquids. The final simulant definition was based on the composition estimated for an actual saltcake waste composite that was prepared and retrieved (dissolved in water) at the 222-S Laboratory.

Certain constraints were placed on the cold simulant composition by the needs of the processes that were to use the simulant for tests. These constraints are described in Section 2.1. The initial approach to defining the simulant, which was based on retrievable inventories of salts, is discussed in Section 2.2. Section 2.3 sets forth the manner in which the waste composite was used as the basis for the final simulant.

2.1 Constraints on Simulant Composition

For the bulk vitrification process, Na, sulfate (SO_4), phosphate (PO_4), halides, radioactive cesium (Cs) and technetium (Tc), and soluble transuranic (TRU) species are the primary species of concern. The concentration of SO_4 is considered more important than that of PO_4, except at atypically high concentrations of phosphorus. Of the species listed above, the halides, Cs, and Tc were considered unimportant for crucible tests because such tests would not well characterize their disposition (e.g., relative amounts retained and vaporized) in an actual process. A minimum concentration of 0.025 M SO_4 was required, with 0.1 M SO_4 being considered desirable.[a]

The containerized grout tests require sufficient concentrations of NO_3 and NO_2,[b] with

$$(NO_3+NO_2) > 0.1 \text{ M}$$
$$NO_2 > 0.01\text{M}$$

The concentrations of aluminum (Al) and silicon (Si) in the simulant were not of concern for either of these processes because of the large amounts of these species in the glass-former and grout feeds.

CH2M HILL has set maximum concentration limits for the component concentrations in the dissolved saltcake waste used in process studies. These limits are expressed in terms of the

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[a] Personal communication from JD Vienna, PNNL, September 4, 2002.

[b] Personal communication from LM Bagaasen, PNNL, August 28, 2002, and RJ Serne, PNNL, August 30, 2002.

maximum ratio of the species to Na.[(a)] At the standardized sodium concentration of 5-M Na, the maximum acceptable concentration limits for the major species are as stated in Table 2.1.

Table 2.1. Maximum Acceptable Concentrations in Dissolved Saltcake Waste

Species	Maximum Species Molarity
Al^{+3}	1.07
Ca^{+2}	0.0101
Cl^{-}	0.162
CO_3^{-2}	1.03
Cr (total)	0.049
F^{-}	0.575
Fe^{+3}	0.00448
K^{+}	0.0454
Mn^{+4}	9.25×10^{-4}
Ni^{+2}	0.00367
NO_2^{-}	1.57
NO_3^{-}	4.58
OH^{-}	4.16
Pb^{+2}	5.00×10^{-4}
PO_4^{-3}	0.91
Si^{+4}	0.0288
SO_4^{-2}	0.339
Sr^{+2}	8.45×10^{-4}
TOC	0.73
^{137}Cs	8.78×10^{-5} Ci/L
^{99}Tc	2.84×10^{-5} Ci/L

2.2 Initial Simulant Definition (inventory-based)

As an initial approach to defining the cold saltcake simulant, PNNL estimated a composition for the average waste liquid that could be produced by using water to dissolve the waste from some or all of the 68 saltcake SSTs. The starting point was data from the Best Basis Inventories (BBIs) for the tanks, downloaded from TWINS on May 13, 2002.

(a) Information included in three CH2M HILL documents: (a) Request for Proposal Number 93505, Bulk Vitrification, Statement of Work, Attachment B, Tables TS-2.1; (b) Request for Proposal Number 94427, Supplemental Technology – Containerized Grout, Section C, Tables TS-2.1; and (c) Statement of Work Number 95311, Steam Reforming.

A standardized procedure was used to determine the fraction of each BBI species in each tank that was in the liquid and solid phases. These calculations depended on the assumption that, of the four BBI species, potassium (K), chloride (Cl), nitrite (NO_2), and ^{137}Cs, at least one was present only in the liquid and could therefore serve as a tracer to calculate the amount of liquid in the tank inventory. The dissolved concentration of the tracer, $x_{T,L}$, expressed as μg of species per mL of liquid, was taken from the BBI data on TWINS on September 12, 2002. This tracer concentration in the liquid and the bulk concentration of the tracer, $x_{T,a}$, expressed as μg of species per g of bulk waste, were used to calculate the average liquid volume per unit mass waste, ω_L, in the inventory.

$$\omega_L = x_{T,a} / x_{T,L} \tag{2.1}$$

The liquid volume per mass waste was then used with the liquid and bulk concentrations of the non-tracer species to calculate the phase distribution of each. The phase distribution of all species provided the basis for a calculation of the solid-phase composition. The comparative merits of the results from each candidate tracer (K, Cl, NO_2, and ^{137}Cs) were judged by performing a mass balance on the calculated dry-solids composition. The tracer that produced the best mass balance was chosen as the final basis of the phase distribution fractions for all species. A deviation of less than 10% from a mass balance of 1.0 was considered good.

The phase distribution fractions were then used to estimate what fraction of each BBI species in each tank could be retrieved by water dissolution. It was assumed that the dissolution of saltcake wastes would continue until all the sodium salts had dissolved, including any sodium oxalate (C_2O_4), and that the resulting liquid would be retrieved. The following rules were applied to estimate the fraction of the tank inventory of each species that could be retrieved by water dissolution:

- Al: 90% of the Al initially present in the liquid and none of the Al initially present in the solid is retrieved by water
- Bismuth (Bi), calcium (Ca), Cr, Cs, iron (Fe), lanthanum (La), manganese (Mn), nickel (Ni), lead (Pb), U: only the mass of species that is initially in the liquid is retrieved
- Cl, carbonate (CO_3), fluoride (F), K, Na, NO_2, nitrate (NO_3), PO_4, SO_4, total organic carbon (TOC): all the species are retrieved
- Si, zirconium (Zr): 50% of the species initially present in the solid, and all of the species initially present in the liquid, is retrieved by water dissolution
- Strontium (Sr): 15% of the Sr initially present in the solid, and all of the Sr initially present in the liquid, is retrieved by water dissolution.

These rules were based on the results from modeling S-112 and U-107 water-only dissolution retrieval using Version 6.5 of the solution thermodynamics program ESP$^{TM(a)}$ with the XBASE and PUBLIC databases (OLI 1998).

The method just outlined was used to calculate the extent to which species could be retrieved by water dissolution for 67 of the 68 saltcake SSTs. (Tank SX-109 BBI lacked liquid concentration data, so the method could not be applied.) In the cases of Tanks A-101, AX-101, BY-112, S-101, S-105, and S-111, the BBI had been updated since May 13, 2002. Thus the phase distribution fractions calculated here were out-of-date with the current BBI. This is unlikely to introduce any great error into the determination of the retrievable SST liquid composition.

The May 2002 phase distribution fractions were combined with the BBIs (current as of September 12, 2002) to calculate the mass of each species' inventory that would be retrieved by dissolution with water. The retrieved inventories were converted to moles. The product of this process was 67 sets of retrievable liquid inventories, including those for Al, Bi, Ca, Cl, CO_3, Cr, F, Fe, Hg, K, La, Mn, Na, Ni, NO_2, NO_3, free OH, PO_4, Si, SO_4, TOC, U, Zr, ^{137}Cs, ^{90}Sr, and ^{99}Tc.

Summing up all 67 inventories for each species gave the total retrievable inventory in moles for the saltcake SSTs. Another total was calculated for each species over the smallest subset of the 67 tanks that, taken together, contained 50% of the Na in the 67-tank set. These 100%-Na and 50%-Na inventories of species were then scaled to molar concentrations on the assumption that in each case the Na concentration would be reconcentrated to 5 M, with all other species scaled proportionally. Note that after retrieval and reconcentration, some species reprecipitate, notably oxalate, fluoride, phosphate, and aluminum. So the fact that a species was retrieved in liquid does not mean that it is still dissolved when blended in the receiving DST or when subsequently concentrated to 5 M Na.

Table 2.2 shows the BBI nonradioactive (cold) species concentrations (scaled to 5 M Na) contained in the 100% Na and the 50% Na retrievable saltcake waste products. These saltcake products include not only the liquid but also the solids that may be created by blending and reconcentration. All of the cold concentrations are below the maximum limits set in Table 2.1. The Si concentration is closer to its limit than any of the other nonradioactive species.

The radioactive species ^{137}Cs and ^{99}Tc are also included in the table, though these will not be present in the cold simulant. The ^{137}Cs and ^{99}Tc concentrations are above the maximum limits, consistent with the already recognized need for pretreatment to remove these species.

(a) ESP (the Environmental Simulation Program) is a trademark of OLI Systems, Inc., Morris Plains, New Jersey.

Table 2.2. Estimated Composition of Saltcake Product Retrieved by Water Dissolution

Analyte	**Concentration in mol/L (M)** **SST saltcake product when 50% of Na is retrieved** [(a,b)]	 **SST saltcake product when 100% of Na is retrieved**[(a)]
Al	0.19	0.23
C_2O_4	0.033	0.049
CO_3	0.41	0.39
Cl	0.040	0.048
Cr	0.0096	0.0094
F	0.071	0.120
K	0.019	0.021
Na	5	5
NO_2	0.36	0.43
NO_3	2.85	2.52
PO_4	0.10	0.13
Si	0.021	0.022
SO_4	0.11	0.11
soluble TOC	0.072	0.086
^{137}Cs	0.038 Ci/L	0.045 Ci/L
^{99}Tc	3.5×10^{-5} Ci/L	4.4×10^{-5} Ci/L

(a) All concentrations include both solid and liquid phases and are based on the estimated tank inventories that can be retrieved by water dissolution alone, with concentrations scaled to a 5 M Na concentration. The saltcake tanks include 67 of the 68 listed in Table D-1 of Gasper et al. (2002). Only SX-109 is excluded.

(b) The tanks that contribute to this waste are the 21 saltcake SSTs with the highest Na BBIs: S-112, TX-113, TX-112, A-101, S-109, TX-105, TX-115, TX-116, S-108, BY-105, TX-114, SX-103, S-105, AX-101, BY-106, U-108, BY-101, S-106, BY-112, TX-110, and TX-117.

2.3 Final Simulant Definition (waste composite)

The initial PNNL approach to simulant definition (as described in Section 2.2) was changed because of the need for the cold simulant to be consistent with the "hot" saltcake solution that was being prepared for waste treatment process testing. The 222-S Laboratory made a bulk waste composite that was a mixture of saltcake material from a number of core samples taken from tanks in the S and U farms. The saltcake solution that was to be used for supplemental treatment process testing purposes was prepared from this saltcake waste composite by adding water until the concentration of sodium in the resulting liquid was nominally 5 M.

The 222-S Laboratory provided a list of the samples that were used in the composite and a description of the method by which the composite was prepared.[(a)] This list is slightly different from that in the Test Plan (Callaway 2002) because not all the core samples listed in the Test Plan were needed to provide the desired quantity of solution with 5-M Na concentration. Table 2.3 shows the amount of each core sample that was used. The italicized samples are those for which no composition data were found in TWINS.

The listed samples were combined and mixed. Enough water was added to produce 5.1 L of supernatant above the remaining solids. At this point the sodium concentration in the liquid was higher than desired, so a further 0.7 L of water was added. This last dilution produced a measured sodium concentration of 5.10 M Na in the liquid. (The analysis results are given in Table 5.1 and are discussed in Section 5.)

To define the cold simulant composition that would match the composition of the 222-S saltcake solution before obtaining analytical results for the actual hot liquid, PNNL predicted the composition using the following calculation scheme.

First, the composition of the bulk saltcake composite was calculated as a weighted average of the compositions of all the core samples that were used, weighting each composition by the mass of the sample that went into the composite. The sample compositions were taken from the Hanford TWINS database. The few samples for which no TWINS data were available were treated as having the weighted-average composition of the rest of the samples from the same tank.

Constituent concentration measurements that were below the minimum detection limit (MDL) were treated as equal to the MDL in generating the weighted averages. When a constituent was measured by more than one method (for example, by acid prep and fusion prep), and both values were above the MDL, the larger of the values was used. When both were below the MDL, the smaller MDL was used. Where there were no data for a constituent, the tank average concentration derived from the BBI was used.

The calculated composite composition was used as an input to the ESP code. Most of the measured species concentrations could be used as ESP model inputs without any modification. The exceptions were chromium and TOC, because in both of these the soluble and insoluble fractions of the constituents had to be distinguished from one another in the ESP inputs. The phase distribution fractions were calculated (using the method described in Section 2.1) on the basis of the weighted-average composition of all the samples from each tank. In other words, the

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(a) October 22, 2002, personal communication, e-mail, from JN Appel to SD Rassat, containing the spreadsheet “MAI Sample 1 Composite-Final.xls.”

Table 2.3. Samples Used in the 222-S Saltcake Composite

Sample	**Jar No.**	**g**	**Sample**	**Jar No.**	**g**
S-101-142:01	15923	128.3	S-111-149:07-LH	10549	89.3
S-109-158:01-UH	10678	59.3	S-111-149:08-UH	10550	85.0
S-109-158:01-LH	10679	33.1	S-111-149 composite	19324	15.1
S-109-158:03-UH	10639	45.3	*S-111-150:02-UH*	*16517*	*85.1*
S-109-158:03-UH	10640	25.1	*S-111-150:03B*	*10586*	*11.5*
S-109-158:04	10684	20.1	*S-111-150:03C*	*10511*	*22.7*
S-109-158:02A-LH	10674	11.3	S-111-237:05-UH	14440	105.0
S-109-158:02B-UH	10507	17.3	S-111-237:05-LH	14443	39.9
S-109-158:02B-LH	10509	9.5	S-111-237:07-LH	14233	90.7
S-109-158:03A-LH	10683	72.0	S-111-237:07-UH	14236	116.4
S-109-158 composite	*18601*	*14.7*	S-111-237:09-UH	14231	111.2
S-109-160:01	10337	8.2	S-111-237 composite	14970	79.1
S-109-160:02	10641	19.3	U-106-147:02-UH	10313	16.9
S-109-160:02B-LH	10675	19.3	U-106-147:02-UH	16974	78.7
S-109-160:02B-UH	10676	9.0	U-106-147:03-UH	10457	39.5
S-109-160 composite	*18653*	*13.4*	U-106-147:03-LH	10458	67.1
S-110-140:01-UH	9902	59.4	U-106-147:03-LH	16662	81.0
S-110-140:01-LH	9903	82.6	U-106-147:03-UH	16910	54.9
S-110-140:02-LH	16924	82.5	U-106-147:04-LH	10459	80.8
S-110-140:02-UH	9904	106.9	U-106-147:04-UH	10460	72.2
S-110-140:02-LH	9905	86.1	U-106-147:04-UH	16978	83.1
S-110-140:03-UH	15575	76.9	U-106-147:04-LH	17029	41.0
S-110-140:03-UH	9906	113.7	U-106-147:05-UH	10461	73.6
S-110-140:03-LH	9907	86.6	U-106-147:05-LH	10462	3.5
S-110-140:04-UH	9908	25.3	U-106-147:05-UH	16672	55.3
S-110-140:04A	9909	46.1	U-106-148:04-UH	10467	70.7
S-110-140:04B-UH	9809	34.2	U-106-148:05-UH	10469	85.0
S-110-140:04C	10202	22.6	U-106-148:05-LH	10470	56.3
S-111-149:04-LH	10506	106.5	*U-109-124:03*	*9154*	*55.3*
S-111-149:05-UH	10333	117.2	U-109-124:04	9155	50.1
S-111-149:06-UH	10546	105.7	U-109-124:05-UH	9157	57.4
S-111-149:06-LH	10547	93.2	U-109-124:07-LH	9160	108.6

composition of a sub-composite was calculated for each tank, based on the amounts of samples taken from that tank, and the distribution fractions for soluble/insoluble Cr and soluble/insoluble TOC were calculated on this basis. These distributions were carried through to the total composite by calculating the total composite distribution as the weighted average of the tank sub-composites' distributions. Soluble TOC was treated as acetate for simulant purposes; insoluble (i.e., not initially dissolved) TOC was treated as oxalate; soluble Cr was treated as chromate ion, and insoluble Cr as Cr(III).

The WaterAnalyzer module of the ESP solution thermodynamics model (version 6.5) was used with the LAB, PUBLIC, and XBASE databases to calculate the composition of the supernatant liquid at the point when enough water had been added to the composite to give the liquid a sodium concentration of 5.0 M Na. The ESP-predicted liquid composition was used as the initial attempted composition for the cold simulant liquid.

Table 2.4 compares the bulk 222-S waste composite with the saltcake product formed by a blend of waste from the 67 saltcake SSTs (Table 2.2). Both materials are scaled to 5 M Na. The total 222-S bulk composite is nearly comparable in its basis to the SST saltcake product. The difference in basis is that the 222-S composite includes both the water-retrievable and non-retrievable fractions of all species, while the SST saltcake product contains only the water-retrievable fractions. This difference in basis accounts in part for the higher content of Al and Cr in the 222-S composite reported in the table. While the tabulated 222-S composite composition includes all the Al and Cr in the composite, the tabulated SST saltcake product includes only the Al and Cr that were initially present in the liquid in the SST. Al and Cr in the SST solids were not considered to be retrieved, so the SST saltcake product composition excludes Cr(III).

The 222-S composite can also be seen to contain more CO_3 and soluble TOC than the retrievable saltcake product. The 222-S composite contains less C_2O_4, Cl, F, K, PO_4, Si, and SO_4 than the retrievable saltcake product. The differences in concentration are particularly large for F, K, Si, and PO_4.

The table also includes two ESP-modeled liquids, one the 222-S saltcake solution produced by adding water to the 222-S composite until a 5 M Na concentration is reached, the other a solution produced by similarly adding water to the SST saltcake product. These two liquids are by definition both on a "water-retrievable" basis. Of the species considered important to waste treatment processes (Section 2.1), the 222-S composite solution is lower in fluoride and sulfate and higher in chloride and phosphate than the SST saltcake product solution. Nitrate, nitrite, and chromium are at similar concentrations in the two solutions.

The insoluble species (Bi, Ca, Fe, Mn, Ni, Pb, U, and Zr) are negligibly present in the liquids. Some other species also appear as precipitate: Al, C_2O_4, F, Na, PO_4, and Si. It should be noted that these latter components are the species that can be brought over in dissolved form during retrieval, then reprecipitate as a result of blending or reconcentration.

Table 2.4. Comparison of Simulant Liquid with Retrievable Saltcake Product

Analyte	Concentration in mol/L			
	Total 222-S composite[(a)]	ESP-modeled 222-S dissolved composite liquid[(b,c)]	SST saltcake product when 100% of Na is retrieved[(d)]	ESP-modeled liquid from dissolved 100% Na saltcake product[(b)]
Al	0.29	0.064	0.23	0.042
Bi	0.0002	-- 0 --		
C_2O_4	0.037	0.012	0.049	0.014
CO_3	0.47	0.48	0.39	0.40
Ca	0.0086	-- 0 --		
Cl	0.043	0.044	0.048	0.032
Cr	0.069	0.010	0.009	0.0097
F	0.036	0.032	0.120	0.078
Fe	0.011	-- 0 --		
K	0.012	0.012	0.021	0.022
Mn	0.0036	-- 0 --		
Na	5.01	4.98	5	4.77
Ni	0.0010	-- 0 --		
NO_2	0.42	0.42	0.43	0.44
NO_3	2.47	2.51	2.52	2.60
free OH		0.44		0.30
Pb	0.00031	-- 0 --		
PO_4	0.075	0.062	0.13	0.045
Si	0.0082	0.0083	0.022	0.019
SO_4	0.088	0.090	0.11	0.12
Soluble TOC	0.26	0.26	0.086	0.12
U (total)	0.0009	-- 0 --		
Zr	0.00034	-- 0 --		

(a) Bulk 222-S composite values were calculated by taking a mass-weighted average of the composition of the samples in the composite and scaling them to a 5 M Na concentration. This scaled composite includes both retrievable (relatively soluble) and nonretrievable (insoluble) species.

(b) Bulk composite concentrations were used as inputs to the ESP model (version 6.5 with PUBLIC, LAB, and XBASE databases). The soluble Cr was modeled as CrO_4^{-2} and the soluble TOC as acetate. Values in this column are model-predicted concentrations of species in the liquid only. Solids $Al(OH)_3$, $Na_2C_2O_4$, $Na_7F(PO_4)_2.19H_2O$, and $NaAlSiO_4$ were predicted to precipitate.

(c) The decantable liquid created by diluting the composite to 5 M Na amounted to a total of 6.6 L.

(d) All concentrations include both solid and liquid phases and are based on the estimated tank inventories that can be retrieved by water dissolution alone. Concentrations are scaled to 5 M Na concentration. Saltcake tanks include 67 of the 68 listed in Table D-1 of Gasper et al. (2002) Only SX-109 is excluded.

The ESP prediction of the dissolved aluminum contains significant uncertainty because the exact form of the aluminum in the waste solids is not well known. Boehmite (AlOOH) has been observed in S-101 solids (Rapko and Lumetta 2000), but other forms of precipitated aluminum have also been observed in saltcake waste, these being aluminosilicates and hydrated aluminum oxides. Other observed forms of precipitated aluminum in tank wastes include gibbsite and nordstrandite, which are different crystalline forms of $Al(OH)_3$, as well as amorphous $Al(OH)_3$. All of these precipitates exhibit different aluminum solubilities. In the temperature range below 100°C, the only solids modeled by ESP are gibbsite and the simplest aluminosilicate, $NaAlSiO_4$. The solubility of gibbsite is lower than that of other forms of aluminum hydroxide that can exist in tank waste.

Another aspect of aluminum chemistry that makes it difficult to verify ESP predictions against measured concentrations is that aluminum dissolution and precipitation reactions, especially the latter, are slow at room temperature. Aluminum that is subjected to precipitation-causing conditions may take days or weeks to reach the final low solubility associated with gibbsite, so that analyses that are carried out before equilibrium show higher concentrations of dissolved aluminum than are predicted by ESP. In fact, the composite saltcake solution, when prepared, was measured as having a higher dissolved aluminum concentration than was predicted by ESP These differences are discussed further in Section 5.

3.0 Simulant Formulation, Preparation Procedure, and Laboratory Evaluations

Several 1-L batches of simulant of varying formulation were prepared and evaluated in the laboratory using simulant compositions described in Section 2 as a basis. The composition of the simulant evolved as a result of several factors: 1) a decision was made to try to match an actual waste composite of a limited number of tank samples instead of representing a blend of all salt-cake SSTs (see Section 2); 2) our understanding of the samples used in the actual waste composite changed over time; and 3) solids precipitation was observed in laboratory batches of some formulations. This section discusses the laboratory evaluations, including Raman spectroscopic analysis of precipitated solids, leading to modification of the simulant composition. The final simulant formulation and method of preparation are also described.

3.1 Laboratory Evaluations Leading to Final Simulant Composition

Table 3.1 summarizes the concentrations of analytes in the dissolved saltcake solution simulant. These concentrations match those shown in Table 2.4 for the ESP-modeled 222-S dissolved composite liquid, with a few notable exceptions, as discussed below. Except for cesium, the simulant formula contains no species predicted in very low concentrations (<0.001 M).

Generally speaking, exclusion of the minor constituents is not expected to have a significant effect on bulk vitrification, containerized grout, and steam reforming processes. A possible exception is the lack of soluble technetium (pertechnetate, TcO_4^{4-}). Radioactive pertechnetate is a potentially volatile and mobile species that could affect processing and/or waste form performance. Perrhenate (ReO_4^{4-}), a possible nonradioactive surrogate for pertechnetate, might be difficult to detect chemically in very low concentrations. Spiking the simulant with appropriate concentrations of radioactive pertechnetate or nonradioactive perrhenate is an option considered for supplemental technology process testing. Table 2.2 shows the estimated concentrations of ^{99}Tc and ^{137}Cs for blended saltcake waste.

The concentrations of the key constituents shown in Table 3.1 match those obtained from the model predictions for the sample of dissolved actual waste composite with two primary exceptions. First, in deference to the great excess of silicon containing formers that would be added to bulk vitrification glass and containerized grout formulations, the relatively small quantity of silicon expected in the actual waste sample (~0.008 M Si) is omitted. Additionally, early laboratory preparations including Si (added as silica, SiO_2, or hydrated sodium metasilicate, $Na_2SiO_3•9H_2O$) resulted in a significant amount of insoluble species. The Si-containing species were assumed to contribute to the insoluble solids. Secondly, the formulation in Table 3.1 includes 20% less phosphate (0.049 M) than the model predicted solubility limit (0.062 M) for the composite of actual waste samples. To maintain the Na concentration at 5 M with a reduced

Table 3.1. Cold Dissolved Saltcake Solution Simulant Analyte Concentrations

Metals	**Concentration (M)**
Al	0.0637
Cs(a)	5.1E^{-08}
Cr	0.0104
K	0.0124
Na	5.00
Anions/Other	**Concentration (M)**
Cl	0.0438
CO_3 (or TIC)(b)	0.475
F	0.0316
NO_2	0.424
NO_3	2.51
PO_4	0.0492
SO_4	0.0900
C_2O_4 (oxalate)	0.0118
Other TOC (as carbon, from acetate)	0.263
TOC total(c)	0.287
OH Total	0.740
Free OH	0.485

(a) The concentration of cold Cs in the simulant is based on the estimated concentration of ^{137}Cs in the actual waste solution prior to ion exchange and then reduced by a factor of 100, accounting for a conservatively low ion exchange decontamination factor. Because of the very low Cs chemical concentration in the simulant solution, its concentration in simulant batch preparations is estimated by formulation. Analysis of ^{137}Cs in the actual waste solution is possible because radiochemical methods (e.g., GEA) are highly sensitive.

(b) In the simulant solution preparations, ion chromatography or, alternatively, a total inorganic carbon (TIC) analysis will be used to determine carbonate.

(c) For the simulant, TOC can be calculated from the analysis of TOC contributors oxalate and acetate, or it can be measured directly with a TIC/TOC analysis.

quantity of phosphate (added as a sodium salt), a corresponding increase was made in sodium hydroxide concentration. This resulted in a free hydroxide concentration in the simulant of 0.48 M compared with 0.44 M predicted for the higher phosphate level shown in Table 2.4.

Laboratory preparation of a cold simulant batch containing the higher amount of phosphate (~0.06 M) resulted in a small amount of precipitate. Using Raman spectroscopy to analyze the solids, it appeared that primarily the sodium fluoride-phosphate double salt [$Na_7F(PO_4)_2{\cdot}19H_2O$], and to a lesser extent sodium oxalate precipitated. Raman measurements were made using an Inphotonics® Raman Spectroscopy System with a 150-mW, 670-nm laser. Raman measurements were run directly on a small quantity of filtered solid sample and were an average of 10 acquisitions of 0.2 second each. Figure 3.1 contains Raman spectra of the precipitate isolated from the higher-phosphate formulation, along with standard spectra of solid samples of pure sodium nitrate ($NaNO_3$), sodium oxalate ($Na_2C_2O_4$), and the sodium fluoride-phosphate double salt. Qualitatively, all the peaks observed in the precipitate spectrum can be assigned primarily to the three pure components displayed in Figure 3.1.

The precipitate spectrum is shown in Figure 3.2 with all the relevant bands assigned to the three components $NaNO_3$, $Na_2C_2O_4$, and $Na_7F(PO_4)_2{\cdot}19H_2O$. Figure 3.3 is a fit of the precipitate spectrum using a weighted sum of the spectral intensities (Raman responses) of the three pure spectra shown in Figure 3.1. The weights of the pure spectra were chosen to qualitatively match the precipitate spectrum with the calculated spectrum; the weighted values for the pure spectra are 85% $Na_7F(PO_4)_2{\cdot}19H_2O$, 9% $NaNO_3$, and 7% $Na_2C_2O_4$. It must be made clear that these weights are only a qualitative indication of the contribution of the pure salts within the precipitate sample, primarily because the Raman measurement probed only the solid surfaces of the sample and is not a quantitative measure of the bulk property.

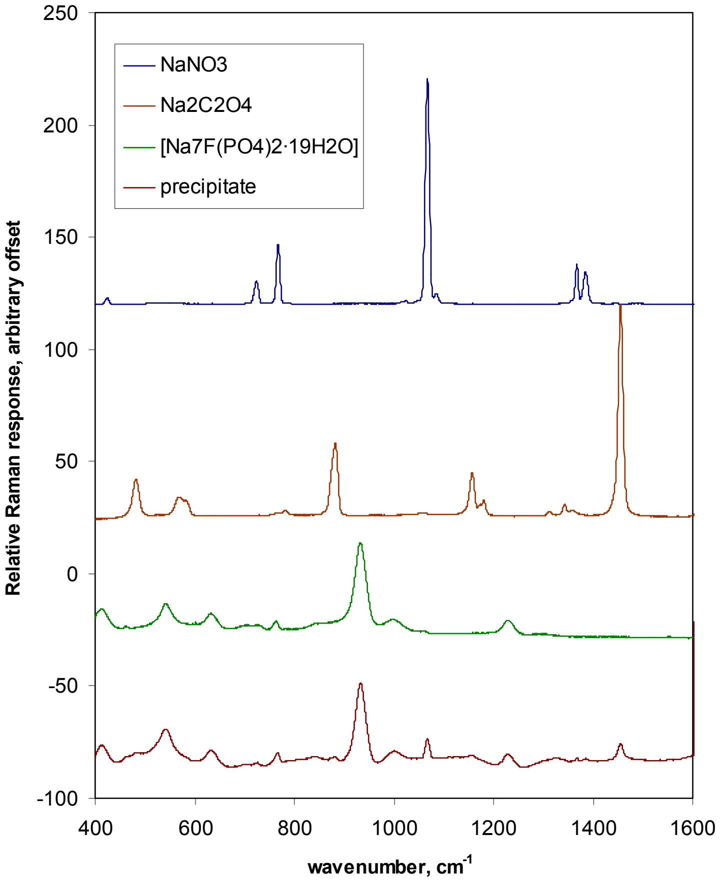

Figure 3.1. Raman Spectra of the Precipitate Obtained from the Higher-Phosphate Saltcake Simulant Formulation (lower), along with Spectra of Pure Sodium Nitrate (upper), Sodium Oxalate (upper middle), and the Sodium Fluoride-Phosphate Double Salt (lower middle)

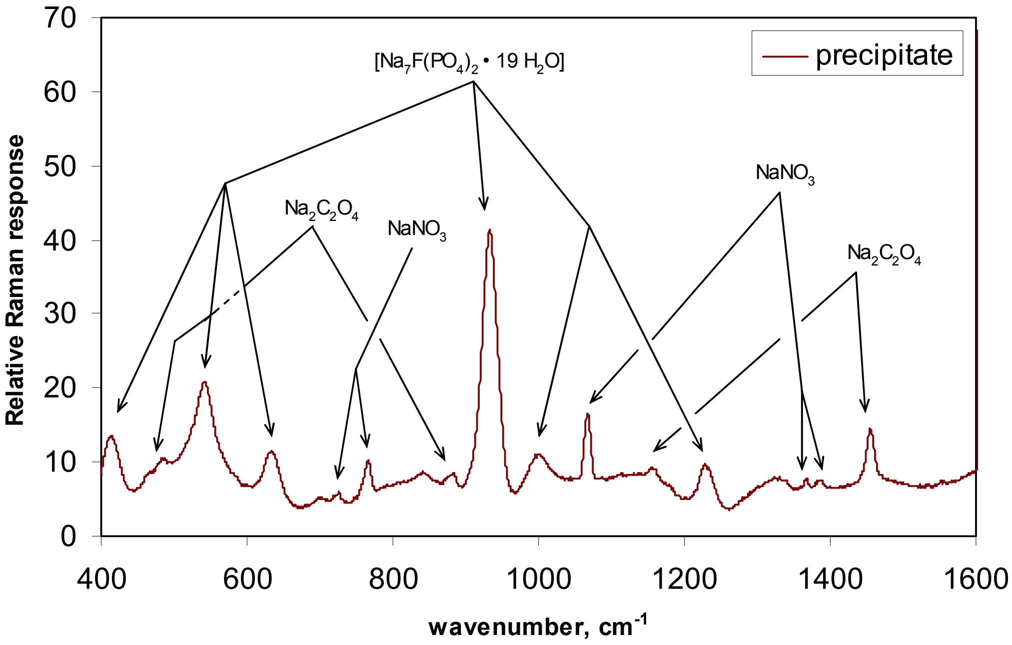

Figure 3.2. Raman Spectrum of the Precipitate Obtained from the Higher-Phosphate Saltcake Simulant Formulation. The Raman bands are labeled according to their source.

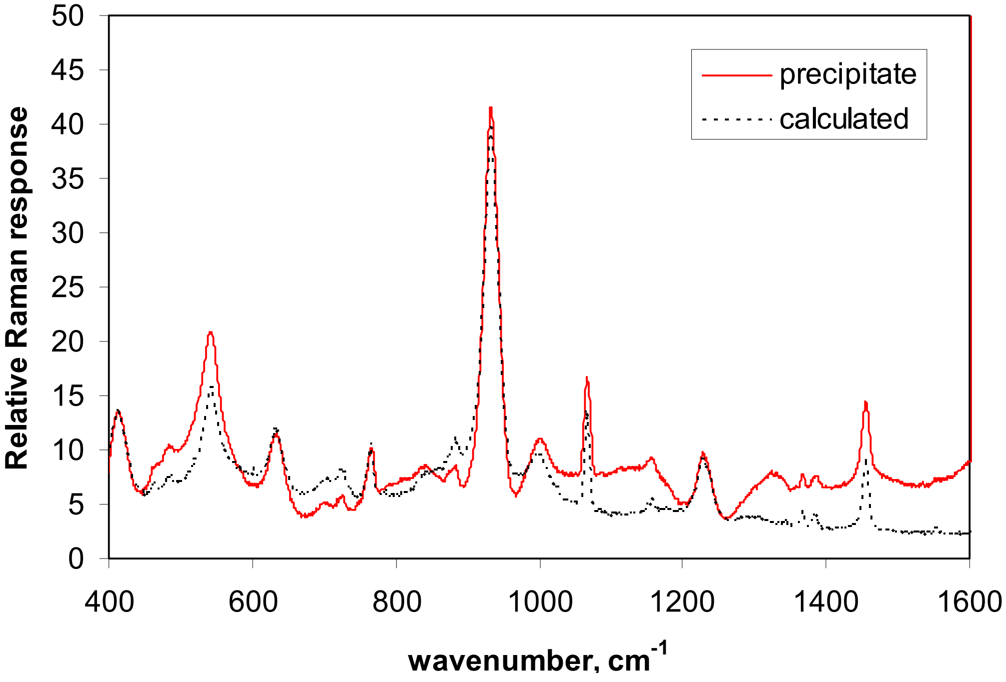

Figure 3.3. Calculated Fit of Precipitate Raman Spectrum. The weights of pure spectra were chosen to qualitatively match the precipitate spectrum with the calculated spectrum; the weighted values for the pure spectra are 85% $Na_7F(PO_4)_2 \cdot 19H_2O$, 9% $NaNO_3$, and 7% $Na_2C_2O_4$.

While the precipitate spectrum suggests that $NaNO_3$ is a contributor, it is doubtful that the nitrate salt was actually precipitated in the simulant solution. The nitrate in the precipitate more likely resulted from liquid in contact with the filtered solids. Before obtaining the spectrum, the filtered solids were washed with only a very small volume of water to minimize the dissolution of the precipitate sample. It is probable that nitrate-rich simulant liquid was not thoroughly washed from the sample, and $NaNO_3$ bands were thereby evident in the Raman spectrum.

The Raman analysis indicates that primarily the sodium fluoride-phosphate double salt, and to a lesser extent sodium oxalate, precipitated from a higher-phosphate simulant formulation. The phosphate concentration was reduced to minimize the potential formation of the double salt. (Reducing the fluoride concentration instead of or in addition to the phosphate reduction was considered as an alternative.) It should be noted that the phosphate concentration in the final simulant composition (0.049 M, Table 3.1), while low compared with that predicted for the composite of actual waste samples (0.062 M, Table 2.4), is still significant. According to ESP model predictions for the dissolved liquid resulting from a blend of waste retrieved from 67 saltcake SSTs, the expected soluble phosphate concentration is 0.045 M (Table 2.4). Therefore, the phosphate content of the simulant is slightly greater than that nominally expected from the saltcake tanks.

The final simulant composition characterized in Table 3.1 was clear yellow solution on preparation. After sitting for a few days, an extremely small amount of precipitate formed in a room temperature sample. The amount of solids was visually estimated to be <0.1 g in 500 mL (<0.02 wt%). These solids were not filtered and analyzed because the amount of solids was extremely small and thought to be inconsequential to supplemental technology process testing. Approximately three months after preparation, portions of a batch of the final simulant formulation held at room temperature and ~50°C appeared as they did a few days after preparation. To this date, only a very small amount of solids was noted at the bottom of each sample container. This suggests that the simulant formulation has good shelf stability.

A single density measurement was made on the laboratory batch of the simulant (composition given in Table 3.1 and prepared as described in Section 3.2). Room temperature solution was filled to the mark of a 100-mL volumetric flask and weighed. The resulting “information-only” density estimate for the solution is 1.237 g/mL.

3.2 Final Simulant Formulation and Preparation Procedure

Table 3.2 shows the reagents and the appropriate masses to prepare 1 L of cold dissolved saltcake solution simulant matching the composition specified in Table 3.1. The masses of pure reagents other than water are exact; the mass of water is estimated to achieve the expected solution density of 1.24 g/mL. Reagents are added in the order listed, except that a fraction of the water is reserved for dilution to final volume. Appropriate safety precautions must be

Table 3.2. Reagent Masses for 1 L of Cold Dissolved Saltcake Solution Simulant

Component	**Reagent**	**Mass (g)**	**Concentration (M)**
Water	H_2O	860	
Sodium oxalate	$Na_2C_2O_4$	1.58	0.0118
Sodium acetate	CH_3COONa	10.79	0.132
Sodium nitrate	$NaNO_3$	196.11	2.308
Potassium nitrate	KNO_3	1.25	0.0124
Sodium hydroxide	NaOH	29.58	0.740
Aluminum nitrate	$Al(NO_3)_3 \cdot 9\ H_2O$	23.90	0.0637
Sodium carbonate	Na_2CO_3	50.35	0.475
Sodium sulfate	Na_2SO_4	12.78	0.0900
Sodium chromate	Na_2CrO_4	1.68	0.0104
Sodium phosphate	$Na_3PO_4 \cdot 12\ H_2O$	18.70	0.0492
Sodium chloride	NaCl	2.56	0.0438
Sodium fluoride	NaF	1.33	0.0316
Sodium nitrite	$NaNO_2$	29.26	0.424
Cesium nitrate	$CsNO_3$	1.0e-05	5.1e-08

employed during solution preparation. In particular, sodium hydroxide must be added slowly and carefully because the dissolution process is highly exothermic.

The components contributing to the TOC concentration in the cold simulant include acetate and oxalate salts. Lacking speciation details for the organic carbon components in the actual waste composite, these salts were selected to represent the completely soluble and less-soluble organic contributors, respectively. Concentrations of higher molecular organic complexants such as ethylenediaminetetraacetic acid (EDTA) are not expected to be significant in the saltcake wastes and therefore are not included as TOC components.

4.0 Instrumental Analyses of a Simulant Batch

This section describes the instrumental analyses of a 25-L simulant batch prepared by NOAH using the formulation given in Section 3. Section 4.1 discusses the different instrumental analyses used to confirm the simulant composition. Section 4.2 presents the analysis results and compares the measured simulant composition with the target composition.

4.1 Instrumental Analyses for Quality Assurance

This section will describe each analytical method as well as its related accuracy and precision. The purpose of the PNNL analyses was to provide analytical results of the NOAH prepared simulant that comply with the QA requirements of the project. The instrumental analyses performed at PNNL comply with the HASQARD and the relevant elements of ASME NQA-1 (Nuclear Quality Assurance) program. Five separate instrumental methods were required to analyze the complete set of analytes shown in Table 3.1.

The accuracy of each analyte is different and can be affected by several different factors, including the sample matrix, other analytes present, and how far from the detection limit the analyte concentration is, among others. In general, if the concentration is significantly above the detection limit and no significant interferences are present, the accuracy of the analytical methods is within a relative 10%. The Environmental Protection Agency (EPA) uses the matrix spike (MS) results to determine accuracy. A MS is a known amount of standard added to the sample. If based on the measurement, the known amount of standard is recovered and the results are considered accurate. The MS results for each analytical method are in the appendix.

The cations (Al, Cr, K, Na, and P) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES). The samples were acid digested according to procedure PNL-ALO-128, *HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*. The acid digested samples required additional five-fold dilutions to quantify all analytes of interest according to procedure PNL-ALO-211, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry*. The detected analytes at or above the estimated quantitation limit (EQL) [equivalent to 10 times the method detection limit (MDL)] were reported with an uncertainty of ±15% (2- σ). As the MDL was approached, the uncertainty increased to 100%. Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g., 2% v/v HNO_3 or less) at analyte concentrations greater than 10 times the detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 0.5 wt%. When the total dissolved solids are near or above 0.5 wt%, the efficiency of the nebulizer in the instrument can be affected resulting in concentration values that may be slightly low (~3% to 5%). The analytical report along with all of the QC data can be found in Appendix A.1.

The anions (Cl, F, NO_3, NO_2, PO_4, SO_4, and C_2O_4) were analyzed by ion chromatography (IC) according to procedure PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. The method was used to evaluate the anions of interest on unprocessed sub-samples of simulant. Routine precision and bias is typically ±15% or better for noncomplex aqueous samples that are free of interferences and have concentrations similar to those of the measured anions. The analytical report and the QC data can be found in Appendix A.2.

The simulant samples were analyzed in duplicate for free hydroxide (OH) content following procedure PNL-ALO-228, *Determination of Hydroxyl and Alkalinity of Aqueous Solutions, Leachates, & Supernates*. Direct sample aliquots were analyzed using a Brinkman 636 Auto-Titrator. A 0.1018 M NaOH solution was prepared for use as a standard and spiking solution. The titrant was 0.2098 M HCl. The relative standard deviation (RSD) was ±2% or less of the OH molarity. The analytical report along with all of the QC data can be found in Appendix A.3.

The total organic carbon (TOC) and total inorganic carbon (TIC) were analyzed by the hot persulfate method. The hot persulfate wet oxidation method uses acid decomposition for TIC and acidic potassium persulfate oxidation at 92° to 95°C for TOC, all on the same sample. The total carbon (TC) is the sum of the TIC and TOC. All sample results were corrected for average percent recovery of system calibration standards and for contribution from the system blanks, as per procedure PNL-ALO-381 calculations. Routine precision and bias is typically ±15% or better for noncomplex samples that are free of interferences. The analytical report with all of the QC data can be found in Appendix A.4.

The fluoride (F), acetate, and oxalate were analyzed by organic acid ion chromatography. This method pumps the sample through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn and a separator column, are packed with a low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The eluent solution is a sodium bicarbonate-sodium carbonate mixture. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared with known standards. These samples required quite a bit of dilution because of the high nitrate and acetate concentrations. Routine precision and bias is typically ± 15% or better for noncomplex aqueous samples that are free of interferences and have concentrations similar to those of the measured anions. The analytical report and the QC data can be found in Appendix A.5.

4.2 Measured Analyte Concentrations and Simulant Properties

This section summarizes the results of the PNNL instrumental analyses and other independent analyses that are provided as information-only. The measured results are also compared with the simulant target concentrations.

NOAH produced a 25-L batch of simulant to match the formulation provided to them by PNNL. NOAH identified their product as Dissolved Salt Cake Waste Simulant for Battelle, Lot 117987/1.1. Dissolved saltcake simulant samples from NOAH were received in three bottles. Two of the bottles were 0.5-L (subportions of the two 10.5-L samples split out for delivery to supplemental treatment process vendors) and one bottle was a 3-L sample for PNNL to retain and observe. A sample was taken from each bottle and submitted for analysis. The two 0.5-L bottle samples were designated as DSS-1 and DSS-2, and the 3-L bottle sample was designated as DSS-3. The simulant samples received from NOAH were clear yellow liquids with no visible precipitate. They appeared to be very stable at room temperature.

Table 4.1 shows the results of the PNNL analyses for the three individual samples. Except for hydroxide, the PNNL analyte concentrations (*C*) were reported in µg/mL (see Appendix A) and converted to molar concentration units M (mol/L) using the following equation:

$$C(\mathrm{M}) = \frac{C(\mu\mathrm{g/mL})}{1000 * MW} \tag{4.1}$$

where *MW* is the analyte molecular weight in g/mol. Table 4.1 also provides the numerical average of the three individual sample measurements, the standard deviation of the three results referenced to the average, and the percent difference between the average and target concentrations [i.e., % difference = 100*(average conc.-target conc.)/target conc.]. As indicated by the standard deviation, the analytical results were generally consistent for the three samples. Also, all of the analyte concentrations were within 10% of the target values except for oxalate and acetate.

Oxalate analyzed with the inorganic anions was 59% higher than the target concentration, whereas oxalate analyzed with the organic acids was 18% lower than the target concentration. The large difference in results obtained with the two oxalate analysis methods adds significant uncertainty to knowing the actual concentration. Additionally, the PNNL acetate results shown in Table 4.1 were higher than expected, but acetate at this relatively large concentration presents an analytical problem; higher dilutions are required for analysis, and this may affect measurement precision and accuracy. Also, because acetate and fluoride elute very close together, there may have been chromatographic interference between the two peaks.

All of the results from the organic acids analysis (F, C_2O_4, and acetate) had relatively high standard deviations indicating less precision in the measurements. Again, this may have been a result of the higher dilutions necessary to accommodate the high level of acetate present in the samples.

Table 4.1. PNNL Measured Results Compared with Target Values

Analyte	Target Conc. (M)	DSS-1 PNNL Measured (M)	DSS-2 PNNL Measured (M)	DSS-3 PNNL Measured (M)	Average PNNL Measured (M)	PNNL Standard Deviation	% Diff. Target and Average
Al	0.0637	0.0584	0.0578	0.0589	0.0584	0.00056	-8.4
Cs	5.12E-08	---(a)	---(a)	---(a)	---(a)	---(b)	---(b)
Cr	0.0104	0.00968	0.00964	0.00983	0.00972	0.000099	-6.6
K	0.0124	0.0120	0.0116	0.0117	0.0118	0.00019	-5.1
Na	5.00	4.72	4.70	4.83	4.75	0.070	-5.0
Cl	0.0438	0.0429	0.0429	0.0432	0.0430	0.00016	-1.8
CO_3 (as TIC)	0.475	0.490	0.483	0.480	0.484	0.0048	2.0
F	0.0316	0.0263	0.0295	0.0342	0.0300	0.0040	-5.1
NO_2	0.424	0.413	0.413	0.415	0.414	0.0013	-2.4
NO_3	2.51	2.32	2.34	2.35	2.34	0.012	-6.9
P	0.0492	0.0478	0.0469	0.0452	0.0466	0.0013	-5.2
PO_4	0.0492	0.0466	0.0466	0.0449	0.0461	0.0010	-6.4
SO_4	0.0900	0.0891	0.0888	0.0893	0.0891	0.00024	-1.0
C_2O_4(c)	0.0118	0.0092	0.0097	0.0102	0.0097	0.00051	-18
C_2O_4(d)	0.0118	0.0219	0.0175	0.0168	0.0187	0.0028	59
Acetate	0.132	0.186	0.186	0.169	0.181	0.0098	37
TOC (direct measure)	0.287	0.286	0.285	0.285	0.285	0.00054	-0.6
TOC (acetate + C_2O_4)	0.287	0.390	0.391	0.358	0.380	0.019	32
Free OH	0.485	0.534	0.512	0.516	0.521	0.012	7.4

(a) Not measured.
(b) Not applicable.
(c) Results from organic acids analysis.
(d) Results from inorganic anions analysis.

Table 4.1 shows TOC concentrations determined from the PNNL analyses using two methods. First, as discussed in Section 4.1, the TOC content is measured directly using the hot persulfate method. Secondly, the TOC is calculated from the acetate and oxalate concentrations determined in the organic acid analysis and converting them to carbon equivalents. The direct-measured TOC, which measures contributions from all organic carbon sources (e.g., oxalate and acetate), is within 1% of the target value, whereas the calculated value is 32% higher than the target. The analytical uncertainty in the oxalate and acetate measurements for the simulant is a contributing factor in the discrepancy of the calculated TOC compared with the direct-measured TOC.

For information purposes and per contract agreement with NOAH, a sample of the simulant was analyzed at Southwest Research Institute (SwRI). The SwRI analyses are included here for completeness, but do not bear the QA program pedigree of the PNNL analyses. Therefore, the SwRI results are for information only. Information-only ICPAES analysis results were also obtained at the NOAH facility where the simulant was prepared.

Table 4.2 shows the NOAH-measured concentration of the metals and the SwRI-measured concentrations for most of the analytes. The table also shows the NOAH expected concentration for each analyte based on the amount of chemical reagents added to the simulant and the measured reagent purity (as reported on certificates of analysis). The SwRI and NOAH measured analyte concentration results were reported as wt% of the solution and converted to M concentration using the following equation:

$$C(\mathrm{M}) = \frac{10 * C(wt\%) * \rho}{MW} \tag{4.2}$$

where ρ is the sample density in g/mL. A density of 1.23 g/mL, as determined at PNNL for a 100-mL portion of simulant, was used in these calculations. However, this density measurement was obtained as information-only, lacking the QA of the PNNL instrumental analyses.

The analytical results from SwRI generally agreed with the PNNL analyses, with the largest discrepancies noted for potassium, oxalate, carbonate (TIC), and fluoride. The SwRI results for direct-measured TOC and oxalate shown in Table 4.2 are within 7% and 1% of the target values, respectively. The SwRI results suggest that the oxalate concentration is closer to target than the PNNL results indicate. The relative consistency of the PNNL and SwRI TOC results (direct measurements) is an indicator that the simulant organic content is near to target.

With the possible exception of oxalate and acetate, as noted above in the discussion of PNNL results, the simulant analyte concentrations are all within the relative analytical method error (~10%) of the target values. This indicates that the dissolved saltcake simulant was nominally prepared to specifications.

Table 4.2. NOAH and SwRI Results Compared with Target Values (information only)

Analyte	Target Conc. (M)	NOAH Expected (M)	NOAH Measured (M)	SwRI Measured (M)
Al	0.0637	0.0643	0.0510	0.0598
Cs	5.12E-08	5.10E-08	---(a)	---(b)
Cr	0.0104	0.0105	0.00823	0.00964
K	0.0124	0.0125	0.0101	0.0144
Na	5.00	5.05	5.08	4.70
Cl	0.0438	0.0442	---(a)	0.0441
CO_3 (as TIC)	0.475	0.479	---(a)	0.569
F	0.0316	0.0319	---(a)	0.0255
NO_2	0.424	0.427	---(a)	0.421
NO_3	2.51	2.53	---(a)	2.64
PO_4	0.0492	0.0497	---(a)	---(a)
P	0.0492	0.0497	---(a)	0.0500
SO_4	0.0900	0.0908	---(a)	0.0915
C_2O_4(d)	0.0118	0.0119	---(a)	0.0117
Acetate	0.132	0.133	---(a)	---(b)
TOC (direct measure)	0.287	0.290	---(a)	0.307
TOC (acetate + C_2O_4)	0.287	0.290	---(a)	---(c)
Free OH	0.485	---(b)	---(a)	---(a)

(a) Not given.
(b) Not measured.
(c) Not applicable.
(d) Results from inorganic anions analysis.

5.0 Comparison of Simulant and Actual Waste Solution Compositions

It was noted in Section 1 that development of the cold dissolved saltcake simulant formulation was estimated on the basis of calculations and modeling because the composition of actual dissolved saltcake waste was not available early enough to meet the project schedule. Preliminary results of instrumental analyses completed on samples of the pretreated actual waste solution to be delivered to supplemental treatment process vendors are now available. This section shows that the measured analyte concentrations of the pretreated actual waste and simulant solutions agree to within ±10% for the majority of analytes. Additionally, bases for the differences in the solution compositions are discussed, and the expectation that the differences will not have a significant impact on supplemental treatment process testing is expressed.

5.1 Comparison of Simulant and Actual Waste Analyte Concentrations

The measured analyte concentrations for simulant and actual waste solutions are compared with model predictions and the simulant formulation in Table 5.1. The first column in the table is the ESP-predicted composite solution composition that was given in Table 2.4, and it is based on the liquid in equilibrium with the remaining solids after the actual waste sample composite was dissolved to 5 M Na. The as-formulated simulant composition in the second column is reproduced from Table 3.1. As discussed in Section 3.1, the phosphate level of the simulant formulation was reduced to 80% of the model-predicted concentration, resulting in a difference in the free hydroxide concentration as well. The instrumental analysis results shown in Table 5.1 for the batch of cold saltcake simulant solution were presented in Section 4 (Table 4.1), and the pretreated actual waste liquid data are reproduced from a preliminary analysis report.(a)

Except as noted in the footnotes to Table 5.1, the procedures and instrumentation used to ascertain the actual dissolved composite waste liquid analyte concentrations were identical to those for the cold simulant solution described in Section 4.1 and Appendix A.1. Because the overall composition of the two solutions is generally in agreement, it is appropriate to assume that factors affecting the performance of instrumental analyses and measurement accuracy (Section 4) are similarly biased. Thus it is instructive to compare the results of solution measurements directly, as is done in the last column of Table 5.1. The percent difference of the measured simulant analyte concentration from the pretreated actual waste baseline result is tabulated for each analyte [i.e., % difference = 100*(simulant conc-actual waste conc)/actual waste conc].

(a) Results provided in a letter report by BM Rapko and TG Levitskaia, *Removal of ^{137}Cs from Dissolved Hanford Tank Saltcake by Treatment with IE-911.* TWS 03.030, February 2003, Pacific Northwest National Laboratory, Richland, WA. A final PNNL report describing the pretreatment process and containing the analytical results is expected in April 2003.

Table 5.1. Comparison of Simulant and Actual Waste Compositions

Concentration in mol/L					
Analyte	**ESP-Modeled Dissolved Composite Liquid(a,b)**	**Cold Simulant Liquid As-Formulated**	**PNNL Measured Cold Simulant Liquid(c)**	**PNNL Measured Pretreated Actual Waste Liquid(d)**	**% Difference, Simulant vs Actual Waste Measurements**
Al	0.064	0.0637	0.058 ± 0.00056	0.208 ± 0.0025	-72
B		0	n/a	0.0021 ± 0.000057	n/a
C_2O_4	0.012	0.0118	0.0097 ± 0.00051	0.0105 ± 0.000032(e)	-7.4
CO_3 (TIC)	0.48	0.475	0.484 ± 0.0048	0.533 ± 0.0017	-9.1
Ca	0	0	n/a	0.0014 ± 0.00024	n/a
Cl	0.044	0.0438	0.0430 ± 0.00016	0.0415 ± 0.0	3.6
Cr	0.010	0.0104	0.0097 ± 0.000099	0.0186 ± 0.00015	-48
F	0.032	0.0316	0.030 ± 0.0040(f)	0.018 ± 0.00026(f)	63
K	0.012	0.0124	0.0118 ± 0.00019	0.0090 ± 0.00054(g)	30
Na	4.98	5.00	4.75 ± 0.070	5.10 ± 0.11	6.9
NO_2	0.42	0.424	0.414 ± 0.0013	0.414 ± 0.0046	-0.09
NO_3	2.51	2.51	2.34 ± 0.012	2.44 ± 0.011	-4.4
free OH	0.44	0.485	0.52 ± 0.012	0.51 ± 0.0035	2.2
PO_4	0.062	0.0492	0.0461 ± 0.0010	0.0515 ± 0.0014	-11
Si	0.0083	0	n/a	0.0039 ± 0.00043	n/a
SO_4	0.090	0.0900	0.0891 ± 0.00024	0.0932 ± 0.000074	-4.5
other soluble TOC (e.g., acetate)	0.26	0.263	0.36 ± 0.020	n/a	n/a
TOC (direct measure)	0.29	0.287	0.285 ± 0.00054	0.233 ± 0.0049(h)	22.6

(a) The bulk composite concentrations were used as inputs to the ESP model (version 6.5, with the PUBLIC, LAB, and XBASE databases).

(b) The decantable liquid created by diluting the composite to 5-M Na amounted to an estimated total of 6.6 L.

(c) The uncertainty interval is one standard deviation based on triplicate measurements.

(d) The uncertainty interval is one standard deviation based on duplicate measurements.

(e) The actual waste result was obtained as an upper bound from inorganic anion ion chromatography and is provided as an information-only result; the simulant result was determined from organic acid ion chromatography (Section 4.1).

(f) Result agreed to in a personal communication with BM Rapko of PNNL on February 6, 2003; the result reported above does not include an apparent outlier that was included in the average presented in the letter report cited for the other actual waste analyses reported here. The final actual waste result is to be discussed in a PNNL report expected in April 2003.

(g) Result provided in a personal communication from BM Rapko of PNNL on January 16, 2003 for a sample dilution equivalent to that applied for the simulant analysis. This actual waste result is higher than shown in the letter report cited for the other actual waste analyses reported here. In the letter report, the K concentration is reported as 0.0061 M (± 0.0035 M) for a 5x-diluted sample. The difference in actual waste results for the different dilutions is to be discussed in a PNNL report expected in April 2003.

(h) Result provided in a personal communication from BM Rapko of PNNL on January 22, 2003. The final result is to be published in a PNNL report expected in April 2003.

As indicated in the last column of Table 5.1, most of the analyte concentrations for the simulant and actual waste solutions agree to within ±10%, including the four analytes with the highest concentrations (Na, NO_3, CO_3, and NO_2). For these four species, the simulant measurements are consistently lower. The most significant discrepancies (>20% difference) between the cold dissolved composite simulant liquid and the actual dissolved composite waste liquid are in the Al, Cr, F, K, and TOC concentrations. The simulant is more concentrated than the actual waste in F, K, and TOC, but less concentrated in Al and Cr.

5.2 Assessment of Differences in Simulant and Actual Waste Compositions

The apparent differences in the simulant and actual waste solution compositions are likely attributed to the following factors: 1) errors in the model prediction for the simulant; 2) variations in dilution in the simulant and actual waste solution preparations; 3) effects due to the ion-exchange process applied to the actual waste solution; and 4) inconsistent analytical measurement error for the two solutions. Given the similarity of the analytical methods applied to the solutions, the latter factor is considered insignificant. The other three factors are assessed below.

It was shown in Section 4 that the measured analyte concentrations for the batch of simulant substantially match the formulation targets within the expected analytical measurement accuracy. Therefore, large deviations (>±20%) in the simulant and actual waste compositions in Al, Cr, F, K, and TOC are likely due, at least in part, to errors in model predictions (Section 2). Three sources of error are possible. First, some discrepancies could be the result of actual waste core sample heterogeneity, causing differences in composition between the bulk core segments and the core segment subsamples on whose analyses the cold dissolved composite simulant composition was based (Section 2.3). This is a form of model input error.

Secondly, another source of model input error is possible. Most of the measured species concentrations for the actual waste composite could be used as ESP model inputs without any modification. The exceptions were Cr and TOC, because in both these cases the soluble and insoluble fractions of the constituents in the waste composite (before dissolution by water addition) had to be distinguished from one another in the ESP model inputs. Thus, discrepancies in Cr (-48%) and TOC (+23%) concentrations could be partly the result of assumptions of how these species are initially phase distributed in the waste. Waste sample composition estimates noted above would also play a significant role.

The aluminum solubility uncertainties also result from input assumptions, in that the form of aluminum in the waste solids was unknown and the standard form of gibbsite, aluminum hydroxide, was assumed to dominate. It is quite possible that the aluminum hydroxide in the core composite was a more soluble crystalline form than the gibbsite phase used by the ESP model. This could account for the extremely low concentration of Al in the simulant compared with the actual waste solution (-72%).

Finally, the thermodynamics databases and models used by ESP may not completely represent the highly complex matrix of saturated solution in contact with saltcake waste solids. Differences in the fluoride concentration in the two solutions (+63%) could be related to the model's representation of the sodium fluoride-phosphate double salt [$Na_7F(PO_4)_2 \cdot 19H_2O$] solubility. As discussed in Section 3.1 and reiterated in Table 5.1, the PO_4 concentration in the simulant formulation was reduced from the ESP model predicted solubility limit to overcome precipitation of the double salt in preliminary recipes. Alternatively, it would have been possible to eliminate the precipitation problem by reducing the F concentration in concert with (or instead of) the PO_4 reduction. The measured actual waste PO_4 concentration (0.052 M) was in between the simulant solution measurement (0.046 M) and the ESP model prediction (0.062 M).

While model predictions may have contributed to large discrepancies on a few analytes, the overall agreement of simulant and actual waste solutions is quite good, especially for the most concentrated species. Other factors help explain the less significant differences in the majority of species.

Assuming the results of the measurement of metals by ICPAES as shown in Table 5.1 are perfectly accurate, then the Na concentration is ~2% higher than target in the actual waste solution and ~5% lower in the simulant. This suggests that the actual waste solution may not have been diluted sufficiently with water to reach the 5.0-M Na target, whereas an excess of water may have been added in the simulant batch. However, as noted in Section 4.1 (and Appendix A.1), a method accuracy of 100% is not assured given the many variables in the instrumental analyses. In any case, there appears to be an actual ~7% difference in Na concentration in the two solutions, and this is likely attributable to the effects of water dilution, which similarly effects the concentration of all analytes (as long as small differences in dilution do not result in dissolution or precipitation of new species).

It is assumed that the ion-exchange pretreatment process applied to remove ^{137}Cs from the actual waste solution had a negligible impact on the analyte concentrations, except perhaps on potassium. Because the crystalline silicotitanate ion-exchange resin employed targets selective removal of Cs cations [(a)], it is likely that the concentrations of other alkali cations (K, Na) would be reduced after passing through the ion exchange column. The relative affinity (selectivity factors) of crystalline silicotitanate Cs-specific ion exchange media for alkali cations generally proceeds in the order Cs>K>Na. Therefore, the ion exchange process is likely to impact the relative concentration of K more than Na. The change in analyte concentrations in the actual

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[(a)] The ion-exchange resin is IONSIV® IE-911, available from UOP, as noted in the letter report by BM Rapko and TG Levitskaia, *Removal of ^{137}Cs from Dissolved Hanford Tank Saltcake by Treatment with IE-911.* TWS 03.030, February 2003, Pacific Northwest National Laboratory, Richland, WA. A final PNNL report describing the ion-exchange pretreatment process is expected in April 2003.

dissolved saltcake waste solution resulting from the ion-exchange process will be discussed in greater detail in an upcoming report [a]. Preliminary reported results indicate that the K concentration in the actual waste feed solution prior to ion exchange was 0.0104 M.[b] Compared with this result, the K concentration is only 13% higher in the simulant, not 30% higher as indicated in Table 5.1 for the pretreated actual waste solution.

While the magnitude of the relative difference in the simulant and actual waste composition is large for a few analytes, the absolute differences in concentration are in general not appreciable, and the differences are not expected to have a significant impact on bulk vitrification or containerized grout supplemental treatment process testing. For example, in light of the great molar excess of Na compared with K, which differ by a factor of ~400 in the simulant solution, the discrepancy in absolute K concentration in the actual waste and simulant solutions is negligible. It is unlikely that bulk vitrification and containerized grout supplemental treatment processes would need to modify their formulations to account for the 0.003 M difference in measured K in the two solutions. This difference is dwarfed by the Na concentration difference (0.35 M), which might warrant a formulation adjustment.

Of the other species with large relative differences in the simulant and actual waste solutions (Al, Cr, F, and TOC), the F and TOC are in excess in the simulant and therefore represent a slight challenge to the supplemental treatment processes and/or waste forms. Additionally, the F and TOC concentrations in the simulant are well within the bounds of what might be expected from a saltcake tank waste stream (see Table 2.1 for reported limits).

The concentrations of Al and Cr in the simulant solution are both lower than in the actual waste solution, but not adversely so. To validate Cr retention in the supplemental treatment waste forms, higher Cr concentrations in the simulant (as well as in the actual waste) might be beneficial. However, the Cr concentration in the simulant is on the same order of magnitude as the actual waste solution and is probably "representative" of many saltcake tank waste streams that might be encountered.

PNNL vitrification and grout experts were consulted about the potential impact of aluminum on supplemental treatment processes. They responded that the lower Al concentration would not be expected to affect the formulation used, the simulant/waste processing characteristics, or the derived waste form properties in any significant way because of the great excess of aluminum-containing species added as formers and the ready incorporation of Al in the waste forms.[c] A possible exception is the effect of Al on heat evolution during the cure of grout waste forms, which is not expected to be an issue for smaller containerized grout pours.

(a) A final PNNL report describing the ion-exchange pretreatment process is expected in April 2003.

(b) As noted in the letter report by BM Rapko and TG Levitskaia, *Removal of ^{137}Cs from Dissolved Hanford Tank Saltcake by Treatment with IE-911.* TWS 03.030, February 2003, Pacific Northwest National Laboratory, Richland, WA.

(c) Personal communications with PNNL grout expert LM Bagaasen and PNNL vitrification expert JD Vienna on November 16, 2002.

The effect of the aluminum concentration difference in the simulant and actual waste solutions on steam reforming waste processing and waste forms is less clear. An expert in steam reforming waste form properties noted that the low Al content in the simulant could affect the mineralogical makeup of the aluminosilicate steam reformer product, and the sensitivity of the process to waste stream variability is not well established.(a) However, as with the bulk vitrification and containerized grout processes, an excess of aluminum-containing species (e.g., kaolinite) is added in the steam reforming process. Further steam reformer testing is needed to address these uncertainties.

(a) Personal communication from BP McGrail, PNNL, February 13, 2003.

6.0 References

Callaway WS. 2002. *222-S Laboratory Test Plan for Preparation of Ex-Situ Vitrification Test Solution.* RPP-13046, Fluor Hanford Inc., Richland, WA.

Gasper KA, KD Boomer, ME Johnson, GW Reddick Jr, AF Choho, and JS Garfield. 2002. *Recommendation for Supplemental Technologies for Potential Mission Acceleration.* RPP-11261 Rev. 0, CH2M HILL Hanford Group, Inc., Richland, WA.

OLI. 1998. *A Guide to Using the OLI Engine.* OLI Systems, Inc., Morris Plains, NJ.

Rapko BM and GJ Lumetta. 2000. *Status Report on Phase Identification in Hanford Tank Sludges.* PNNL-13394, Pacific Northwest National Laboratory, Richland, WA.

Appendix

Instrumental Analysis Reports for Simulant

A.1 ICPAES Report

Battelle PNNL/RS&E/Inorganic Analysis ... ICPAES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#:	44832 / F40026
ASR#:	6668
Client:	R. Russell
Total Samples:	3 (liquid)

	First	Last
RPL#:	03-00464	03-00466
Client ID:	DSS-1	DSS-3
Sample Preparation: PNL-ALO-128 (SRPL/ms)		

Procedure: PNNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry" (ICPAES).

Analyst: D.R. Sanders

Analysis Date (File): 01-08-2003 (A0877)

See Chemical Measurement Center 98620 file: ICP-325-405-1
(Calibration and Maintenance Records)

M&TE Number: WB73520 (ICPAES instrument)
360-06-01-029 (Mettler AT400 Balance)

B.M. Oliver 1/13/03
Preparer

MW Urie 1-14-03
Review and Concur

Three aqueous saltcake solution simulant samples submitted under Analytical Service Request (ASR) 6668 were analyzed by ICPAES. The samples were prepared by acid extraction following procedure PNL-ALO-128 in the RPL Sample Preparation and Receiving Laboratory (SRPL) using a nominal 1.0 mL of sample and diluting to a final volume of approximately 25 mL.

Analytes of interest (AOIs) were specified in the ASR and are listed in the upper section of the attached ICPAES Data Report (2 pages). The quality control (QC) results for each of these analytes have been evaluated and are presented below. Analytes other than those identified as AOIs are reported in the bottom section of the data report, but have not been fully evaluated for QC performance.

The results are given as µg/mL for each detected analyte, and have been adjusted for all laboratory processing factors. Normally, results for the least diluted sample are preferred as this provides the highest analyte levels to the instrument. However, for the present case, where the total dissolved salt levels in the samples were ~0.5 wt.%, results for 5x dilutions are reported where applicable. For high dissolved salt levels, the efficiency of the instrument can be reduced, resulting in indicated analyte concentrations that can be slightly low (~3 to 5%). Results for undiluted samples are given for those cases were the data are subject to less uncertainty, i.e., where the 5x data are <EQL or <MDL and the 1x data are >EQL or >MDL, respectively.

The following is a list of quality control measurement results relative to ICPAES analysis requirements of the controlling QA plan. For the extraction processing, a process blank, blank spike, matrix spike, and duplicate were prepared along with the samples. The blank spike and matrix spike were prepared using 1.5 and 0.5 mL respectively of multi-element spike solutions BPNL-QC-1A and -2A. All AOIs were included in the combined spike solution. QC evaluation was done using 5x dilutions where available. Results for lower dilutions are reported as applicable.

<u>Process Blank:</u>

A process blank (reagents only) was prepared with the samples. Except for calcium, the concentration of all AOIs in the blank were within the acceptance criteria of <EQL (estimated quantitation level) or < 5% of the concentration in the samples. Calcium was detected at a level of ~21 µg/mL in the blank. In the samples, calcium was detected at levels of ~12 µg/mL, which was <EQL. Since the same reagents were used for all samples, the slightly higher level of calcium in the blank is considered to be an anomaly.

<u>Blank Spike:</u>

A blank spike (reagents and spike solution) was prepared with the samples. The recovery values were within the acceptance criterion of 80% to 120% for all AOIs.

<u>Duplicate Relative Percent Difference (RPD):</u>

A duplicate was prepared for Sample 03-00464. RPDs are listed for all analytes that had a concentration ≥ EQL. The RPDs were within the acceptance criterion of ±15% (±3.5% for sodium) for all AOIs meeting the above requirement.

Laboratory Control Standard (LCS):

No LCS was provided for analysis.

Matrix Spiked Sample:

A matrix spike was prepared using Sample 03-00466. Recovery values are listed for all analytes in the spike that were measured above the EQL, and that had a spike concentration > 20% of that in the sample. The recovery values were within the acceptance criterion of 75% to 125% for all AOIs meeting the above requirements. Recovery values for analytes with a spike concentration < 20% of the concentration in the sample are listed as "nr".

Post-Spiked Samples (Spike A Elements):

A post-spike A was conducted using Sample 03-00464-Dup. Recovery values are listed for all analytes in the spike that had a concentration > 20% of that in the sample. The recovery values were within the acceptance criterion of 75% to 125% for all AOIs meeting the above requirement. Recovery values for analytes with a spike concentration < 20% of the concentration in the sample are listed as "nr".

Post-Spiked Samples (Spike B Elements):

A post-spike B was conducted using Sample 03-00464-Dup. Recovery values are listed for all analytes in the spike that had a concentration > 20% of that in the sample. No AOIs were included in the post-spike B spike.

Serial dilution (Percent Difference):

Five-fold serial dilution was conducted on all samples. For QC evaluation, however, the results for the first serial dilution (Sample 03-00464) were used. Percent differences (%Ds) are listed for all analytes that had a concentration > EQL in the diluted sample. The %Ds were within the acceptance criterion of ±10% for all AOIs meeting the above requirement.

Other QC:

All other instrument-related QC tests for the AOIs passed within the appropriate acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the IDL by the "Multiplier". The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Multiplier".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight).

Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -".

4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
5) The maximum number of significant figures for all ICP measurements is two.

		Run Date=	1/8/2003	1/8/2003	1/8/2003	1/8/2003	1/8/2003	1/8/2003	1/8/2003	1/8/2003	1/8/2003
		Multiplier=	25.3	25.8	128.9	24.0	120.0	24.7	123.6	26.4	131.8
		RPL/LAB #=	03-00464-PB	03-00464	03-00464 @5	03-00464-DUP	03-00464-DUP @5	03-00465	03-00465 @5	03-00466	03-00466 @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID=	process blank	DSS-1		DSS-1-Dup		DSS-2		DSS-3	
(ug/mL)	(ug/mL)	(Analyte)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)
0.0310	0.446	Al	--		1,570		1,580		1,560		1,590
0.0450	0.450	Ca	20.8	[11]		[11]		[9.0]		[11]	
0.0060	0.060	Cr	--		504		503		501		511
1.0000	10.000	K	--	482		455		455		458	
0.0870	0.870	Na	[4.9]	over-range	108,000	over-range	109,000	over-range	108,000	over-range	111,000
0.0240	0.236	P	--		1,480		1,480		1,450		1,400
Other Analytes											
0.0050	0.069	Ag	--	[0.35]		[0.14]		[0.13]		--	
0.0360	0.360	As	--	[1.8]		[1.7]		[2.0]		[1.7]	
0.0100	0.031	B	--	1.94		1.79		1.79		1.77	
0.0011	0.010	Ba	--	[0.092]		[0.085]		[0.088]		[0.083]	
0.0002	0.002	Be	--	--		--		--		--	
0.0250	0.250	Bi	[6.3]	[1.7]		[1.6]		[1.5]		[1.4]	
0.0038	0.038	Cd	[0.28]	[0.27]		[0.2]		[0.17]		[0.12]	
0.0400	0.400	Ce	--	[1.1]		--		--		--	
0.0050	0.050	Co	--	[0.14]		--		[0.13]		--	
0.0070	0.070	Cu	[0.72]	[0.78]		[0.91]		[0.59]		[0.47]	
0.0100	0.100	Dy	--	--		--		--		--	
0.0050	0.050	Eu	--	--		--		--		--	
0.0100	0.100	Fe	[0.5]	[0.99]		[0.96]		[0.77]		[0.82]	
0.0130	0.130	La	--	[0.35]		--		[0.36]		--	
0.0058	0.058	Li	--	[1.0]		[0.55]		[0.52]		[0.48]	
0.0250	0.335	Mg	--	[4.4]		[4.0]		[3.1]		[3.0]	
0.0006	0.012	Mn	--	[0.052]		[0.043]		[0.043]		[0.039]	
0.0057	0.057	Mo	--	[0.4]		[0.29]		[0.29]		[0.25]	
0.0450	0.400	Nd	--	[1.4]		--		[1.3]		[1.2]	
0.0130	0.130	Ni	--	--		[0.39]		--		--	
0.0230	0.264	Pb	[2.2]	[4.2]		[1.2]		[1.2]		[0.9]	
0.1250	1.250	Pd	--	[12]		[11]		[12]		[12]	
0.0510	0.510	Rh	--	[1.9]		--		[1.7]		[1.4]	
0.0200	0.200	Ru	--	[0.91]		[0.62]		[0.74]		[0.72]	
0.0280	0.280	Sb	--	--		--		--		--	
0.0360	0.360	Se	--	[1.4]		[0.88]		[1.5]		[1.2]	
0.0300	0.298	Si	[0.88]	[4.0]		[3.6]		[3.7]		[3.5]	
0.1300	1.234	Sn	--	[5.1]		--		[4.4]		[3.6]	
0.0015	0.015	Sr	--	[0.07]		[0.062]		[0.058]		[0.061]	
0.0500	0.500	Te	--	[1.8]		[1.4]		[1.8]		[1.6]	
0.0250	0.278	Th	--	--		--		--		--	
0.0025	0.025	Ti	--	[0.069]		--		--		--	
0.0210	0.210	Tl	[0.53]	[1.2]		[0.99]		[1.2]		[1.1]	
0.5400	4.971	U	--	[23]		[16]		[21]		[18]	
0.0039	0.040	V	--	[0.45]		[0.39]		[0.42]		[0.4]	
0.0380	0.130	W	--	--		--		--		--	
0.0019	0.020	Y	--	--		--		--		--	
0.0070	0.070	Zn	[0.82]	[1.5]		[1.5]		[1.2]		[1.2]	
0.0043	0.043	Zr	--	[0.81]		[0.75]		[0.8]		[0.78]	

1) "--" indicates the value is ≤MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values > EQL is estimated to be within ±15%.

2) Values in brackets [ ] are > MDL but ≤EQL, with errors likely to exceed 15%.

3) Blank cells are not reported.

QC Performance 1/8/03

Criteria>	<15%$^{(a)}$	80% - 120%	75%-125%	75%-125%	75%-125%	< ±10%
QC ID=	03-00464 & 03-00464-D (@5)	LCS/BS	03-00466 & 03-00466-MS (@5)	03-00464-Dup + Post Spike A (@5)	03-00464-Dup + Post Spike B (@5)	03-00464 @5/@25 Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	0.4	95	103	96		1.5
Ca		93	101	99		
Cr	0.1	95	nr	103		2.5
K	5.9 (b)	96	99	96		
Na	0.4	98	nr	nr		3.7
P	0.2	101	nr	96		0.9
Other Analytes						
Ag				96		
As				100		
B	7.6 (b)	101	105	97		
Ba		97	99	95		
Be		90	95	94		
Bi		96	97 (b)	96		
Cd		97	104	106		
Ce		94	91		92	
Co				101		
Cu		98	98	98		
Dy					97	
Eu					97	
Fe		101	107	102		
La		97	98		95	
Li		97	101	97		
Mg		98	109	105		
Mn		98	102	100		
Mo		100	109	101		
Nd		97	97		94	
Ni		97	103	102		
Pb		91	97	98		
Pd					90	
Rh					93	
Ru					96	
Sb				99		
Se				99		
Si		107	119	108		
Sn				95		
Sr		98	104	98		
Te					101	
Th		95	100		98	
Ti		99	102	95		
Tl				99		
U		95	96		95	
V		93	99	95		
W		102	109	96		
Y				94		
Zn		98	104	102		
Zr		107	111	99		

Shaded results exceed acceptance criteria

Bold results for information only - spiked concentration less than EQL

nr = not recovered; spike concentration less than 20% of sample concentration.

(a) ±3.5% for Na (only); (b) Value for undiluted samples

A.2 Inorganic Anions Ion Chromatography Report

Battelle - Pacific Northwest National Laboratory
Radiochemical Science and Technology – IC Report
PO Box 999, Richland, Washington 99352

Project Number:	44832
Charge Code:	F40026
ASR Number:	6668
Client:	R. Russell
Total Samples:	3

	First	**Last**
RPL Numbers	03-0464	03-0466
Client IDs	DSS-1	DSS-3

Analysis Procedure	PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography"
Prep Procedure	None
Analyst	MJ Steele
Analysis Date	01/09/2003 – 01/10/2003
Calibration Date	01/09/2003
Cal/Ver Stds Prep Date	Cal 08/26/2002, Ver 04/11/2002
Excel Data File	ASR 6663 Rapko 6668 Russell.xls
M&TE Numbers	IC system (WD25214)
	Balance (360-06-01-031)
All Analysis Records	Chemical Measurement Center 98620 RIDS IC System File (IC-0035)

1-16-03

Prepared By **Date**

MJ Steele 1-16-03

Reviewed By **Date**

Sample Results

		F		Cl		NO_2		Br	
RPL Number	**Sample ID**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**
03-00464DB	Dilution Blank	0.013	0.013 U	0.013	0.029 J	0.025	0.025 U	0.013	0.013 U
03-00464	DSS-1	13	1,300(b)	13	1,520	25	19,000	130	130 U
03-00465	DSS-2	13	1,300(b)	13	1,520	25	19,000	130	130 U
03-00466	DSS-3	13	1,400(b)	13	1,510	25	19,200	130	130 U
03-00466 D	DSS-3 Dup	13	1,400(b)	13	1,550	25	19,000	130	130 U
	RPD		0%		3%		1%		(a)
QC Samples	**Sample ID**		**%Rec**		**%Rec**		**%Rec**		**%Rec**
03-00466MS	Matrix Spike @10000x		102		105		101		95
03-00466MS	Matrix Spike @20000x		96		95		96		94
LCS BS030108	Lab Control Sample		97		97		95		95
LCS BS030108	Lab Control Sample		99		100		97		96

		NO_3		PO_4		SO4		C_2O_4	
RPL Number	**Sample ID**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**	**MDL µg/mL**	**Result µg/mL**
03-00464DB	Dilution Blank	0.025	0.025 U	0.025	0.025 U	0.025	0.025 U	0.025	0.025 U
03-00464	DSS-1	250	144,000	25	4,430	25	8,560	25	1,930
03-00465	DSS-2	250	145,000	25	4,430	25	8,530	25	1,540
03-00466	DSS-3	250	147,000	25	4,340	25	8,660	25	1,480
03-00466 D	DSS-3 Dup	250	144,000	25	4,190	25	8,490	25	1,480
	RPD		2%		4%		2%		0%
QC Samples	**Sample ID**		**%Rec**		**%Rec**		**%Rec**		**%Rec**
03-00466MS	Matrix Spike @10000x		105		97		100		99
03-00466MS	Matrix Spike @20000x		89		95		98		97
LCS BS030108	Lab Control Sample		93		94		96		93
LCS BS030108	Lab Control Sample		95		96		98		96

RPD: relative percent difference EQL: estimated quantitation limit
MDL: method detection limit [(EQL/10)*Dil.Factors, where EQL is defined as the lowest calibration standard]
U flag: not detected above the MDL; MDL value is entered as the Result and is flagged with a 'U'

(a) RSD/RPD not calculated unless both sample and duplicate results >10*MDL.
(b) Results are upper bounds. Severe interferences from coeluting anions; e.g., formate, acetate.

Sample Analysis/Results Discussion

The samples submitted under ASRs 6668 required additional laboratory dilutions from 1,000x to 10,000x in order to ensure that the anions were measured within the calibration range and that the IC column was not overloaded during the analysis. The estimated method detection limit (MDL) are provided, and are based on one-tenth the lowest calibration standard adjusted for the dilutions used for reporting the results.

Data Limitations

Peak resolution and retention times were acceptable for all analytes except fluoride. The fluoride peak area exhibited significant broadening, which is indicative of the presence of one or more coeluting anions. Therefore, the fluoride results from this analysis should be considered an upper bound. (Note: Fluoride and acetate are measured using another method and the fluoride results reported above are for information only.)

Quality Control Discussion

Duplicate: A laboratory duplicate sample was prepared for sample 03-0466 (DSS-3). The RPD meets the laboratory's QA Plan acceptance criterion of <20% for all anions measured above EQL.

Laboratory Control Sample/Blank Spike (LCS/BS): A LCS/BS (LCS BS030108) was prepared by diluting the high range verification check standard (HVC020411) by 3x. The recoveries for all anions are well within the 80% to 120% acceptance criterion.

Matrix Spike: Two matrix spikes (MS) were prepared for sample 03-0466 by adding a known quantity of the mid-range calibration check standard (CCV020411). All MS recoveries were within the 75% to 125% acceptance criterion.

IC System QC samples: Eight calibration verification standards and nine calibration verification blanks were analyzed with the samples. All IC System QC produced results within the acceptance criteria of the laboratory's QA Plan.

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- The low calibration standards time the sample dilution factors are defined as the EQL for the reported results and assume non-complex aqueous matrices. Matrix-specific method detection limits or EQLs may be determined, if requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

A.3 Hydroxide Analysis Report

Battelle
. . . *Putting Technology To Work*

Client: Renee Russell — Date: 01/09/03

Subject: Hydroxide Analyses for: Cold Dissolved Saltcake Solution Simulant
ASR: 6668
Sample ID. 03-0464 DSS-1
03-0465 DSS-2
03-0466 DSS-3

A direct sample aliquot of three Fractions of Cold Dissolved Saltcake Solution Simulants (DSS-1 -3) were analyzed in duplicate for the hydroxide content following procedure PNL-ALO-228 using a Brinkman 636 Auto-Titrator. The titrant used was 0.2098 M HCl and the base standard, 0.1018 M NaOH was used for QC verification standards and matrix spike. -- see attached Chemrec_86..

The attached Report Summary indicates good RSD +/- 2% or less on the OH molarity (1st inflection point) on all three samples. The hydroxide Standard recoveries were 96 and 99% and the matrix spike recovery on the DSS-3 sample was 90%. No hydroxide was detected in the reagent blank.

The second and third inflection point frequently associated with carbonate and bicarbonate respectively, showed an excellent RSD 5% or less on all samples, well within the required RSD of +/- 15%. The results are accepted based on the QC data meeting the acceptance criteria as specified in the ASR.

Following is the report summary, the sample results calculated from the raw data, and the record file for the standardized acid and base used. Copies of the titration curves are available upon request.

Prepared by: ______________________ Date: 1/13/03
Reviewed by: ______________________ Date: 1/10/03

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # **6668**

WP# **F40026**

Hydroxide and Alkalinity Determination
Procedure: **PNL-ALO-228** Equip # **WB76843**

Report Summary for ASR # -- 6668

RPG #	Client ID	OH conc ug/mL	Concentration, moles / Liter First Point Molarity	RSD	Second Point Molarity	RSD	Third Point Molarity	RSD
03-0464	**DSS-1**	9.2E+03	**0.540**		**0.641**		**0.59**	
03-0464	**DSS-1**	9.0E+03	**0.527**	2%	**0.597**	5%	**0.61**	2%
03-0465	**DSS-2**	8.7E+03	**0.513**		**0.614**		**0.65**	
03-0465	**DSS-2**	8.7E+03	**0.511**	0.3%	**0.612**	0.3%	**0.63**	1%
03-0466	**DSS-3**	8.7E+03	**0.511**		**0.601**		**0.61**	
03-0466	**DSS-3**	8.8E+03	**0.520**	1%	**0.613**	1%	**0.64**	3%

OH conc (ug/mL) = M (g/L) * 17,000

mg/L MRQ	Molarity MRQ	Required RSD
7.5E+04	4.41	+/- 15%
not specified in ASR		

		Allowed Recovery Range
Reag. Blk.1	**0**	
Standard 1	**96%**	+/- 25%
Standard 2	**99%**	+/- 25%
MS 03-0466 Matrix spike	**90%**	+/- 20%

Note: Results are presented for the first, second, and third inflection points on the titration curves, as applicable. The first inflection point is generally associated with the hydroxide concentration. The second and third points generally represent the carbonate and bicarbonate concentrations.

Analyst: 1/13/03

Reviewer: 1/10/03

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

Batched with ASR's

ASR # **6668**
Client: Renee Russell
WP# F40026

File: R:\radchem\hydroxide\asr 6668
Analysis Date: **01/08/03**
Report Date: **01/09/03**

Procedures: RPG-CMC-228: Determination of Hydroxyl (OH-) and
Alkalinity of Aqueous Solutions, Leachates and Supernates
and Operation of Brinkman 636 Auto-Titrator

Analyst: 1/13/03

Equip # WB76843 Lab Loc. 525

	Titrant	Molarity	Chem Rec#
Strong	HCl	**0.2098**	**86**

Std. & Spike	Molarity
NaOH	**0.1018**

RPG #	Sample ID		Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	**Diluted** Initial pH reading	**OH** **1st Equivalence** Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
03-0464	DSS-1		na	0.200	0.2564	1.282	7	12.469	0.515	11.184	0.108	0.540	
03-0464	DSS-1	Replicate	na	0.400	0.5027	1.257	8	12.572	1.004	11.143	0.211	0.527	2.56%
03-0465	DSS-2		na	0.400	0.5035	1.259	9	12.589	0.978	11.201	0.205	0.513	
03-0465	DSS-2	Replicate	na	0.400	0.5011	1.253	10	12.608	0.974	11.117	0.204	0.511	0.41%
03-0466	DSS-3		na	0.400	0.4949	1.237	11	12.634	0.974	11.180	0.204	0.511	
03-0466	DSS-3	Replicate	na	0.400	0.5057	1.264	12	12.507	0.992	11.196	0.208	0.520	1.83%
Reag. Blk.1				5.00			1	10.834				**OH % Recovery**	
Standard 1	0.1018 M NaOH			5.000	5.0481	1.010	2	12.613	2.323	7.881	0.4874	**95.7%**	
Standard 2	0.1018 M NaOH			5.000	5.0409	1.008	15	12.622	2.405	7.848	0.5046	**99.1%**	
MS 03-0466	+ 2mL 0.1018 M NaOH			0.200	0.2456	1.228	13	12.759	1.368	11.071	0.2870	**90.3%**	MS

Buffer	ORION Lot #	CMS#	Expire Date
10	910110-GY-1	186909	Apr-04
4	910104-GX-1	186908	Mar-04
7	910107-GY-2	186907	Feb-04

Initial	pH 7.0 reading =	7.002
Final	pH 7.0 reading =	6.992

Performance checks using Balance # 360--01-06-037

Pipet #	Vol.	Wt.	Pipet #	Vol.	Wt.
C301764	5.00	5.0049	92501	0.200	0.1984
C301764	5.00	4.9987	92501	0.200	0.1991
C301764	5.00	5.0121	92501	0.200	0.1995

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # 6668

WP# F40026

File: R:\radchem\hydroxide\asr

Procedures: RPG-CMC-228: Determination of Hydroxyl (OH-) and
Alkalinity of Aqueous Solutions, Leachates and Supernates
and Operation of Brinkman 636 Auto-Titrator
Equip # WB76843

Analyst: 1/13/03

Titrant	Molarity
HCl	0.2098

RPG #	0	Sample Vol. (mL	2nd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	nillimole RPD	3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
03-0464	0	0.200	1.126	7.500	0.128	0.641		1.688	4.661	0.118	0.590	
03-0464	Replicat	0.400	2.142	8.121	0.239	0.597	7.12%	3.305	4.651	0.244	0.610	3.41%
03-0465	0	0.400	2.149	8.169	0.246	0.614		3.380	4.542	0.258	0.646	
03-0465	Replicat	0.400	2.140	8.003	0.245	0.612	0.43%	3.349	4.552	0.254	0.634	1.80%
03-0466	0	0.400	2.120	8.099	0.240	0.601		3.292	4.628	0.246	0.615	
03-0466	Replicat	0.400	2.160	8.197	0.245	0.613	1.90%	3.376	4.610	0.255	0.638	3.69%
						2-nd Recovered						
Standard 1		5.000	2.399	4.039	0.01594	3.1%						
Standard 2		5.000	2.491	3.839	0.01804	3.5%						
MS 03-0466		0.200	1.997	7.811				2.605	4.650			

Matrix spike recovery is calculated as follows:
Spike = 2.00 mL 0.1018 N NaOH was added to the 0.100-mL of sample for each matrix spike.
SpikeTitrant vol. (sample @ .1mL + spike) - SampleTitrant vol. (average sample only equated to .1mL) * 0.2034 N (HCl titrant) = meq. OH
meq OH / 2.00 mL added = meq OH/mL found / 0.1018 N OH added * 100 = % recovered.

Chem Rec_86 Prep date: 7/15/02

Preparation and Standardization of 0.1 M, and 0.01M NaOH
and Preparation and Standardization of 0.2 M HCl and dilutions

WP# K88426 Prepared by: rg Swoboda

Request: *I need more NaOH and HCl solutions made up for the OH- analysis procedure --- rgs*

Preparation: Prepared ~ 0.1M NaOH and 0.2M HCl from reagent grade stock . Standardize the ~0.1M NaOH solution against NIST Potassium Acid Phthalate KHC8H4O4 (KAP) . Then prepare 0.2M HCl and standardize against the calibrated 0.1M NaOH. Do a verification check on all the subsequent dilutions of NaOH and HCl.

Standardization : Use NIST SRM 84j, Potassium Acid Phthalate KHC8H4O4 (KAP) --CMS# 52232
Technique used will be via hand-titration to the phenopthalein endpint. Project titration for about 20-25 mL of a 50 mL burrette.
----- KHC8H404 = 204.23 g/mole or mg/meq
Hence, ~20 mL * 0.1M NaOH = 2 meq. and ~2 meq of KAP = 204.22 mg/meq * 2 = ~ 400 mg KAP weighed on 5-place balance --- All preparations will be certified for 2 yrs beyond calibration date --- rgs.

0.1M NaOH and dilutions

Verification Test #	Wt. of **KAP**	Vol. Of ~ **0.1M NaOH** to neutralize	NaOH Molarity =a * 1000 / b * 204.23	Molarity Error +/- @ 1 s	% error
1	0.43336	20.85	0.10177		
2	0.49981	24.05	0.10176		
3	0.63432	30.50	0.10183		
Standardized Average NaOH Molarity =			**0.10179**	0.00004	0.04%

10X cut of ~ 0.1M NaOH

Verification Test #	Wt. of **KAP**	Vol. Of ~ **0.01M NaOH** to neutralize	NaOH Molarity =a * 1000 / b * 204.23	Molarity Error +/- @ 1 s	% error
1	0.06842	33.05	0.01014		
2	0.07756	37.42	0.01015		
3	0.07141	34.42	0.01016		
Standardized Average NaOH Molarity =			**0.01015**	0.00001	0.11%

0.2M HCl and dilutions

Titration Id.	aliquot of acid	Vol. of **0.10179M NaOH** to neutralize	**Molarity of Acid** in Sample	Molarity Error +/- @ 1 s	% error
1	20.00	41.20	0.2097		
2	20.00	41.25	0.2099		
3	20.00	41.20	0.2097		
Standardized Average HCl Molarity =			**0.2098**	0.00015	0.07%

Titration Id.	aliquot of acid	Vol. of **0.01015M NaOH** to neutralize	**Molarity of Acid** in Sample	Molarity Error +/- @ 1 s	% error
1	20.00	41.05	0.0208		
2	20.00	41.10	0.0209		
3	20.00	41.00	0.0208		
Standardized Average HCl Molarity =			**0.0208**	0.00003	0.12%

0.0052 M HCl was prepared by making an exact 40X cut of 0.2098 M HCl -- Error ~ 0.5%

Analyst/Date r. g. Swoboda 1/9/03

Expiration Date on Stds.
7/15/04

A.4 TIC/TOC Report

Battelle - Pacific Northwest National Laboratory
Radiochemical Science and Technology
TOC/TIC Report – Hot Persulfate Oxidation Method
PO Box 999, Richland, Washington 99352

Project Number:	44832
Charge Code:	F40026
ASR Number:	6668
Client:	Renee Russell
Total Samples:	3

	ASR 6668
RPL Numbers	03-00464 to 03-00466
Client IDs	DSS-1, DSS-2, DSS-3

Analysis Procedure	PNL-ALO-381, "Direct Determination of TC, TOC, and TIC in Radioactive Sludges and Liquids by Hot Persulfate Method"
Prep Procedure	None
Analyst	M. Steele
Analysis Date	1/10/2003
Cal/Verify Standards	TOC CMS-53219, TIC CMS-161359
LCS/MS Standards	TOC CMS-161713, TIC CMS-161732
Excel Data File	ASR 6663 6668 HP rev1.xls
M&TE Numbers	Carbon System (WA92040)
	Balance (360-06-01-023)
All Analysis Records	Project File

1-22-03

Prepared By **Date**

1-22-03

Reviewed By **Date**

Laboratory Control Sample/Blank Spike: A LCS/BS was analyzed with the samples. At 99% TIC and 99% TOC, the LCS/BS recoveries are well within acceptance criterion of 80% to 120%.

Duplicate: Precision of the carbon measurements is demonstrated by the RPD between sample and duplicate. No duplicate sample was provided by the client. A laboratory duplicate was prepared from sample 'DSS-3'. The TIC RPD result of 1% and the TOC result of 3% are both well within the ASR-defined acceptance criterion of <15% RPD. Note: the RPD is only calculated if both the sample and duplicate result exceed 5xMDL.

Matrix Spike: The accuracy of the carbon measurements can be estimated by the recovery results from the MS. A MS was prepared from sample 'DSS-3', an inorganic standard, and an organic standard (see cover page for standard identification). The TIC and TOC MS recoveries are well within the acceptance criterion of 75% to 125% recovery.

Deviation from Procedure

None

General Comments

1) The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
2) Routine precision and bias are typically ±15% or better for non-complex samples that are free of interferences.
3) The estimated quantitation limit (EQL) is defined as 10 times the MDL. Results <10xMDL have higher uncertainties, and RPDs (or RSDs, if applicable) are not calculated if the results are <5xMDL.
4) For both the TC and TOC, the analysis MDL is based on three times the standard deviation of a set of historical 'system blank' data. The sample MDL (in µgC/mL or µgC/g) are calculated by using the analysis MDL adjusted for the sample volume or mass.

PNNL Radiochemical Processing Group: TOC/TIC/TC Calculations **Review** Report - Hot Persulfate Method PNL-ALO-381

Client:	**R. Russell/ B. Rapko**	Analyzer M&TE: WC01713 -- 701		
Project :		Balance M&TE: 360-06-01-023		
Work Pkg:	**CMC**	TOC STD: alpha-D-glucose Aldrich CMS#53219(Cal/ICV), Sigma CMS#161713(MS/LCS)	40.00% Carbon	<<[G]
Analyst/date:	**MJ Steele 1/15/2003**	TIC STD: Calcium Carbonate Baker CMS#161359(Cal/ICV), Mallinckrodt CMS#161732(MS/LCS)	11.99% Carbon	<<[C]
ASR:	**6668/6663**			

Sample Results		Note: Sample weights are on "as received" basis; i.e., wet weight											
		[I] Raw	[J]	[K] Sam	TIC	TIC	[M] Raw	[N]	[O] Sam	TOC	TOC	TC	TC
ACL Number	Client Sample ID (Liquids)	TIC (ug C)	Blk (ug C)	Vol (ml)	(ug C/ml)	RPD (%)	TOC (ug C)	Blk (ug C)	Vol (ml)	(ug C/ml)	RPD (%)	(ug C/ml)	RPD (%)
03-00451	MAI Feed Final A	1317	18	0.20	6,383		569	35	0.20	2,752		9,135	
03-00452	MAI Feed Final B	1323	18	0.20	6,412	0.5	585	35	0.20	2,835	3	9,247	1
03-00464	DSS-1	1215	18	0.20	5,882		701	35	0.20	3,432		9,314	
03-00465	DSS-2	1199	18	0.20	5,803		699	35	0.20	3,422	0	9,225	1
03-00466	DSS-3	1186	18	0.20	5,739		690	35	0.20	3,376		9,115	
03-00466 DUP	DSS-3	1198	18	0.20	5,798	1	707	35	0.20	3,463	3	9,261	2
03-00466 MS	DSS-3	3041	18	0.20	see below		1519	35	0.20	see below		see below	
	(Note: For any TOC or TIC result displayed as "# (<mdl)" the final reported "less than" concentration is calculated by dividing the Method Detection Limit by [K])												

Matrix Spike Results										
		[Q] Raw MS	[R] MS Blk	[S] Sam	[T] MS Sam	[V] Sample	Spike	[U] Spike	MS	
ACL Number	Client Sample ID	(ug C)	(ug C)	(ug C/ml)	Vol (ml)	(ug C)	wt (g)	(ug C)	% Recovery	
03-00466 MS	TIC Recovery	3041	18	5739	0.20	1148	0.0155	1858	**98.1**	**TIC**
	TOC Recovery	1519	35	3376	0.20	675	0.0020	800	**106.7**	**TOC**
	Total Carbon Recovery (TIC + TOC)							2658	**100.7**	**TC**

Reviewer/date: 1-22-03

R/ MWUrie 1-22-03

HOT PERSUL E WORKSHEET

M. Steele 1-15-03

Client R. Russell / B. Rapko ASR 6668/6663 Analyst M. Steele Date January 10, 2003

Procedure: PNL-ALO-381 Analyzer M&TE: Balance M&TE: 360-06-01-023

Standards:
TOC STD: alpha-D-glucose Aldrich ~~CAS~~ cms #53219 (Cal/ICV), Sigma ~~CAS~~ cms #161713 (ms/LCS) : 40.00% Carbon

TIC STD: Calcium Carbonate Baker Cms #161359 (Cal/ICV), Mallinckrodt Cms #161732 (ms/LCS); 11.99% Carbon

		Standard WT (g)		Sample		TIC			TOC		
Lab ID	Client ID	TIC	TOC	Vol.	Wt.(g)	std value	inst. Reading	% recovery	std value	inst. Reading	% recovery
Blank 1							17.54			33.65	
Blank 2							14.85			30.64	
ICV I		0.0119	0.0042				1553			1635	
ICV 2		0.0111	0.0023				1329			925	
BS		0.0095	0.0037				1163			1463	
03-00451	MAI Feed Final A			0.2mL			1317			569	
03-00452	MAI Feed Final B						1323			585	
03-00464	DSS-1						1215			701	
03-00465	DSS-2						1199			699	
03-00466	DSS-3						1186			690	
03-00466 Dup							1198			707	
03-00466 MS	↓	.0155	.0020	↓			3049			1519	
CCV	—	.0140	.0068				1683			2728	
Blank 3	—						21.02			39.46	

Review DC [illegible] 1-16-03

Carbon Bench sheet.xls

A.5 Organic Acids Ion Chromatography Report

Pacific Northwest National Laboratory (PNNL) // Battelle Northwest
Advanced Organic Analysis Group (AOAM)

Organic Anions/Fluoride by Ion Chromatography Report

Project / WP#:	44832 / F40026
ASR#:	6668
Client:	Renee Russell
Total Samples:	3

RPL #	Client ID
03-464	DSS-1 Simulant
03-465	DSS-2 Simulant
03-466	DSS-3 Simulant

Procedure: TPR-RPP-WTP-212, *Analysis and Quantification of Fluoride and Other Inorganic and Organic Anions in Hanford Tank Waste*

M&TE Number:	WD12888	Dionex IC Analyzer System
	P37596	Mettler AE50 Balance

Analyst: GM Mong

Analysis Date: 1-17-03

Analysis Files: Data: gm0117E01
Standards: BNW14062, p. 54, p.61
Spreadsheets: IC Std 14062-61

Prepared By

Blandina Valenzuela 2-10-03
Reviewed By (analysis, report)

Blandina Valenzuela 2-10-03
Reviewed By (QC data)

Three samples, DSS-1, DSS-2, DSS-3 (Cold Dissolved Saltcake Simulant), were submitted for fluoride analysis and organic anion analysis. The requested analytes (fluoride, acetate, and oxalate) fall within the capacity of separation using a Dionex AS-15 column and the procedure originally developed for fluoride analysis (TPR-RPP-WTP-212, *Analysis and Quantification of Fluoride and Other Inorganic and Organic Anions in Hanford Tank Waste)* All QC acceptance criteria found within the procedure were followed. Preliminary analysis of a single sample indicated a large individual difference in the native concentration of the organic ions and fluoride. This requires two separate analyses to be performed in order to bring the native concentrations of the analytes within working concentrations. The samples were given a 250 fold dilution by volume, and then two separate analytical solutions were prepared: one that was a 5 fold dilution of the initial dilution, and one which was a 50 fold dilution of the initial dilution. The reported values for fluoride and oxalate result from the 1250 fold overall dilution; and acetate, due to the large amount present, results from the 12500 fold dilution.

All analytical work was done on a volume dilution basis, using class A volumetric glassware and calibrated pipets. When V/V dilutions are done, no density factors enter into the calculation of analyte concentration.
This work utilizes the QC acceptance criteria developed in test plan TP-RPP-WTP-024 MDL/EQL.

Table 1. **Analysis**

The results from the analysis of the saltcake solutions are provided in Table 1 below. The data reported are the average of duplicate injections

Table 1. Organic Anion Results for DSS-1,2,3 Dissolve Saltcake Simulant

RPD success criteria: <20% when >10x MDL **RPD success criteria: <15% when >10x MDL**			
Sample ID	**Fluoride mg/L**	**Acetate mg/L**	**Oxalate mg/L**
DSS-1	500	11000	810
DSS-2	560	11000	850
DSS-3	650	10000	900
MDL (est)	22	660	57
EQL (est)(1)	130	2000	170
Preparation DF	250	250	250
Analysis DF	5	50	5
Total DF	1250	12500	1250
MDL (at the instrument)	0.018	0.053	0.045

(1) In the absence of other supporting data, the EQL has been set at 3 times the MDL. The EQL for fluoride is set at the LLS level, adjusted for the appropriate dilution factor.

2. Quality Control Sample Comments

Duplicate (DUP) and Triplicate (TRIP). No duplicate samples were delivered for this sample set. Duplicate injections of diluted samples were done on every sample.

Post Spike (PS) and Post Spike Duplicate (PSD). These samples cannot be successfully spiked in the delivered matrix so that the included volume of spike would be <10% of the sample. Several of the analytes would exceed their respective solubilities in water if this exercise was undertaken. Therefore, a spike was added to the initial 250 fold dilution of sample DSS-2 (03-465). The QC available is therefore a **Post Spike**. The spike recoveries as well as the RPD between the PS and PSD meet the QC success criteria. The resulting data for PS and PSD is derived from a 50 fold dilution of the PS and PSD dilution. All values used for the calculation are above the estimated MDL. PS samples were also run at the 5 fold dilution level in anticipation of better estimation of the recovery of fluoride and oxalate; these were found to be outside the calibration curves for these analytes. Regardless, the data (not reported here) was found to be within the acceptance criteria for fluoride and oxalate at this lower dilution level.

Table 2. Organic Anion Results for the AP-104 Supernatant PS and PSD samples (ASR 6668)

Post Spike Success Criteria: 75% to 125% of expected value						
Analyte/Sample	**MDL* mg/L**	**Spike mg/L**	**Sample mg/L**	**Measured mg/L**	**Rec %**	**RPD %**
FluoridePS	0.9	5.0	2.2	7.6	109	
FluoridePSD		5.0	2.2	7.4	105	4
	mg/L	**mg/L**	**mg/L**	**mg/L**	**%**	**%**
Acetate PS	2.7	45	43	96	118	
Acetate PSD		45	43	97	119	1
	mg/L	**mg/L**	**mg/L**	**mg/L**	**%**	**%**
Oxalate PS	2.3	8.9	3.3	11	89	
Oxalate PSD		8.9	3.3	12	95	6

*MDL's are derived from the instrument MDL multiplied by the dilution factor applied to the post spike

Preparation Blank (PB) and Laboratory Control Standard (LCS).

The preparation blank is an in-laboratory sample of deionized water, treated as a sample, and subjected to dilution (1: 1250) and included in the batch. The EQL values are derived from this lower dilution value, and this affords a lower EQL for acetate than in the analysis data. The LCS is an in-laboratory standard similar to the mid-range of the calibration curve. The values reported for the LCS are represented as those at the instrument.

Table 3. Organic Anion Results for the PB and LCS

PB success criteria : <EQL **LCS success criteria: 80% - 120% Recovery**			
Sample ID	**Fluoride mg/L (Rec)**	**Acetate mg/L (Rec)**	**Oxalate mg/L (Rec)**
PB	<130 (EQL)U	<200 (EQL)U	<170 (EQL)U
LCS measured	0.42(105%)	0.64(100%)	0.51(98%)

Explanation of flag: U: analyte is either not observed or the determination was below the included MDL level.

Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Standards.

ICB and CCB standards met the success criteria. All analytes were below the MDL levels shown below. CCB values are collected after CCV values, with 10 total samples between CCV samples.

Table 4. Organic Anion Results for the ICB and CCB Standards

ICB/CCB success criteria: <MDL at the instrument			
Sample ID	**Fluoride mg/L**	**Acetate mg/L**	**Oxalate mg/L**
MDL	0.018	0.053	0.045
ICB	< 0.018 U	< 0.053 U	< 0.045 U
CCB-1	<0.018 U	<0.053 U	<0.045 U
CCB-2	< 0.018 U	< 0.053 U	< 0.045 U
CCB-3	<0.018 U	<0.053 U	<0.045 U

Explanation of flag: U: analyte is either not observed or the determination was below the included MDL level.

Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) Standards.

ICV and CCV met the acceptance criteria. CCV samples are run with a maximum of 10 samples between CCV data points.

Table 5. Organic Anion Results for the ICV and CCV Standards

ICV/CCV success criteria: 90% to 110% Recovery at the instrument			
Sample ID	**Fluoride mg/L (Rec)**	**Acetate mg/L (Rec)**	**Oxalate mg/L (Rec)**
ICV measured	0.43 (105%)	0.65 (105%)	0.57 (103%)
ICV expected	0.41	0.62	0.56
CCV-1 measured	0.43 (107%)	0.70 (109%)	0.54 (104%)
CCV-1 expected	0.40	0.64	0.52
CCV-2-measured	0.44 (109%)	0.70 (108%)	0.54 (104%)
CCV-2 expected	0.40	0.64	0.52
CCV-3 measured	0.44 (110%)	0.61 (95%)	0.56 (107%)
CCV--3 expected	0.40	0.64	0.52

Low-Level Standard (LLS).

The LLS met the success criteria. By examination of the integrated area of the LLS analytes, the MDL level is approximated by 1/3 of the LLS (or EQL) level. The response for fluoride is somewhat higher than for the organic acids; hence the MDL for fluoride is set at 1/6 the LLS level. This criteria is applied to all data released by this laboratory.

Table 6. Organic Anion Results for the LLS

LLS success criterial: 75% to 125% Recovry at the instrument			
Sample ID	**Fluoride mg/L (Rec)**	**Acetate mg/L (Rec)**	**Oxalate mg/L (Rec)**
LLS measured	0.11 (107%)	0.16 (98%)	0.14 (105%)
LLS expected	0.10	0.16	0.13

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