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# Investigation of Thermolytic Hydrogen Generation Rate in Tank 44 Dissolved Saltcake Samples

**C.J. Martino**
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August 2021
SRNL-STI-2019-00730, Revision 1

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# EXECUTIVE SUMMARY

Saltcake core samples collected from Tank 44 in 2006 were dissolved to provide material for HGR measurements applicable to F-Area dissolved saltcake material. Additionally, characterization was performed on the Tank 44 saltcake material.

The following are key results from the Tank 44 saltcake characterization.

- The Tank 44 Upper Saltcake Composite, corresponding to the 171 to 285 inch tank level, contained by mass approximately 69% sodium nitrate, 11% sodium carbonate, 8% sodium nitrite, smaller amounts of other salts and components, and 9% unquantified (which includes water, water of hydration, oxygen/hydrogen content of oxides and hydroxides, and uncertainty).
- The Tank 44 Lower Saltcake Composite, corresponding to the 76 to 114 inch tank level, contained by mass approximately 49% sodium carbonate, 18% sodium nitrate, smaller amounts of other salts, at least 8% sludge, and 9% unquantified (see above).
- The dissolved saltcake contained free hydroxide less than quantifiable (<0.01 M) due to the limited quantity of material that could be removed from the Shielded Cells based on the sample radioactivity. Measurement by pH paper provided an approximate pH of 12.

The following are key results from the Tank 44 HGR testing.

- During boiling at 106.7 °C, HGR for Tank 44 dissolved saltcake without added glycolate was $7.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$.
- During boiling at 106.9 °C, HGR for Tank 44 dissolved saltcake with 1000 mg/L of added glycolate was $8.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$.
- For the test without added glycolate, the first several HGR measurements at 70, 85, and 100 °C gave indication of the release of dissolved hydrogen and should not be used to represent the sustained thermolytic HGR for those temperatures. The measurements at boiling are the best representation of thermolysis in this testing.
- Carbon dioxide was observed at concentrations up to 6 vol% in the flow-system offgas for the test at boiling.
- Methane generation was observed at 100 °C and boiling. Methane concentration in the total gas generated during testing remained well below the lower flammability limit for methane in air.
- The addition of 1000 mg/L of glycolate did not have a significant impact on the hydrogen generation rates measured during this testing.
- The low hydroxide concentration in the Tank 44 dissolved saltcake likely influenced the relatively low thermolytic HGR and high carbon dioxide release observations in this testing.

Based on the observation that methane was generated or released upon heating SRS radioactive Tank 44 waste samples to 100 °C and above, we recommend gaining a greater understanding of the cause and mechanism of its generation. First, the applicable literature should be reviewed to reveal the thermolytic methane generation mechanisms of possible methane generating species in the SRS CSTF. If warranted, a plan should be developed for simulant tests with methylated siloxanes and other applicable compounds in order to gain a better mechanistic understanding of methane generation in the SRS CSTF.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| CI | Confidence Interval |
| CPC | Chemical Processing Cell |
| CSTF | Concentration, Storage, and Transfer Facilities |
| DAC | Data Acquisition and Control |
| DMA | Direct Mercury Analysis |
| DSA | Documented Safety Analysis |
| DWPF | Defense Waste Processing Facility |
| $E_a$ | Activation Energy |
| EPA | Environmental Protection Agency |
| GC | Gas Chromatograph |
| HGR | Hydrogen Generation Rate |
| ICA | Ion Chromatography for Anions |
| ICP-AES | Inductively Coupled Plasma – Atomic Emissions Spectroscopy |
| ICP-MS | Inductively Coupled Plasma – Mass Spectroscopy |
| LOD | Limit of Detection |
| LOQ | Limit of Quantification |
| LTAD | Low Temperature Aluminum Dissolution |
| MMHg | Monomethylmercury |
| MS&E | Measurement Systems and Equipment |
| M&TE | Measuring and Test Equipment |
| n.d. | Not determined |
| NGA | Nitric-Glycolic Acid |
| OMCTS | Octamethylcylclotetrasiloxane |
| PISA | Potential Inadequacy in the Safety Analysis |
| ppmv | Parts per million by volume |
| RSD | Relative Standard Deviation |
| SPF | Saltstone Processing Facility |
| SRNL | Savannah River National Laboratory |
| SRR | Savannah River Remediation |
| SRS | Savannah River Site |
| SVOA | Semivolatile Organics Analysis |
| TC | Total Carbon |
| TIC | Total Inorganic Carbon |
| TOC | Total Organic Carbon |
| TTQAP | Task Technical and Quality Assurance Plan |
| TTR | Technical Task Request |
| VOA | Volatile Organics Analysis |
| WTP | Waste Treatment Plant |

# REVISION HISTORY

| Revision Number | Summary of Changes | Date |
|---|---|---|
| 0 | Initial Issue | February 2020 |
| 1 | • In Tables 3-1 and 3-3, corrected charge on glycolate to -1<br>• In Table 3-5, changed units to wt% for all analytes<br>• In Table 3-6, added units of dpm/g to Np-239 and Am-243 | August 2021 |

# 1.0 Introduction

## 1.1 The Issue of Thermolytic Hydrogen Generation

In February 2017, Savannah River Remediation (SRR) declared a Potential Inadequacy in the Safety Analysis (PISA) in each of three Savannah River Site (SRS) Liquid Waste facilities: Concentration, Storage, and Transfer Facilities (CSTF),[1] Saltstone Processing Facility (SPF),[2] and the Defense Waste Processing Facility (DWPF).[3] The PISAs relate to how organics can impact the radiolytic and thermolytic production of hydrogen, which is a flammable gas.

With the implementation of the Nitric-Glycolic Acid (NGA) flowsheet at DWPF, small amounts of glycolate will transfer into the SRS CSTF from the DWPF recycle stream. A literature survey indicated that glycolate can produce hydrogen via thermolytic reactions.[4] Work performed for the Hanford Reservation tank waste programs indicated that glycolate decomposition in high pH solutions containing soluble aluminum generates hydrogen.[5-6] A prior analysis of this literature data predicted the expected influence of glycolate on radiolytic and thermolytic hydrogen generation in the SRS CSTF, SPF, and DWPF.[7]

## 1.2 Documents Related to This Task

To address these needs, SRR issued a Technical Task Request (TTR) requesting that Savannah River National Laboratory (SRNL) perform simulant and radioactive waste testing to support thermolytic Hydrogen Generation Rate (HGR) determination for CSTF processes.[8] This report covers a portion of the data gathered as Task 2 of the TTR, specifically addressing data from radioactive waste spiked with glycolate. A Task Technical and Quality Assurance Plan (TTQAP) further defines the radioactive-waste and simulated-waste testing.[9] Finally, a Run Plan gives test details specific to the HGR testing of dissolved radioactive waste saltcake samples from Tank 44.[10] Testing was performed in a flow systems consistent with previous radioactive testing[11] with minor modifications as discussed in Section 2.1.

## 1.3 Previous Thermolytic HGR Measurements at SRNL

SRNL conducted initial research to determine the thermolytic HGR with simulated and radioactive waste. Gas chromatography methods were developed and used with air-purged flow systems to quantify hydrogen generation from heated simulated and radioactive waste at rates applicable to the CSTF Documented Safety Analysis (DSA). Initial testing included a measurement of HGR on waste from Tank 38 and simulated waste with the most common SRS CSTF organics at temperatures up to 140 °C.[12] HGR measurements of Tank 50 samples with and without additives (not including glycolate) were performed using a sealed measurement system.[13] After redesign of a flow system to minimize impacts from glass and stainless steel components to the extent possible, HGR was quantified for a Tank 38 sample with and without 1570 mg/L glycolate, [14] for a Tank 50 sample with 350 mg/L glycolate,[14] for a Tank 28 sample with and without 500 mg/L glycolate,[11] and for a Tank 39 sample with and without 2000 mg/L glycolate.[11] In all cases, the addition of glycolate was either at or well above predicted maximum concentrations, depending on the test objectives. Measurement with Tank 22 samples with and without 120 mg/L of added glycolate showed none to minimal thermolytic HGR in that dilute sample matrix with the detection limits of the flow system.[15] In addition, considerable testing with non-radioactive simulants was performed to screen tank farm organics for thermolytic production of hydrogen, quantify thermolytic HGR from glycolate and the most reactive tank farm organics over the range of CSTF conditions, and develop reaction models for thermolytic HGR applicable to SRS waste.[16]

## 1.4 Test Objectives

This report contains HGR measurements of Tank 44 radioactive samples with and without added glycolate. The primary goal for HGR measurements of Tank 44 saltcake is to extend the knowledge from the previous sample measurements[12-15] to dissolved saltcake. The purpose of the heated measurements without added glycolate is to investigate the thermolytic HGR of the mixture of organic compounds currently residing in the Tank 44 saltcake. SRR issued a report that outlined the justification for the tanks selected.[17] Tank 44 may contain legacy organics from F canyon and 1F and 2F evaporator system operation. The objective for measurement of thermolytic HGR of a Tank 44 sample with added glycolate is to provide additional confirmation of the simulant testing.

An additional goal of this testing was to provide characterization information for Tank 44 saltcake.

### 1.5 Thermolytic Hydrogen Generation Background

A background of thermolytic hydrogen generation applicable to current CSTF organic compounds and future additions of glycolate are detailed elsewhere.[7, 12] In work designed to support flammability calculations at the Hanford Waste Treatment Plant (WTP), Hu developed an empirical model describing the thermolytic production of hydrogen from organic molecules as a function of temperature, organic carbon content, and aluminum content.[18] In 2017, Crawford and King used observations and glycolate destruction rate data generated by Ashby et al.[5] to develop a rate expression for hydrogen generation due to glycolate thermolysis.[7] The glycolate thermolysis HGR model was predicted to be a function of temperature, glycolate, nitrite, and aluminum concentration and to have an unconfirmed inverse proportionality to hydroxide concentration.

Simulant work performed at SRNL on thermolysis of glycolate and CSTF organic compounds at conditions applicable to SRS waste has determined relationships that differ from the rate expressions generated by Hu and by Crawford and King.[19] Most strikingly, most of the SRNL testing for glycolate and CSTF organic compounds showed a direct relationship to hydroxide concentration. While hydroxide is a major component of both SRS and Hanford tank waste, hydroxide did not appear in Hu's rate expression and had the opposite functionality relative to expectations in Crawford and King's rate expression. The SRNL simulant testing maintained the direct relationship between concentration of the organic compound of interest and the thermolytic HGR.

### 1.6 Glycolate Concentration Applicable to HGR Testing

A portion of the testing with the Tank 44 dissolved saltcake sample will have added glycolate. Simulant testing to date has shown that the HGR from glycolate primarily increases with increased organic concentration, hydroxide concentration, and overall salt (i.e., sodium) concentration.[16] At the time of HGR test planning and execution, the salt composition of the Tank 44 saltcake samples was unknown. The salt solution resultant from Tank 44 saltcake dissolution was expected to be primarily sodium nitrate with smaller amounts of sodium hydroxide, sodium nitrite, and other salts. However, not enough characterization data was available to predict the thermolytic HGR of glycolate using interim models. With this absence of information, it was recommended that 1000 mg/L of glycolate be added to the Tank 44 dissolved saltcake composite as it gave a good possibility of measurable HGR from glycolate thermolysis at 70 °C and above. Note that based on expected future processing, levels of glycolate in Tank 44 or similar dissolved saltcake material is not expected to approach 1000 g/L. The ability to differentiate the contribution of glycolate from the contribution of the other organics in the sample with respect to the production of hydrogen will be dependent on the concentration and relative reactivity of the other organics.

## 2.0 Experimental

### 2.1 Shielded Cells Flow System Apparatus

The flow-system apparatus used in the Tank 44 thermolytic HGR testing in the Shielded Cells is identical to the system used for Tank 22, Tank 28, Tank 38, Tank 39, and Tank 50 thermolytic HGR testing with the exception that the glass funnel for sample addition was removed.[11, 14-15] The apparatus was based on the simulant testing flow system being used for Task 1 of the TTR and TTQAP.[8-9, 16] The apparatus combined design elements from equipment used for previous one liter and four liter sludge batch qualification Chemical Processing Cell (CPC) testing.[20-21] The vessel holding the radioactive waste sample and the sealing lid (assuring capture of gases during testing) were made of Teflon®, with an internal volume of approximately 1.2 liters. Use of a flow-through system with minimal headspace is consistent with the HGR measurement apparatus recommended and developed for qualification of radioactive-waste feeds at the Hanford WTP, although dimensions are larger for this application.[22-23] Teflon® fluoropolymer was used for HGR flow-system measurements to minimize potential interferences from performing tests in glass or stainless-steel vessels and was chosen based on literature preparations and recommendations from simulant testing.[5, 16]

Figure 2-1 contains two photographs of the HGR measurement system. The photograph on the left is the system with the stainless-steel pot prior to its use in the Low Temperature Aluminum Dissolution (LTAD) tests.[24] The photograph on the right is the same system but with a Teflon® pot installed in SRNL Shielded Cells, A Block Cell 2 (note that the insulation is not shown in the photograph). A separate Teflon® pot is installed for each tank sample to be tested.

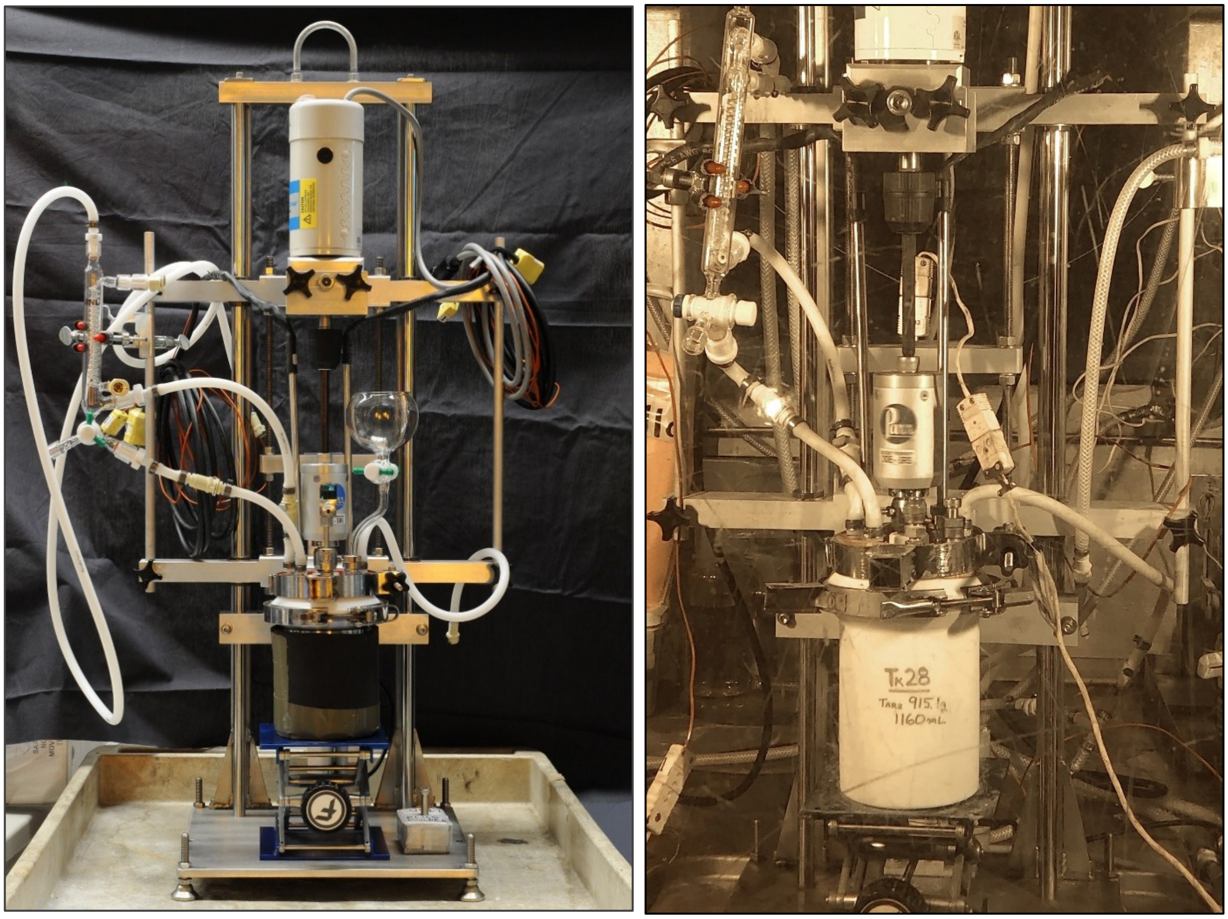

**Figure 2-1. HGR measurement flow system prepared for installation (left) and in operation (right).**

Heating was provided using two 0.375-inch diameter Alloy 800 heating rods powered by an automated direct current power supply (TDK-Lambda Genesys, GEN150-10). Mixing was controlled using a mixer system consisting of a Servodyne mixing head coupled to an agitator shaft via a Parr high torque magnetic drive. A Teflon® pitched turbine impeller was attached to a Teflon®-coated agitator shaft. The slurry was continually stirred over the course of the testing. Purge gas was controlled using an MKS Model 647 Multi Gas Controller and MKS Model 1179 Flow Controller. An offgas condenser allowed condensate to reflux into the reactor containing the sample material. Non-condensable gas exiting the condenser was sampled by a dedicated Agilent 3000A dual column micro gas chromatograph (GC), as described in further detail in a later subsection. A data acquisition and control (DAC) system was utilized for control of the heating rods, mixing, and purge gas flow and for automated data logging. A schematic depicting integration of the primary components of the HGR measurement flow system apparatus is given in Figure 2-2.

Additional details about the flow-system apparatus and its use is contained in the Tank 22 thermolytic HGR testing report.[15]

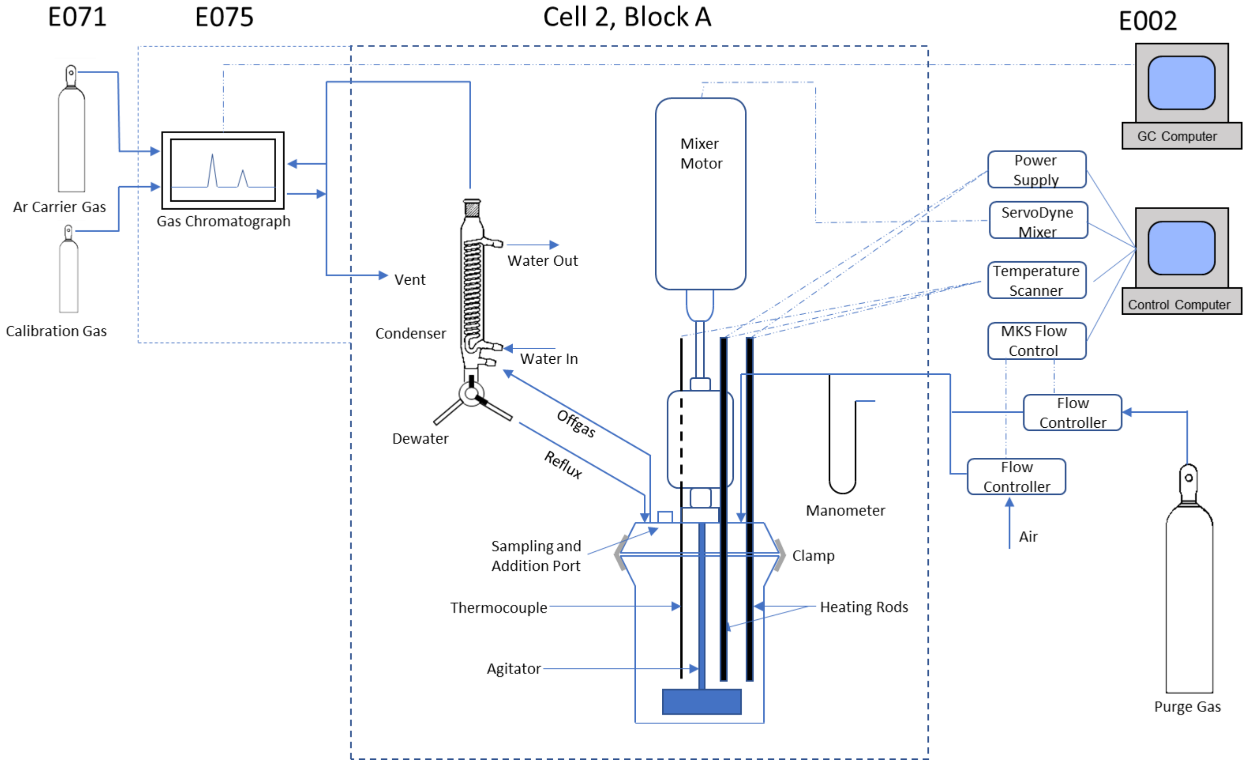

**Figure 2-2. HGR measurement flow system used in Tank 44 testing.**

## 2.2 Test Protocol

### *2.2.1 Samples and Chemicals*

Prior to this task, the salt from the Tank 44 core samples had already been repackaged into a "Tank 44 upper saltcake composite" consisting of 923 grams from samples FTF-44-06-48-1 through FTF-44-06-48-6, and a "Tank 44 lower saltcake composite" consisting of 132 grams from samples FTF-44-06-48-10 and FTF-44-06-48-11. It is not effective to attempt to homogenize and characterize the two composites in this state because the generally hard and dry nature of these salt samples makes homogenization challenging. Instead, the two saltcake composites were partially dissolved with water, supernate was decanted supernate from the remaining undissolved solids, and the supernate and solids portions were characterized.

The dissolution process used a 1.2:1 mass ratio of water to saltcake. The volume was chosen to produce a reasonably concentrated salt solution while providing enough volume of sample for both characterization and a single large aliquot for HGR testing. The salt was allowed to dissolve for a 4 day period with occasional periods of mixing to resuspend the undissolved solids. The dissolved saltcake was separated from the remaining saltcake and sludge by settling for six additional days and decanting. The dissolved portions of the Tank 44 upper and lower saltcake composites were combined and used in HGR testing.

The samples did not contain glycolate, so sodium glycolate (Alfa Aesar, 99.1 wt %) was added to the sample material to achieve the desired concentration, where applicable.

### *2.2.2 Flow System Testing Parameters*

The parameters for flow-system testing of Tank 44 were as follows.

- Measurement apparatus: nominally 1 L flow system, fluoropolymer vessel with fluoropolymer lid. Total volume (liquid and gas) of approximately 1.2 L.
- Test sample: dissolved fraction of Tank 44 saltcake sample FTF-44-06-48
- Sample density: 1.289 g/mL at 25 °C
- Sample volume: approximately 1.08 L
- Sample mass: approximately 1390 g
- Glycolate addition, where applicable: 1000 mg/L of glycolate (as sodium glycolate)
- Equipment total gas volume: approximately 200 mL
- Target measurement purge rate: 3 mL/min at standard conditions (1 atm and 21.1 °C). Higher rates of air without Kr tracer (10 to 80 mL/min) were used during periods of temperature adjustment. A lower rate of purge gas with Kr tracer (3 mL/min to 10 mL/min) was applied once the measurement temperature was attained.
- Expected minimum time to equilibrate for HGR measurement: It required approximately 3 hours to achieve three vapor space volume turn-overs at standard conditions and 3 mL/min purge rate.
- Condenser cooling water set point: 10 °C
- Condenser gas output temperature target: 10 to 30 °C (influenced by ambient Shielded Cell temperature)
- Heating rod temperature target: less than 20 °C above solution temperature when equilibrating at measurement temperature; less than 30 °C above solution temperature when heating to measurement temperature
- Mixer rate: nominally 100 to 300 rpm, or as needed for liquid mixing and foam control. Note that there was no visual confirmation of mixing or foaming.

### *2.2.3 Flow System Testing Process*

Due to the limited volume of dissolved Tank 44 saltcake that was available for testing, a single aliquot of material was used for HGR measurements. The HGR measurements were performed at a series of temperatures without the addition of sodium glycolate, followed by HGR measurements with the same aliquot at a series of temperatures with the addition of sodium glycolate. Using a single aliquot for tests both without and with added sodium glycolate was a departure from the planned Tank 39 and Tank 28 HGR measurements but was in line with the earlier Tank 38 HGR measurement.[11, 14]

The measurement was performed by holding the Tank 44 dissolved saltcake material in a fluoropolymer vessel that allowed for mixing, heating, temperature measurement, and gas measurement. Hydrogen, methane, carbon dioxide, and tracer in the offgas was measured by GC. The offgas was carried to the GC by purge gas, which is a mixture containing 20 vol % oxygen, 0.5 vol % krypton tracer, and the balance nitrogen. In parallel with HGR testing, portions of the dissolved Tank 44 saltcake sample test feed without added glycolate was sampled for chemical analysis. The HGR measurements of Tank 44 dissolved saltcake without glycolate occurred at a series of increasing temperatures from 70 °C to the atmospheric pressure boiling point of the material, followed by a second measurement at 70 °C. To this sample, 1000 mg/L of glycolate (added as sodium glycolate) was added. The mixture was again heated to 70 °C, measured for HGR, and sampled for glycolate content. Subsequent HGR measurements with added glycolate occurred at a series of increasing temperatures to the atmospheric pressure boiling point of the material. The material was removed from the HGR measurement apparatus and sampled for post-HGR analysis.

Step-by-step details of the testing process are included in Appendix A.

## 2.3 Data Collection

### *2.3.1 Gas Handling and Analysis (flow system)*

Offgas from the tests was characterized using an Agilent series 3000 micro GC. Column-A collected data related to helium, hydrogen, oxygen, nitrogen, krypton, and methane, while column-B collected data related to carbon dioxide and nitrous oxide. Due to limited GC sensitivity when using argon carrier gas (needed for hydrogen quantification), it was not possible to identify other oxides of nitrogen and carbon. The GC method was modified to quantify low quantities of hydrogen. The instruments have previously been used to quantify offgas from DWPF CPC demonstrations which generally have significantly higher gas generation rates. To quantify the low concentrations of hydrogen, sample injection times were increased by a factor of three relative to DWPF simulations. To improve sensitivity, the GC sensitivity mode was changed from normal to high. Because of these changes, the ability to accurately quantify oxygen and nitrogen, which are present at higher concentrations but are less important for these tests, has been significantly reduced relative to the semi-quantitative results generally seen in CPC simulations. Raw chromatographic data were acquired by the GC from the offgas stream samples using a separate computer interfaced to the data acquisition computer. Sampling frequency was approximately one chromatogram every eight minutes.

The GC was calibrated with a gas mixture containing 50 ppmv hydrogen, 100 ppmv methane, 20.0 vol % oxygen, 0.5 vol % krypton, 1.0 vol % carbon dioxide, 0.5 vol % nitrous oxide, and the balance nitrogen. It was assumed that the GC response (peak area) was linear and proportional to the gas concentration. This assumption was demonstrated to be appropriate for hydrogen with several other hydrogen-bearing gas standards.[12] The calibrations were verified prior to and after completing the week of flow-system testing.

The primary purge gas contained 0.5 vol% krypton, 20.0 vol% oxygen, and 79.5 vol% nitrogen. Air purge was also available and used to partially flush the system between measurement conditions. The Kr-bearing purge gas (as compared to air) served several purposes. First, by using the measured krypton concentration, one could determine if the headspace of the reaction vessel had been purged of air. Second, unlike air, the purge had no helium and hydrogen, which could interfere with quantification of hydrogen produced from radiolysis or thermolysis. Third, Kr measurements were used to adjust for bulk gas generation from the sample, air leakage into the system, and back-mixing at the GC.

The relationship identified in Equation 1 was used to calculate the HGRs. With this equation, it was assumed that flow out of the vessel was equal to flow into the vessel. The validity of this assumption was confirmed by checking that the measured Kr concentration was the same as the Kr concentration in the purge gas fed to the reaction vessel.

$$\boldsymbol{HGR = H2_{area} \times \frac{H2_{stdconc}}{H2_{stdarea}} \times \frac{Kr_{stdarea}}{Kr_{stdconc}} \times \frac{Kr_{purgegas}}{Kr_{area}} \times F_{in} \times \frac{\rho}{m} \times 8.126 \times 10^{-6}} \qquad \text{Equation 1}$$

where,

$HGR$ = hydrogen generation rate, $ft^3 \cdot h^{-1} \cdot gal^{-1}$

$H2_{area}$ = GC hydrogen response for a gas sample

$H2_{stdconc}$ = Concentration of hydrogen calibration gas, ppmv

$H2_{stdarea}$ = Average of the GC responses from the hydrogen-bearing calibration gas

$F_{in}$ = flow of krypton-bearing purge gas into the reaction vessel, mL/min

$\rho$ = density of sample, $g \cdot mL^{-1}$

$m$ = mass of sample, g

$8.126 \times 10^{-6}$ = conversion factor and temperature adjustment, $ft^3 \cdot min \cdot mL \cdot cc^{-1} \cdot gal^{-1} \cdot ppmv^{-1} \cdot hr^{-1}$

$Kr_{purgegas}$ = Concentration of krypton in the purge gas, not including any supplemental air, vol %

$Kr_{area}$ = GC krypton response for a gas sample

$Kr_{stdconc}$ = Concentration of krypton calibration gas, vol %

$Kr_{stdarea}$ = Average of five GC responses from the krypton calibration gas

The units of HGR are cubic feet of hydrogen gas per hour per gallon of tank waste supernate, or $ft^3\ h^{-1}\ gal^{-1}$. The gas volume basis of the HGR measurements reported in this document is at a standard condition of 25 °C and 1 atm to match the CSTF HGR calculation standard condition. Purge rates quoted in this document are at a standard condition of 21.1 °C and 1 atm to match the standard condition of the HGR measurement apparatus.

Tabulated average values for HGR, methane generate rate, and carbon dioxide generate were calculated using the final one to two hours of measurement data (8 to 16 data points) for each stable condition.

The software package GUM workbench[25] was used to determine the partial derivatives used to calculate the overall uncertainty for the above equations. The overall uncertainty (using these derivatives) and one sigma uncertainties in the variables was then used to calculate uncertainties for all the data points using the software package JMP Pro Version 11.2.1.[26]

Based on current and previous GC calibration data,[12] the Limit of Quantification (LOQ) for hydrogen was determined to be 2.3 ppmv. Using a simplified version of Equation 1,[a] the minimum LOQ corresponds to between approximately $5 \times 10^{-8}\ ft^3\ h^{-1}\ gal^{-1}$ and $6 \times 10^{-8}\ ft^3\ h^{-1}\ gal^{-1}$for the sample volume, purge rate, and tracer measurements of the Tank 44 flow-system testing. The Limit of Detection (LOD) was determined to be 1.2 ppmv, which corresponds to approximately $3 \times 10^{-8}\ ft^3\ h^{-1}\ gal^{-1}$ for this testing. Measurements below the LOQ are semi-quantitative and should only be applied in a qualitative manner, such as representing general trends (i.e., increasing or decreasing with time). Measurements above the LOD but below the LOQ should be interpreted as positive indications of the presence of hydrogen as distinguishable from the GC baseline measurement. However, measurement uncertainty and bias are greatly increased when below the LOQ, and thus measurement values below the LOQ should not be used in calculations and comparisons.

SRNL evaluated the GC with 2 ppmv and 10 ppmv methane standards (balance air in both cases). The GC was unable to detect 2 ppmv methane. The 10 ppmv methane gas could be detected and quantified. Ten measurements of this calibration gas yielded a relative standard deviation of 15%. Based on the 10 ppm methane calibration gas, the GC's LOD is less than 10 ppmv. Using an Environmental Protection Agency (EPA)[27] and Taylor[28] based methodology, the methane LOQ is approximately 14 ppmv.

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[a] In Equation 1, the first three terms involving hydrogen simplify to the hydrogen measurement concentration in ppm. The four terms involving krypton simplify to unity.

A difference in Tank 44 testing from previous radioactive sample HGR testing[11, 14] is that the purge gas and air sources were combined immediately prior to entering the shielded cell rather than immediately prior to the HGR apparatus. A flow problem with one of the gas lines entering the shielded cell was the reason for this reconfiguration. This system reconfiguration delayed the increase of the Kr tracer in the GC measurements at the start of each test condition but did not sacrifice data quality.

### *2.3.2 Analytical Methods for Sample Analysis*

The analytical plan for the characterization of Tank 44 dissolved saltcake and HGR test samples is presented in Table 2-1. The plan is more complicated than that of previous tank sample HGR testing because it needed to accommodate characterization of the saltcake composites, including the remaining undissolved saltcake that will not be used in the HGR testing. After saltcake dissolution, the supernate and saltcake portions of the Tank 44 upper and lower saltcake composites were prepared in duplicate (for supernate) and triplicate (for saltcake) and underwent characterization for saltcake dissolution mass balance information. The two dissolved saltcake supernate portions were combined into a single sample for HGR testing and the material was prepared in triplicate and underwent characterization as the pre-HGR test feed supernate. The material sampled after glycolate addition was prepared in duplicate and underwent characterization. The material removed from the test apparatus after the HGR test, the post-HGR supernate, was prepared in duplicate and analyzed as the test product.

Small undiluted portions of supernate samples were analyzed by Volatile Organics Analysis (VOA), by Semivolatile Organics Analysis (SVOA), and by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for monomethylmercury (MMHg). Water dilutions of supernates and slurries received analysis by Ion Chromatography for Anions (ICA); titration for total base, free hydroxide, and other base excluding carbonate (TB/OH/OB); and Total Inorganic Carbon/Total Organic Carbon (TIC/TOC). Acid dilutions (of supernate) and aqua-regia digestions (of remaining solids/undissolved saltcake) received analysis for metals by Inductively Coupled Plasma – Atomic Emissions Spectroscopy (ICP-AES) and for mercury by Direct Mercury Analyzer (DMA). Several additional analyses were performed on the upper and lower composite samples for general characterization and mass balance information. The additional analyses include Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), gamma scan without and with cesium removal, plutonium analysis, and strontium-90 analysis.

**Table 2-1. Analytical plan for Tank 44 characterization**

| | Upper and Lower Composites | | Dissolved Saltcake for HGR Tests | | |
|---|---|---|---|---|---|
| | supernate | remaining solids | pre-HGR | post glycolate add | post-HGR |
| *preparation* | | | *none* | | *none* |
| SVOA | | | 2 replicates | | |
| VOA | | | 2 replicates | | |
| MMHg | | | 1 replicate | | 1 replicate |
| *preparation* | *water dilution* | *water dilution* | *water dilution* | *water dilution* | *water dilution* |
| ICA | 2 repl. × 2 comp. | 3 repl. × 2 comp. | 3 replicates | 2 replicates | 2 replicates |
| TIC/TOC | 2 repl. × 2 comp. | 3 repl. × 2 comp. | 3 replicates | 2 replicates | 2 replicates |
| TB/OH/OB | 2 repl. × 2 comp. | 3 repl. × 2 comp. | 3 replicates | | 2 replicates |
| *preparation* | *acid dilution* | *aqua regia digestion* | *acid dilution* | | *acid dilution* |
| ICP-AES | 2 repl. × 2 comp. | 3 repl. × 2 comp. | 3 replicates | | 2 replicates |
| ICP-MS | 2 repl. × 2 comp. | 3 repl. × 2 comp. | | | |
| DMA | 2 repl. × 2 comp. | 3 repl. × 2 comp. | 3 replicates | | 2 replicates |
| PuTTA+Pu-241 | 2 repl. × 2 comp. | 3 repl. × 2 comp. | | | |
| Sr-90 | 2 repl. × 2 comp. | 3 repl. × 2 comp. | | | |
| Gamma scan | 2 repl. × 2 comp. | 3 repl. × 2 comp. | | | |
| Cs-removed gamma | 2 repl. × 2 comp. | 3 repl. × 2 comp. | | | |

repl. – replicates, comp. – composites

### 2.4 Quality Assurance

The customer-identified functional classification for these tasks is Safety Class.[8-9] Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60.[29] This document, including all calculations (e.g., hydrogen generation rates and uncertainties), was reviewed by Design Verification by Document Review. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[30] Data are recorded in the electronic laboratory notebook system as notebook/experiment number A6583-00142-27 and other associated notebooks/experiments.

For the flow system, the DAC software package used to control, display, and log test parameters is software classification level D.[31] The DAC software controls the heating, mixing, and gas purge flow; displays the test measurements to the user; and records a data file for later use. The DAC software does not perform calculations that are used in this report. The logged data that contributes to HGR calculations are the purge gas flows and the reaction temperature. The purge gas flow instruments, thermocouples, and temperature scanner are in the Measuring and Test Equipment (M&TE) program. Each of these instruments has an alternative reading outside of the DAC software. Data is periodically recorded manually (e.g., every 30 minutes) to supplement the files generated by the DAC software.

As described previously, two commercially available statistical software packages (GUM Workbench and JMP® Pro) are utilized for uncertainty analyses for HGR measurements. For these packages, the software classification is level D.[32-33] Both statistical packages have undergone verification and validation.[34] Calculations performed by these software packages are subjected to the technical review process.

Analytical measurements for gas streams were made with GCs. The GCs are in the Measurement Systems and Equipment (MS&E) program and thus their software is controlled through the requirements of Manual 1Q Procedure 2-7. The reprocessed data from the GC software is used in the HGR calculations.

## 3.0 Samples, Dissolved Saltcake Preparation, and Analysis

### 3.1 Tank 44 Saltcake Core Sample Background

A set of eleven Tank 44 saltcake core samples was obtained in October 2006. The samples were collected with Hanford-style universal samplers used with a Boart Longyear™ LM™75 core sampling rig. The samplers have approximately a 1-1/8-inch inner diameter, and are 19 inches long, with an internal volume of approximately 310 mL each. The sample segments were numbered FTF-44-06-48-1 through FTF-44-06-48-11, with sample FTF-44-06-48-1 collected just below the surface of the saltcake and FTF-44-06-48-11 collected at the lowest tank level allowable for this sampling method. A description of the samples and minimal characterization was previously documented.[35]

Eight of the samples contained significant saltcake (30 g to 275 g of salt). In all, 1.27 kg of salt was received over the region between 285 and 76 inches of tank elevation (surface minus 0 to 209 inches). Three mostly empty samples were pulled over the region from 171 to 114 inches of tank elevation, thus this region is underrepresented by the overall Tank 44F saltcake core. Figure 3-1 shows a representation of how much sample material was obtained over the length of the core sample. Figure 3-2 contains photographs of the saltcake portions of the Tank 44 saltcake segments.

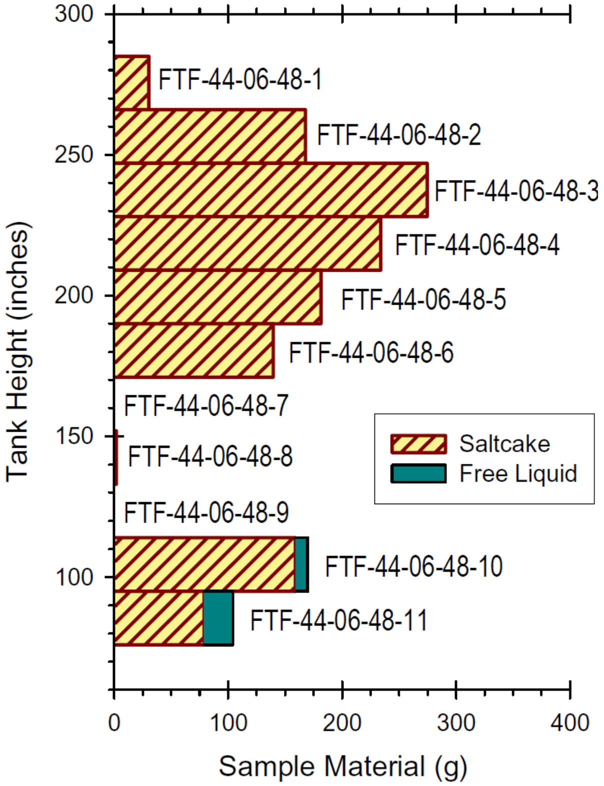


**Figure 3-1. Sample material received from Tank 44[35]**

During storage of the material from 2006 to 2018, significant deterioration of most of the sample jar lids occurred. Several of the samples were open to the cell atmosphere, allowing for the samples to become drier than when they were first collected. During that period, a portion of the hydroxide may have reacted with carbon dioxide in the air, potentially allowing for a decrease in hydroxide content and a corresponding increase in carbonate content. The samples were repackaged into two composites in late 2018: a Tank 44 Upper Saltcake Composite consisting of the saltcake from segments FTF-44-06-48-1 through FTF-44-06-48-6 (171 to 285 inch tank level) and a Tank 44 Lower Saltcake Composite consisting of the saltcake from segments FTF-44-06-48-10 through FTF-44-06-48-11 (76 to 114 inch tank level). Due to drying and loss of material during sample repackaging and compositing, the Tank 44 Upper and Lower Saltcake Composites consisted of 923 g and 132 g of material, respectively.

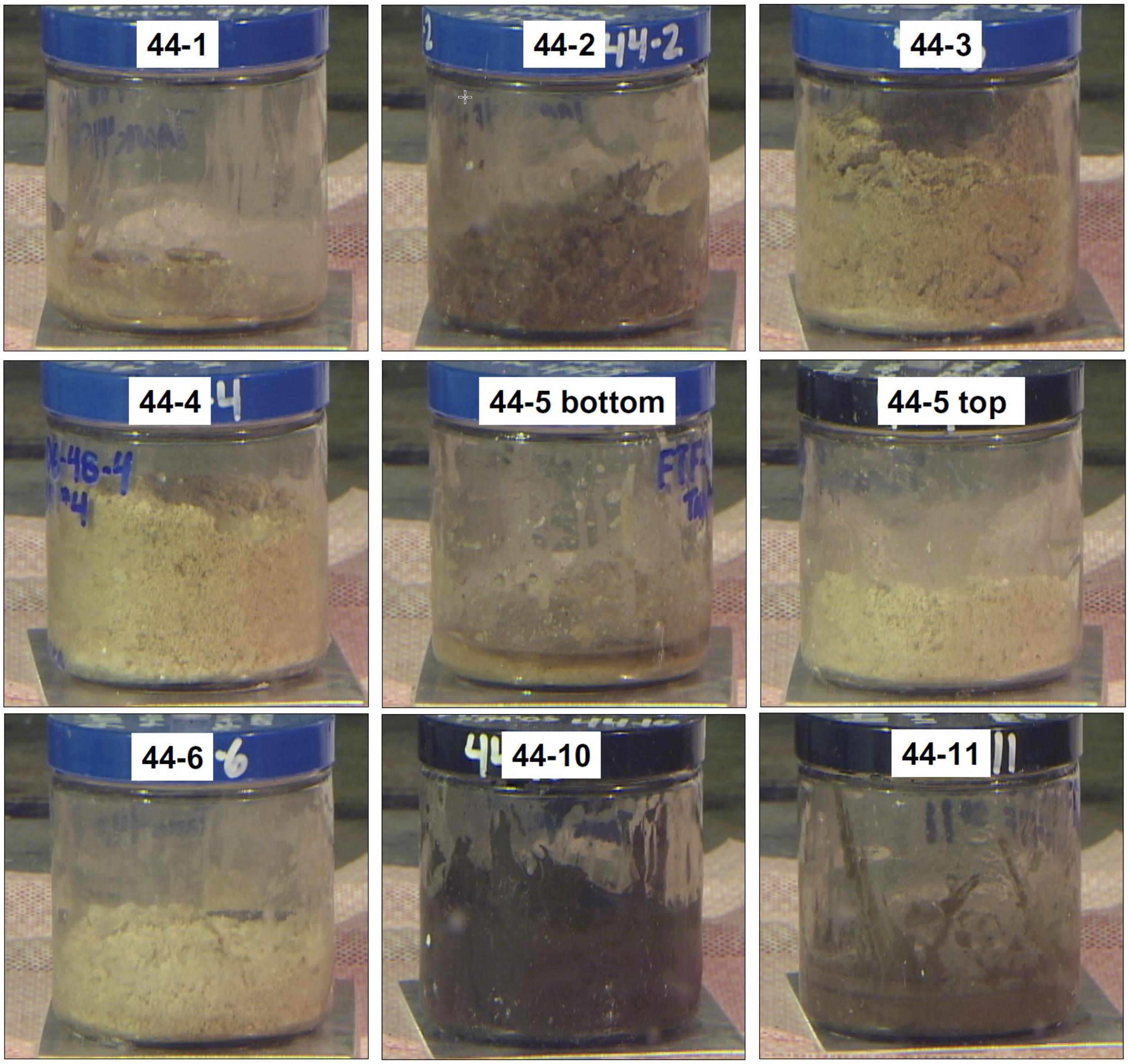


**Figure 3-2. Photographs of the Tank 44 segments in 500 mL glass jars**[35]

3.2 Dissolved Saltcake Preparation

Saltcake dissolution was accomplished by adding 1.2 grams of deionized water per gram of saltcake. This ratio of water to saltcake was used because it was consistent with the goals of this saltcake dissolution, providing sufficient volume for HGR testing and saltcake segment analysis. It was not a goal to attain a very high supernate dissolved solids and density, which would have required less water and would not have provided a sufficient volume. It was also not a goal to dissolve up a greater quantity of the saltcake at equilibrium, which would have required more water and would have produced a supernate that had a lower dissolved solids and density.

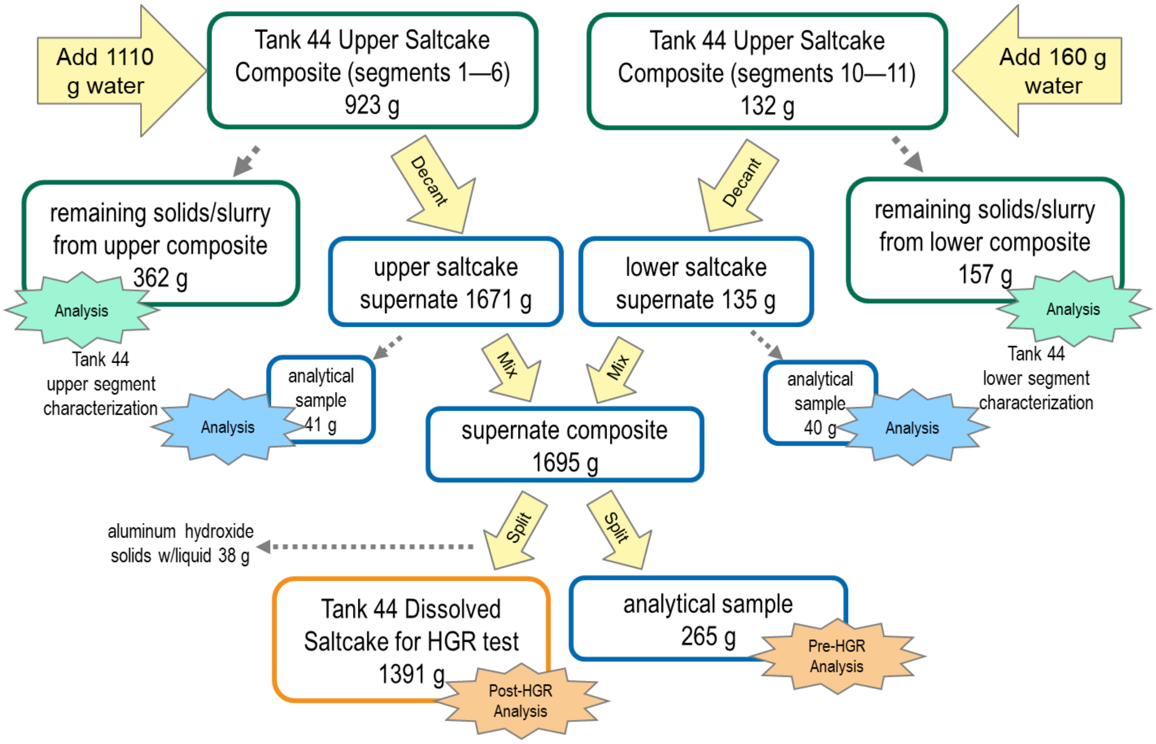


**Figure 3-3. Tank 44 dissolved saltcake preparation and sample processing flow chart**

Figure 3-3 shows a schematic of the dissolution and preparation process for the HGR test and characterization. The 923 g of Tank 44 Upper and 132 g of Tank 44 Lower Saltcake Composite were contacted with 1110 and 160 g of deionized water, respectively. The saltcake and water were held at ambient cell temperature and mixed occasionally over four days. Subsequently, the mixtures sat quiescent for an additional 6 days to allow the undissolved solids to settle. The supernatant portions of the samples were decanted to the maximum extent possible without transferring undissolved solids with the supernate. Analytical samples were removed from the upper and lower saltcake supernates. These supernate samples along with the remaining solids/slurry were analyzed to reconstruct the composition of the upper and lower saltcake segment composites as it was prior to dissolution. The remaining upper and lower saltcake supernates were combined to an overall supernate composite. The mass values shown in Figure 3-3 for the dissolved and undissolved portions and the supernate composite are approximate. The majority of the supernate composite became the Tank 44 dissolved saltcake for the HGR test and the remainder was retained for pre-HGR Tank 44 dissolved saltcake characterization. Light gray or white precipitated solids (assumed to be aluminum hydroxide) were excluded from both HGR testing and pre-HGR characterization.

Figure 3-4 shows the analytical samples from the upper and lower saltcake supernates. Both decanted supernates were relatively clear, but the lower saltcake supernate had a noticeable brown color. Figure 3-5 shows the analytical sample from the overall dissolved saltcake composite. At the bottom of the bottle of the overall dissolved saltcake, a light gray or white layer of fine settled solids is evident. The visual appearance and sample chemistry is consistent with the precipitation of aluminum hydroxide (likely gibbsite and bayerite) as seen in previous saltcake dissolution efforts.[36]

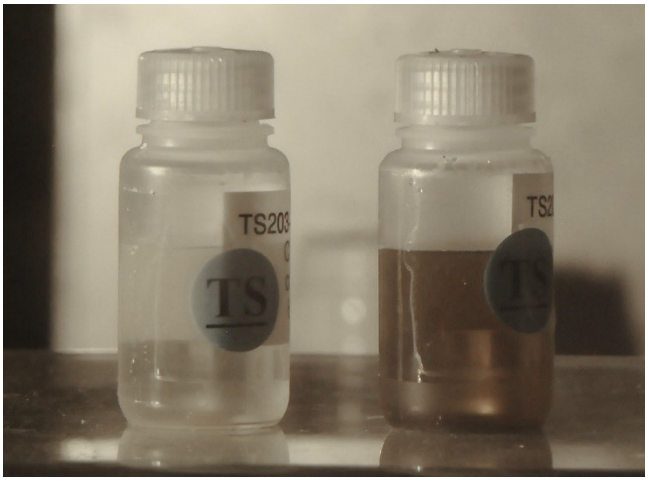


**Figure 3-4. Photograph of the analytical samples from the dissolved Tank 44 saltcake supernate from the upper (left) and lower (right) saltcake segment composites**

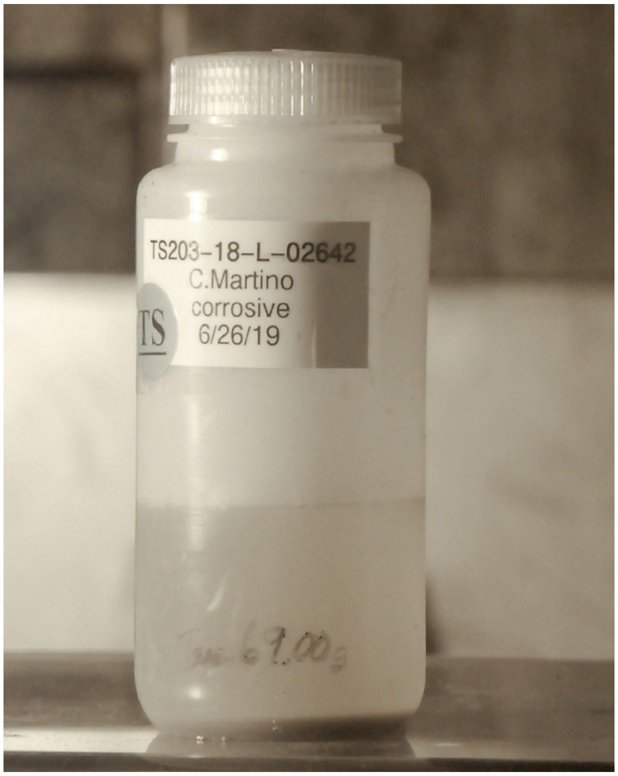


**Figure 3-5. Photograph of the analytical sample from the Tank 44 dissolved saltcake supernate composite for HGR measurement**

### 3.3 Dissolved Saltcake Analytical Results

The analytical results for the characterization of Tank 44 dissolved saltcake supernate from the upper and lower composites, the overall dissolved saltcake composite (pre-HGR) and the post-HGR material are presented in Table 3-1 and Table 3-2. Additional analytical results are contained in Appendix B. Values in tables shown as "n.d." were not determined due to not being analyzed for per the analytical plan (Table 2-1).

The average and percent relative standard deviation (RSD) is given for analytes with multiple results. Values are preceded by "<" when they were below the LOQ.

The results for major chemical components and anions were consistent between the pre- and post-HGR samples, with the exception of the 1000 mg/L added glycolate evident in the post-HGR sample (measured as 1150 mg/L or 0.0153 M). Dissolved segment analyses and the overall composite analyses showed low free hydroxide, which were below the dilution corrected LOQ (i.e., <0.01 M hydroxide for pre-HGR supernate). From pH paper testing of the overall post-HGR supernate composite, the pH was approximately 12, which corresponds to approximately 0.01 M hydroxide. It is likely that the pre-HGR and post-HGR samples had free hydroxide concentrations that were equivalent and slightly below the LOQ of 0.01 M.

From four separate sets of measurements, there is inconsistency in TOC measurements applicable to the original supernate composite used in HGR testing. First, the direct measurement of TOC in the pre-HGR sample was 428 mg C/L. Second, the non-glycolate TOC in the post-HGR sample was 801 mg C/L, which was calculated from the 1169 mg C/L TOC measurement minus the 368 mg C/L TOC attributed to the measured 1150 mg/L of added glycolate. Third, the non-glycolate TOC in the intermediate sample taken after the 70 °C HGR measurement with added glycolate was 244 mg C/L, which was calculated from the 609 mg C/L TOC measurement minus the 365 mg C/L TOC attributed to the measured 1140 mg/L of added glycolate. Fourth, the measurement of TOC based on the approximate mass balance of the TOC measurements of the upper and lower composite supernates was 720 mg C/L. The fourth method may be biased high due to differences noted between oxalate concentrations in the sample, which may have precipitated leading to a reduction in soluble TOC in the supernate composite. The multiple methods of determining TOC in the supernate composite used in HGR testing averaged 548 mg C/L with a 47% RSD.

The dissolved portion of the upper saltcake composite was more concentrated than the dissolved portion of the lower saltcake composite despite the same water to salt mass ratios used in the dissolution of both composites. The dissolved portion of the upper composite contained more sodium, nitrate, nitrite, phosphate, aluminate, and TOC. The dissolved portion of the lower composite contained more carbonate, sulfate, oxalate, chromium, iron, manganese, cesium, uranium, and plutonium. From the aluminum analysis, it is probable that aluminum hydroxide (gibbsite and bayerite) precipitated from a supersaturated mixture when the upper and lower composites were combined to form the overall composite.[36] Iron and oxalate also show signs of precipitation in the overall composite.

VOA analysis of the pre-HGR saltcake composite showed approximately 0.9 mg/L of octamethylcylclotetrasiloxane (OMCTS). OMCTS is similar to the polydimethylsiloxane component of the Dow H-10 antifoam previously used in CSTF HLW evaporators and is a known impurity in antifoamer with chemical similarity to Dow H-10. Other VOA and SVOA analytes were not at detectable levels of < 0.25 mg/L and < 1 mg/L, respectively. MMHg was below detectable levels of < 0.002 mg/L in the pre- and post-HGR supernate samples.

Table 3-3 contains the results of an intermediate sample from after the introduction of 1000 mg/L of glycolate as sodium glycolate and the subsequent HGR measurement at 70 °C. The glycolate measurement in the intermediate sample of 0.0152 M is consistent with the glycolate measurement in the post-HGR sample of 0.0153 M.

### Table 3-1. Tank 44 Dissolved Saltcake Chemical Component Analytical Results for Upper and Lower Segment Composites and the HGR Composite Pre- and Post-HGR Measurement

| analyte | method | units | Tank 44 Upper Composite Supernate | | Tank 44 Lower Composite Supernate | | Tank 44 Composite Pre-HGR | | Tank 44 Composite Post-HGR | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | average | RSD | average | RSD | average | RSD | average | RSD |
| density | gravimetric | g/mL | 1.296 | 0.2% | 1.227 | 0.0% | 1.289 | 0.2% | 1.299 | 0.1% |
| $Na^+$ | ICP-AES | M | 6.27E+00 | 1.1% | 4.71E+00 | 2.3% | 6.28E+00 | 0.1% | 6.23E+00 | 1.0% |
| $OH^-$ | titration | M | <2.28E-01 | -- | <2.10E-01 | -- | <1.00E-02 | -- | <2.67E-01 | -- |
| $NO_3^-$ | IC | M | 4.40E+00 | 1.5% | 1.48E+00 | 2.2% | 4.53E+00 | 0.9% | 4.39E+00 | 0.2% |
| $NO_2^-$ | IC | M | 7.46E-01 | 0.2% | 3.29E-01 | 2.4% | 7.57E-01 | 1.1% | 7.57E-01 | 1% |
| $CO_3^{2-}$ | TIC/TOC | M | 6.21E-01 | 1.5% | 1.94E+00 | 6.2% | 5.08E-01 | 1.2% | 5.67E-01 | 0.2% |
| $Al(OH)_4^-$ | ICP-AES | M | 9.19E-03 | 3.7% | 4.64E-03 | 5.4% | <5.25E-04 | -- | 3.55E-03 | 1.2% |
| $SO_4^{2-}$ | IC | M | 5.25E-02 | 0.3% | 1.46E-01 | 3.3% | 4.36E-02 | 1.9% | 4.92E-02 | 0.1% |
| | ICP-AES | M | 5.06E-02 | 0.0% | 1.57E-01 | 3.1% | 6.03E-02 | 1.3% | 6.41E-02 | 0.1% |
| $PO_4^{3-}$ | IC | M | 1.22E-02 | 1.8% | 7.14E-03 | 1.1% | 1.37E-02 | 3.1% | <2.81E-02 | -- |
| | ICP-AES | M | 1.97E-02 | 3.0% | <5.21E-03 | -- | 1.79E-02 | 1.8% | 1.90E-02 | 0.7% |
| $Cl^-$ | IC | M | <6.42E-03 | -- | 9.28E-03 | 1.7% | <6.97E-03 | -- | <7.53E-02 | -- |
| $F^-$ | IC | M | <1.20E-02 | -- | 1.37E-02 | 2.1% | <1.30E-02 | -- | <1.41E-01 | -- |
| $CHO_2^-$ | IC | M | <5.06E-03 | -- | 1.52E-02 | 1.9% | <5.49E-03 | -- | <5.93E-02 | -- |
| $C_2O_4^{2-}$ | IC | M | 5.02E-03 | 2.3% | 2.46E-02 | 1.7% | <2.81E-03 | -- | <3.03E-02 | -- |
| $C_2H_3O_3^-$ | IC | M | n.d. | -- | n.d. | -- | n.d. | -- | 1.53E-02 | 0.5% |
| TOC | TIC/TOC | mg C/L | 6.03E+02 | 1.6% | 2.72E+03 | 1.8% | 4.28E+02 | 0.3% | 1.17E+03 | 2.1% |
| Ag | ICP-MS | mg/L | 4.20E-02 | n.d. | 5.40E-01 | n.d. | 6.12E-02 | n.d. | n.d. | -- |
| B | ICP-AES | mg/L | 3.88E+00 | 2.7% | 1.55E+01 | 1.2% | 4.89E+00 | 0.1% | <4.70E+00 | -- |
| Co | ICP-MS | mg/L | <2.31E-02 | -- | 2.03E-01 | 1.4% | <2.40E-02 | -- | n.d. | -- |
| Cr | ICP-AES | mg/L | 4.96E+01 | 2.4% | 6.27E+02 | 3.7% | 9.48E+01 | 0.2% | 7.45E+01 | 0.8% |
| Cs-133 | ICP-MS | mg/L | 7.78E-01 | 2.1% | 2.25E+00 | 1.7% | 9.24E-01 | 1.0% | n.d. | -- |
| Fe | ICP-AES | mg/L | 1.13E+01 | 2.2% | 7.99E+01 | 5.4% | 1.48E+00 | 6.7% | <1.05E+00 | -- |
| Hg | DMA | mg/L | <2.3E-01 | -- | 1.00E+00 | 7.5% | <2.4E-01 | -- | <2.6E-01 | -- |
| K | ICP-AES | mg/L | 3.50E+02 | 1.6% | 9.87E+02 | 3.0% | 4.12E+02 | 0.3% | 3.78E+02 | 0.4% |
| Mg | ICP-AES | mg/L | 7.26E-01 | 25.1% | 4.84E+01 | 0.2% | 1.03E+00 | 2.3% | <2.57E-02 | -- |
| Mn | ICP-AES | mg/L | <2.1E+00 | -- | 2.05E+01 | 8.7% | <2.0E+00 | -- | <8.0E-01 | -- |
| Mo | ICP-AES | mg/L | 4.80E+01 | 1.1% | <2.2E+01 | -- | 4.61E+01 | 0.2% | 4.68E+01 | 1.2% |
| Pb | ICP-MS | mg/L | <1.64E-01 | -- | 2.12E-01 | n.d. | <3.61E-02 | -- | n.d. | -- |
| Pd | ICP-MS | mg/L | 6.36E-02 | 2.8% | 1.55E+00 | 0.6% | 5.18E-02 | 8.9% | n.d. | -- |
| Rh | ICP-MS | mg/L | 1.50E-01 | 1.4% | 1.28E+00 | 4.0% | 2.35E-01 | 0.5% | n.d. | -- |
| Ru | ICP-MS | mg/L | 6.65E-02 | n.d. | 1.34E+00 | n.d. | 1.57E-01 | n.d. | n.d. | -- |
| Sb | ICP-MS | mg/L | <4.6E-02 | -- | 3.30E-01 | n.d. | <4.8E-02 | -- | n.d. | -- |
| Si | ICP-AES | mg/L | 1.43E+02 | 2.1% | 4.17E+01 | 8.9% | 1.29E+02 | 2.9% | 1.09E+02 | 3.3% |
| Sr-88 | ICP-MS | mg/L | 3.81E-02 | 6.7% | 1.38E-01 | 16% | 3.20E-02 | 14% | n.d. | -- |
| U | ICP-AES | mg/L | <3.8E+01 | -- | 4.59E+03 | 1.9% | 3.90E+02 | 2.0% | 2.41E+02 | 6.5% |
| W | ICP-MS | mg/L | 1.07E+01 | n.d. | 8.71E-01 | n.d. | 1.01E+01 | n.d. | n.d. | -- |

n.d. – not determined

**Table 3-2. Tank 44 Dissolved Saltcake Radioactive Component Analytical Results for Upper and Lower Segment Composites and the HGR Composite Pre-HGR Measurement**

| analyte | method | units | Tank 44 Upper Composite Supernate | | Tank 44 Lower Composite Supernate | | Tank 44 Composite Pre-HGR | |
|---|---|---|---|---|---|---|---|---|
| | | | average | RSD | average | RSD | average | RSD |
| Al-26 | Cs-rem γ | dpm/mL | <6.3E+01 | -- | <1.5E+02 | -- | n.d. | -- |
| Co-60 | Cs-rem γ | dpm/mL | <8.3E+01 | -- | 1.21E+03 | 7.1% | n.d. | -- |
| Sr-90 | Sr-90 | dpm/mL | 2.36E+04 | 49% | 3.55E+04 | 56% | n.d. | -- |
| Nb-94 | Cs-rem γ | dpm/mL | <1.0E+02 | -- | <1.8E+02 | -- | n.d. | -- |
| Tc-99 | ICP-MS | mg/L | 9.33E-01 | 1.7% | 8.53E+00 | 2.3% | 1.54E+00 | 0.9% |
| Ru-106 | Cs-rem γ | dpm/mL | <1.0E+03 | -- | <2.7E+03 | -- | n.d. | -- |
| Sb-125 | Cs-rem γ | dpm/mL | <7.2E+02 | -- | <2.2E+03 | -- | n.d. | -- |
| Sb-126 | Cs-rem γ | dpm/mL | 4.89E+02 | 1.6% | <2.7E+02 | -- | n.d. | -- |
| Sn-126 | Cs-rem γ | dpm/mL | 4.89E+02 | 1.6% | <1.1E+03 | -- | n.d. | -- |
| Cs-134 | γ | dpm/mL | <1.9E+05 | -- | <2.1E+05 | -- | n.d. | -- |
| Cs-137 | γ | dpm/mL | 4.01E+07 | 0.3% | 1.15E+08 | 5.8% | n.d. | -- |
| Ce-144 | Cs-rem γ | dpm/mL | <1.1E+03 | -- | <2.9E+03 | -- | n.d. | -- |
| Eu-154 | Cs-rem γ | dpm/mL | <2.6E+02 | -- | <5.5E+02 | -- | n.d. | -- |
| Eu-155 | Cs-rem γ | dpm/mL | <3.8E+02 | -- | <1.3E+03 | -- | n.d. | -- |
| Ra-226 | Cs-rem γ | dpm/mL | <4.1E+03 | -- | <9.6E+03 | -- | n.d. | -- |
| Th-232 | ICP-MS | mg/L | <2.7E-02 | -- | 3.50E-01 | 9.0% | 3.54E-02 | 1.4% |
| U-233 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| U-234 | ICP-MS | mg/L | <1.2E-02 | -- | 5.97E-02 | 5.0% | <1.2E-02 | -- |
| U-235 | ICP-MS | mg/L | 7.55E-02 | 3.4% | 9.16E+00 | 3.8% | 8.12E-01 | 0.4% |
| U-236 | ICP-MS | mg/L | <1.2E-02 | -- | 5.03E-01 | 0.9% | 4.11E-02 | 3.2% |
| U-238 | ICP-MS | mg/L | 3.77E+01 | 5.4% | 4.65E+03 | 2.5% | 4.02E+02 | 0.4% |
| Np-237 | ICP-MS | mg/L | <1.2E-02 | -- | 2.03E-01 | 1.1% | 1.74E-02 | 7.7% |
| Np-237 | Cs-rem γ | dpm/mL | <1.2E+03 | -- | <3.3E+03 | -- | n.d. | -- |
| Pu-238 | PuTTA | dpm/mL | 5.14E+03 | 1.8% | 5.73E+05 | 0.6% | n.d. | -- |
| Pu-239 | ICP-MS | mg/L | 7.51E-02 | 1.9% | 3.99E+00 | 1.8% | 3.77E-01 | 0.4% |
| Pu-240 | ICP-MS | mg/L | <1.2E-02 | -- | 2.26E-01 | 2.3% | 2.36E-02 | 7.9% |
| Pu-239/240 | PuTTA | dpm/mL | 9.88E+03 | 5.1% | 5.14E+05 | 0.1% | n.d. | -- |
| Pu-241 | Pu-241 | dpm/mL | 1.63E+04 | 3.0% | 6.53E+05 | 0.6% | n.d. | -- |
| Am-241 | Cs-rem γ | dpm/mL | 1.53E+03 | 23% | 1.34E+04 | 7.7% | n.d. | -- |

n.d. – not determined

**Table 3-3. IC and TIC/TOC results for the intermediate sample taken after glycolate addition and HGR measurement at 70 °C**

| analyte | method | units | Intermediate Sample After Glycolate Add | |
|---|---|---|---|---|
| | | | average | RSD |
| $NO_3^-$ | IC | M | 4.55E+00 | 0.6% |
| $NO_2^-$ | IC | M | 7.60E-01 | 0.5% |
| $CO_3^{2-}$ | TIC/TOC | M | 5.63E-01 | 0.1% |
| $SO_4^{2-}$ | IC | M | 5.00E-02 | 0.5% |
| $PO_4^{3-}$ | IC | M | 1.34E-02 | 1.0% |
| $Cl^-$ | IC | M | <7.2E-03 | -- |
| $F^-$ | IC | M | <1.3E-02 | -- |
| $CHO_2^-$ | IC | M | <5.7E-03 | -- |
| $C_2O_4^{2-}$ | IC | M | 4.10E-03 | 0.0% |
| $C_2H_3O_3^-$ | IC | M | 1.52E-02 | 0.2% |
| | | mg/L | 1.14E+03 | |
| TOC | TIC/TOC | mg C/L | 6.09E+02 | 1.3% |

### 3.4 Saltcake Composite Analytical Results

Through a mass balance, the results from the dissolved saltcake and the remaining solids were combined to provide a characterization of the upper and lower saltcake segment composites. Figure 3-6 contains an approximate representation of the major saltcake components. General salt components were assumed and no attempt was made to determine the exact form of each salt or metal component (such as waters of hydration, double salt, or oxide/hydroxide mineral form). From the graphical depiction, it is evident that the upper segments (171 to 285 inch tank level) contained primarily (69%) sodium nitrate while the lower segments (76 to 114 inch tank level) contained 49% sodium carbonate. The "other" category consists of sample moisture, other minor components, water of hydration in salts, and oxygen and hydrogen in oxides and hydroxides. The relatively low (9%) "other" in both segments is consistent with the samples becoming more dry during storage in the shielded cells. The lower composite contained at least 8% sludge as evident by the iron, uranium, manganese, and chromium. This amount of sludge is atypically large when compared with previous saltcake samples characterized by SRNL.[36-38]

Table 3-4, Table 3-5, and Table 3-6 contain results for the dissolved saltcake, remaining solids, and total composite portions of the Tank 44 upper and lower composites. Due to the way the decanting was performed, the remaining solids portion includes some liquid with the composition of the dissolved saltcake. RSD is listed only for the remaining solids, because the RSD for the supernate was provided previously and the RSD is not applicable for the total because it is determined by calculation.

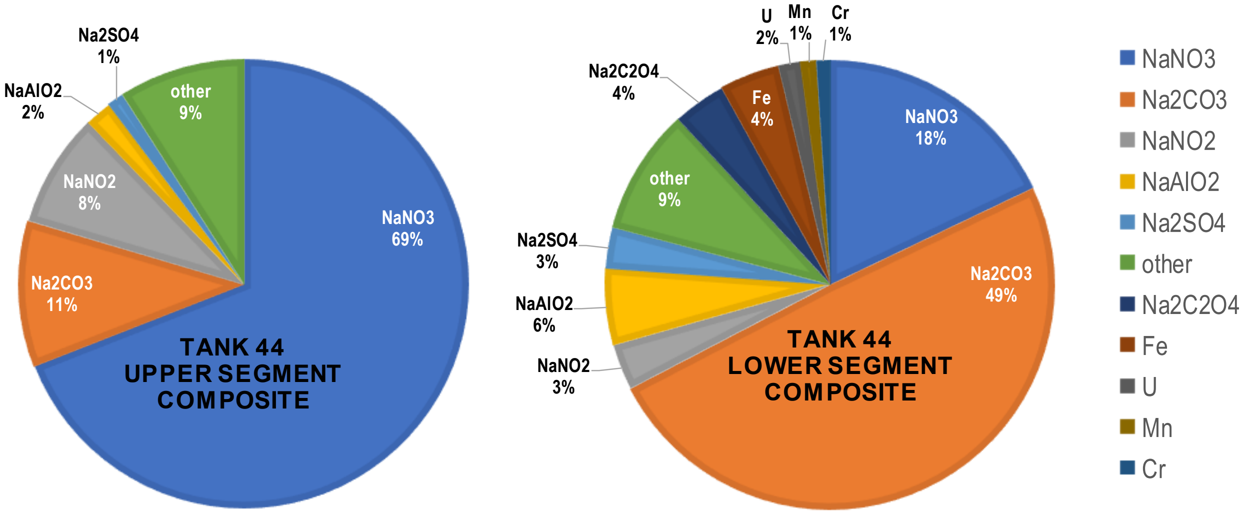


**Figure 3-6. Representation of major saltcake components in the Tank 44 upper and lower segment composites**

**Table 3-4. Tank 44 Upper and Lower Segment Composite Analysis of Major Components**

| | | | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| analyte | method | units | Supernate | Remaining Solids | | Total | Supernate | Remaining Solids | | Total |
| | | | average | average | RSD | sum | average | average | RSD | sum |
| $Na^+$ | ICP-AES | wt% | 1.11E+01 | 1.32E+01 | 2.9% | 2.53E+01 | 8.83E+00 | 1.43E+01 | 1.6% | 2.60E+01 |
| $NO_3^-$ | IC | wt% | 2.10E+01 | 3.14E+01 | 1.8% | 5.04E+01 | 7.50E+00 | 4.54E+00 | 6.3% | 1.31E+01 |
| $NO_2^-$ | IC | wt% | 2.65E+00 | 1.75E+00 | 2.5% | 5.48E+00 | 1.23E+00 | 7.81E-01 | 6.2% | 2.19E+00 |
| $CO_3^{2-}$ | TIC/TOC | wt% | 2.88E+00 | 1.93E+00 | 2.6% | 5.96E+00 | 9.49E+00 | 1.54E+01 | 8.0% | 2.80E+01 |
| $SO_4^{2-}$ | IC | wt% | 3.89E-01 | 2.66E-01 | 1.9% | 8.08E-01 | 1.14E+00 | 7.06E-01 | 7.0% | 2.01E+00 |
| $PO_4^{3-}$ | IC | wt% | 8.92E-02 | 1.51E-01 | 2.0% | 2.21E-01 | 5.53E-02 | <2.4E-02 | -- | 5.65E-02 |
| $Cl^-$ | IC | wt% | <1.8E-02 | <1.7E-02 | -- | -- | 2.68E-02 | <2.4E-02 | -- | 2.74E-02 |
| $F^-$ | IC | wt% | <1.8E-02 | 2.32E-02 | 1.9% | 9.09E-03 | 2.12E-02 | 1.60E-01 | 11% | 2.12E-01 |
| $CHO_2^-$ | IC | wt% | <1.8E-02 | <1.7E-02 | -- | -- | 5.59E-02 | 4.31E-02 | 2.3% | 1.08E-01 |
| $C_2O_4^{2-}$ | IC | wt% | 3.41E-02 | 2.76E-02 | 3.6% | 7.25E-02 | 1.76E-01 | 1.94E+00 | 12% | 2.49E+00 |
| TOC | TIC/TOC | wt% | 4.65E-02 | 4.71E-02 | 18% | 1.03E-01 | 2.21E-01 | 7.54E-01 | 10% | 1.12E+00 |
| Al | ICP-AES | wt% | 1.91E-02 | 2.64E+00 | 17% | 1.07E+00 | 1.02E-02 | 2.49E+00 | 2.8% | 2.97E+00 |
| Fe | ICP-AES | wt% | 8.76E-04 | 2.67E-01 | 16% | 1.06E-01 | 6.51E-03 | 3.61E+00 | 2.7% | 4.30E+00 |
| Mn | ICP-AES | wt% | <1.6E-04 | 1.52E-02 | 16% | 5.95E-03 | 1.67E-03 | 9.47E-01 | 3.3% | 1.13E+00 |
| U | ICP-AES | wt% | <3.0E-03 | 9.61E-02 | 14% | 3.77E-02 | 3.74E-01 | 9.95E-01 | 12% | 1.57E+00 |

## Table 3-5. Tank 44 Upper and Lower Segment Composite Analysis of Other Chemical Components

| | | | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| analyte | method | units | Supernate | Remaining Solids | | Total | Supernate | Remaining Solids | | Total |
| | | | average | average | RSD | sum | average | average | RSD | sum |
| Ag | ICP-MS | wt% | <3.2E-06 | 4.60E-05 | -- | 1.80E-05 | 4.40E-05 | 2.53E-03 | -- | 3.05E-03 |
| B | ICP-AES | wt% | 3.00E-04 | <6.0E-03 | -- | 5.42E-04 | 1.27E-03 | <6.9E-03 | -- | 9.52E-03 |
| Ba | ICP-AES | wt% | <1.4E-05 | 6.50E-04 | 15% | 2.81E-04 | <1.4E-05 | 6.25E-03 | 8.7% | 7.45E-03 |
| Ca | ICP-AES | wt% | <3.5E-04 | 2.72E-02 | 18% | 1.13E-02 | <3.5E-04 | 8.17E-01 | 2.3% | 9.72E-01 |
| Cs-133 | ICP-MS | wt% | 6.00E-05 | 1.12E-04 | 6.6% | 1.52E-04 | 1.84E-04 | 9.75E-04 | 3.1% | 1.35E-03 |
| Ce | ICP-AES | wt% | <1.6E-03 | <1.6E-03 | -- | -- | <1.6E-03 | 5.93E-03 | 10% | 8.70E-03 |
| Co | ICP-MS | wt% | <1.8E-06 | 4.83E-05 | 13% | 1.90E-05 | 1.65E-05 | 1.22E-03 | 4.2% | 1.47E-03 |
| Cr | ICP-AES | wt% | 3.83E-03 | 1.24E-02 | 13% | 1.18E-02 | 5.11E-02 | 1.88E-01 | 8.1% | 2.76E-01 |
| Cu | ICP-AES | wt% | <2.3E-04 | 2.86E-03 | 27% | 1.54E-03 | <2.3E-04 | <1.6E-03 | -- | -- |
| Hg | DMA | wt% | <1.8E-05 | 1.30E-04 | 8.5% | 5.09E-05 | 8.19E-05 | 7.03E-04 | 22% | 9.20E-04 |
| K | ICP-AES | wt% | 2.70E-02 | 2.58E-02 | 5.0% | 5.90E-02 | 8.04E-02 | 8.43E-02 | 6.8% | 1.83E-01 |
| Li | ICP-AES | wt% | <5.5E-05 | <8.1E-04 | -- | -- | <5.5E-05 | 4.67E-03 | 8.7% | 5.61E-03 |
| Mg | ICP-AES | wt% | 5.60E-05 | 7.84E-03 | 16% | 3.17E-03 | 3.94E-03 | 4.53E-01 | 2.8% | 5.42E-01 |
| Mo | ICP-AES | wt% | 3.70E-03 | <3.3E-03 | 4.4% | 6.70E-03 | <1.8E-03 | <3.8E-03 | -- | -- |
| Nd | ICP-MS | wt% | <3.6E-06 | 1.28E-05 | -- | 5.03E-06 | <3.7E-06 | 9.44E-05 | -- | 1.12E-04 |
| Ni | ICP-AES | wt% | <4.1E-04 | 9.15E-03 | 27% | 3.59E-03 | <4.1E-04 | 4.68E-02 | 8.8% | 5.61E-02 |
| P | ICP-AES | wt% | 4.70E-02 | 7.42E-02 | 2.1% | 1.14E-01 | <1.3E-02 | 2.92E-02 | 10% | 4.81E-02 |
| Pb | ICP-MS | wt% | <1.3E-05 | 2.13E-04 | -- | 8.37E-05 | 1.73E-05 | 8.08E-03 | -- | 9.63E-03 |
| Pd | ICP-MS | wt% | 4.91E-06 | 2.16E-05 | -- | 1.73E-05 | 1.26E-04 | 2.92E-04 | -- | 4.76E-04 |
| Rh | ICP-MS | wt% | 1.15E-05 | 1.59E-05 | -- | 2.72E-05 | 1.04E-04 | 1.02E-04 | -- | 2.28E-04 |
| Ru | ICP-MS | wt% | 5.13E-06 | 3.72E-05 | -- | 2.39E-05 | 1.09E-04 | 2.36E-04 | -- | 3.93E-04 |
| S | ICP-AES | wt% | 1.25E-01 | 1.43E-01 | 11% | 2.83E-01 | 4.10E-01 | 3.12E-01 | 10% | 7.90E-01 |
| Sb | ICP-MS | wt% | <3.6E-06 | 3.12E-05 | -- | 1.22E-05 | 2.69E-05 | 2.52E-04 | -- | 3.28E-04 |
| Si | ICP-AES | wt% | 1.11E-02 | 2.49E-02 | 3.6% | 2.98E-02 | 3.40E-03 | 4.52E-02 | 17% | 5.72E-02 |
| Sr-88 | ICP-MS | wt% | 2.94E-06 | 4.68E-04 | 16% | 1.89E-04 | 1.13E-05 | 2.97E-03 | 3.4% | 3.54E-03 |
| Ti | ICP-AES | wt% | <1.3E-04 | 1.18E-04 | 17% | 4.61E-05 | <1.3E-04 | 2.95E-03 | 8.8% | 3.65E-03 |
| W | ICP-MS | wt% | 8.29E-04 | 1.10E-03 | -- | 1.93E-03 | 7.10E-05 | 3.07E-04 | -- | 4.38E-04 |
| Zn | ICP-AES | wt% | <1.0E-04 | 1.95E-02 | 17% | 7.66E-03 | <1.0E-04 | 5.32E-03 | 6.3% | 6.43E-03 |

Table 3-6. **Tank 44 Upper and Lower Segment Composite Analysis of Radioactive Components**

| | | | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| analyte | method | units | Supernate average | Remaining Solids average | RSD | Total sum | Supernate average | Remaining Solids average | RSD | Total sum |
| Al-26 | Cs-rem γ | dpm/g | <4.9E+01 | <4.7E+02 | -- | -- | <1.2E+02 | <4.2E+02 | -- | -- |
| Co-60 | Cs-rem γ | dpm/g | <6.4E+01 | 2.09E+03 | 62% | 9.37E+02 | 9.89E+02 | 2.43E+04 | 3.9% | 2.99E+04 |
| Sr-90 | Sr-90 | dpm/g | 1.82E+04 | 1.18E+06 | 16% | 4.94E+05 | 2.90E+04 | 3.21E+06 | 15% | 3.84E+06 |
| Nb-94 | Cs-rem γ | dpm/g | <7.9E+01 | <6.1E+02 | -- | -- | <1.4E+02 | <5.8E+02 | -- | -- |
| Tc-99 | ICP-MS | wt% | 7.20E-05 | 2.15E-04 | 11% | 2.15E-04 | 6.95E-04 | 1.55E-03 | 4.7% | 2.55E-03 |
| Ru-106 | Cs-rem γ | dpm/g | <7.7E+02 | <4.6E+03 | -- | -- | <2.2E+03 | <5.9E+03 | -- | -- |
| Sb-125 | Cs-rem γ | dpm/g | <5.5E+02 | <3.2E+03 | -- | -- | <1.8E+03 | <5.1E+03 | -- | -- |
| Sb-126 | Cs-rem γ | dpm/g | 3.77E+02 | 7.20E+02 | 14% | 9.66E+02 | <2.2E+02 | 1.07E+04 | 1.4% | 1.27E+04 |
| Sn-126 | Cs-rem γ | dpm/g | 3.77E+02 | 7.20E+02 | 14% | 9.66E+02 | <8.9E+02 | 1.07E+04 | 1.4% | 1.27E+04 |
| Cs-134 | γ | dpm/g | <1.5E+05 | <3.9E+05 | -- | -- | <1.7E+05 | <4.4E+05 | -- | -- |
| Cs-137 | γ | dpm/g | 3.09E+07 | 5.90E+07 | 4.4% | 7.92E+07 | 9.37E+07 | 5.26E+08 | 3.4% | 7.22E+08 |
| Ce-144 | Cs-rem γ | dpm/g | <8.4E+02 | <5.6E+03 | -- | -- | <2.4E+03 | <7.4E+03 | -- | -- |
| Eu-154 | Cs-rem γ | dpm/g | <2.0E+02 | 2.63E+03 | 6.6% | 1.40E+03 | <4.5E+02 | 6.17E+03 | 11% | 7.33E+03 |
| Eu-155 | Cs-rem γ | dpm/g | <3.0E+02 | <2.6E+03 | -- | -- | <1.0E+03 | <4.5E+03 | -- | -- |
| Ra-226 | Cs-rem γ | dpm/g | <3.2E+03 | <1.9E+04 | -- | -- | <7.9E+03 | <2.7E+04 | -- | -- |
| Th-232 | ICP-MS | wt% | 2.06E-06 | 8.61E-06 | 15% | 3.38E-06 | 2.85E-05 | 4.44E-04 | 4.3% | 5.57E-04 |
| U-233 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| U-234 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 4.86E-06 | 1.30E-05 | 13% | 2.04E-05 |
| U-235 | ICP-MS | wt% | 5.82E-06 | 1.93E-04 | 15% | 8.61E-05 | 7.46E-04 | 2.04E-03 | 12% | 3.19E-03 |
| U-236 | ICP-MS | wt% | 8.94E-07 | 6.82E-06 | 13% | 2.67E-06 | 4.10E-05 | 8.76E-05 | 14% | 1.46E-04 |
| U-238 | ICP-MS | wt% | 2.91E-03 | 9.68E-02 | 14% | 4.32E-02 | 3.79E-01 | 1.01E+00 | 12% | 1.59E+00 |
| Np-237 | ICP-MS | wt% | 8.94E-07 | <2.6E-06 | 8.1% | 1.00E-06 | 1.66E-05 | 4.67E-05 | 8.1% | 7.25E-05 |
| Np-237 | Cs-rem γ | dpm/g | <9.3E+02 | <6.8E+03 | -- | -- | <2.7E+03 | <7.0E+03 | -- | -- |
| Np-239 | Cs-rem γ | dpm/g | -- | -- | -- | -- | -- | 6.59E+03 | 18% | 7.84E+03 |
| Pu-238 | PuTTA | dpm/g | 3.96E+03 | 1.38E+05 | 20% | 6.13E+04 | 4.67E+05 | 4.61E+06 | 11% | 5.96E+06 |
| Pu-239 | ICP-MS | wt% | 5.80E-06 | 2.03E-04 | 14% | 9.00E-05 | 3.25E-04 | 3.00E-03 | 3.8% | 3.90E-03 |
| Pu-240 | ICP-MS | wt% | <8.9E-07 | 1.26E-05 | 15% | 4.94E-06 | 1.85E-05 | 1.90E-04 | 4.3% | 2.44E-04 |
| Pu-239/240 | PuTTA | dpm/g | 7.62E+03 | 2.99E+05 | 16% | 1.31E+05 | 4.19E+05 | 5.00E+06 | 13% | 6.38E+06 |
| Pu-241 | Pu-241 | dpm/g | 1.26E+04 | 4.81E+05 | 20% | 2.12E+05 | 5.32E+05 | 6.24E+06 | 13% | 7.97E+06 |
| Am-241 | Cs-rem γ | dpm/g | 1.18E+03 | 1.74E+05 | 13% | 7.05E+04 | 1.09E+04 | 5.66E+06 | 6.5% | 6.74E+06 |
| Am-243 | Cs-rem γ | dpm/g | -- | -- | -- | -- | -- | 7.65E+03 | 7.9% | 9.09E+03 |

## 4.0 HGR Test Results and Discussion

Over the course of the testing with Tank 44 dissolved saltcake at elevated temperatures, the generation and/or release of hydrogen, carbon dioxide, and methane were noted. The bottom portion of Figure 4-1 presents the HGR for the progressive stages of the Tank 44 saltcake dissolution HGR testing as a function of time. Likewise, the bottom portion of Figure 4-2 presents the carbon dioxide and methane measured during the HGR tests. In addition to those gasses, minor amounts of nitrous oxide, up to approximately 0.006 vol%, were observed at 100 °C and boiling conditions for Tank 44 dissolved saltcake without and with added sodium glycolate.

In the bottom portion of Figure 4-1, the filled circles represent quantitative HGR data collected during equilibration, which are adjusted for the tracer gas measurements. The open circles are HGR measurements during transition which are qualitative due to recent changes in temperature and purge flow. The transition is deemed complete when $Kr/Kr_0 \geq 0.8$, which corresponds to greater than one vessel headspace turn-over. The earliest time that measurements were concluded was the time required for three vessel headspace turn-overs plus allowing the time for air to reach the GC, which will total approximately 3.5 hours for the test conditions. Tests at most temperatures were extended slightly to allow for time for the trend in hydrogen concentration to stabilize.

The upper portion of Figure 4-1 shows the supernate temperature, the $Kr/Kr_0$ measurement, the purge gas flow rate with Kr, and the total purge gas flow rate. Due to equipment issues early in Tank 44 testing, the total purge rates during transition periods are not accurate until the HGR test without glycolate at 100 °C (approximately 7/29/2019 1500). This deviation does not impact the accuracy of the HGR measurements because the reported flow rates for purge gas with Kr are accurate. Additionally, note that per the $Kr/Kr_0$ measurement, purge air was not added between the tests without glycolate at 70 °C and 85 °C. The LOQ for HGR is also shown on Figure 4-1. The LOQ value is adjusted for $Kr/Kr_0$. Although the LOQ for hydrogen concentration is constant, the LOQ for HGR decreases with testing time as $Kr/Kr_0$ increases toward one.

The first 70 °C HGR measurement showed a generally increasing trend that stabilized near $1.1\times10^{-6}$ $ft^3$ $h^{-1}$ $gal^{-1}$. However, the subsequent HGR measurements at 85 °C and 100 °C showed continually decreasing HGR measurements despite the increase in temperature. At 100 °C, the HGR decreased to below the LOQ of approximately $5.3\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$. This observation is not due to steady or persistent thermolysis. This decrease in hydrogen is due to the release of dissolved hydrogen gas, the presence of organic compounds that are rapidly destroyed upon heating, or some other hitherto unknown gas generation mechanism. Similar observations were seen in some of the previous testing, most notably with Tank 22 supernate.[15] In this case, evidence points toward release of dissolved hydrogen. If the measured hydrogen rate was due to generation and not release, the observed result at the first 70 °C condition for the Tank 44 dissolved saltcake material would be inconsistent with all previous simulant testing of multiple organics and SRS radioactive testing of HGR. The inconsistency would stem from two factors, that the low level of hydroxide in the Tank 44 sample would lead to relatively low hydrogen generation for all organics investigated and that subsequent higher temperatures would be expected to generate relatively larger amounts of hydrogen for thermolytic generation. Rather, the shape of the HGR curve in the initial measurements at 70, 85 and 100 °C is consistent with the behavior of mass-transport limited gas release, such as that observed during release of dissolved gasses. After the measurement at boiling, the subsequent measurement at 70 °C showed HGR below the LOQ. Once glycolate was added, HGR measurements below the boiling condition were all below the LOQ. This supports the hypothesis that the previously observed hydrogen release at 100 °C and below was due to dissolved hydrogen. Based on the HGR models, the low HGR observed here without and with added glycolate was likely due to the relatively low concentration of hydroxide in the Tank 44 dissolved saltcake.[16]

The HGR measurements of Tank 44 dissolved saltcake without and with added glycolate were quantified for the boiling condition. Without added glycolate, HGR was $7.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$ (95% CI = 5.3%; RSD = 5.0%) while boiling at 106.7 °C. With 1000 mg/L of added glycolate, HGR was $8.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$. (95% CI = 5.3%; RSD = 3.7%) while boiling at 106.9 °C. Figure 4-3 graphically displays the 16 points used to determine the HGR for each test at boiling, comparing the tests without and with added glycolate. The figure also represents the uncertainty of the measurements as the 95% CI. Due to the overlap in the 95% CI values for the HGR measurements with and without added glycolate, the impact of glycolate on HGR cannot be deemed statistically significant for this testing.

Figure 4-2 shows the concentrations of carbon dioxide measured during the Tank 44 dissolved saltcake HGR testing. Because the data in this figure are in concentration units, it is highly dependent on the purge rate used during testing. Carbon dioxide could be quantified at all temperatures and methane could be quantified at 100 °C and boiling. The addition of glycolate did not appear to influence the production of methane or carbon dioxide. During boiling, the HGR test without glycolate generated 73.0 ppmv methane (RSD = 2.7%) at 106.7 °C and the test with 1000 mg/L added glycolate generated 80.3 ppmv methane (RSD = 3.8%) at 106.9 °C. Carbon dioxide was released at significantly higher levels, roughly increasing with temperature. Near the start of boiling, carbon dioxide was approximately 6 vol% in the testing without and with added sodium glycolate. By the end of the HGR measurements at boiling, carbon dioxide was below 5 vol%. The high production of carbon dioxide is one of the factors influencing the deviation of $Kr/Kr_0$ below 1 at the boiling conditions. Carbon dioxide release during testing was higher than observed for previous tank sample HGR measurements due to a combination of factors driving carbon dioxide into the vapor phase: the relatively low hydroxide concentration, the relatively high carbonate concentration, and the elevated temperatures

Table 4-1 contains a tabulated version of the generation rates of hydrogen, methane, and carbon dioxide. As explained previously, the first measurement at 70 °C and the subsequent measurement at 85 °C are likely representative of the release of dissolved hydrogen gas rather than the generation of hydrogen. The right-most column is the volume percentage of the methane of the total gas (primarily carbon dioxide) that was generated during HGR measurements. This shows that methane stays below 5 vol%, the Lower Flammability Limit (LFL) for methane[39], in the gas released during testing and is thus inherently non-flammable.

Consistent with this testing, methane generation was also seen in previous radioactive waste sample HGR tests with Tanks 38 and 28.[11-12, 14] Along with this Tank 44 observation, the radioactive waste samples that generated methane were either current or previous evaporator drop tanks that contain saltcake. HGR testing also showed methane generation from trimethylsilanol in a Tank 38 simulant, which generated larger volumes of methane than hydrogen. Methane generation was thermolytic and seen primarily at the highest test temperatures. OMCTS and other residual H-10 antifoam or antifoam degradation products are potential sources of the methane generated during elevated-temperature testing of the Tank 44 sample.

**Table 4-1. HGR measurements for Tank 44 dissolved saltcake without and with added glycolate**

| Temperature (°C) | Hydrogen ($ft^3\ h^{-1}\ gal^{-1}$) | Methane ($ft^3\ h^{-1}\ gal^{-1}$) | Carbon Dioxide ($ft^3\ h^{-1}\ gal^{-1}$) | Methane / Total Generated (vol%) |
|---|---|---|---|---|
| *Tank 44 without added glycolate* | | | | |
| 70, first | 1.1E-06 | < 3.2E-07 | 4.3E-06 | N/A |
| 70, second | < 5.4E-08 | < 3.2E-07 | 2.32E-05 | N/A |
| 85 | 2.4E-07 | < 5.8E-07 | 1.42E-05 | N/A |
| 100 | < 5.3E-08 | 5.4E-07 | 2.97E-05 | 1.8% |
| 106.7 (boiling) | 7.2E-08 | 1.8E-06 | 1.21E-03 | 0.1% |
| *Tank 44 with 1000 mg/L of added glycolate* | | | | |
| 70 | < 5.6E-08 | < 3.4E-07 | 6.5E-06 | N/A |
| 85 | < 5.6E-08 | < 3.4E-07 | 8.1E-06 | N/A |
| 100 | < 5.6E-08 | 5.9E-07 | 2.49E-05 | 2.3% |
| 106.9 (boiling) | 8.2E-08 | 2.0E-06 | 1.19E-03 | 0.2% |

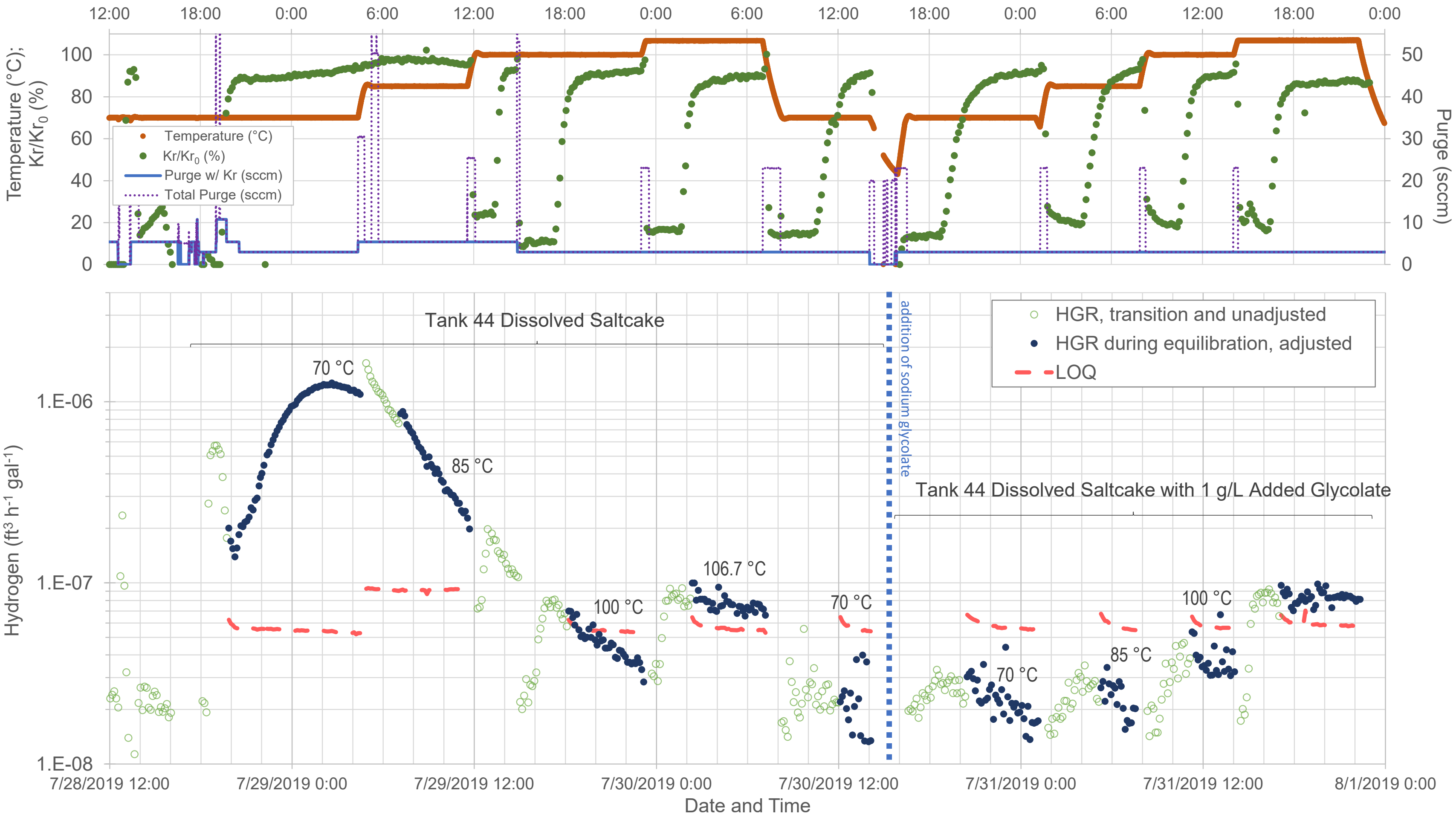
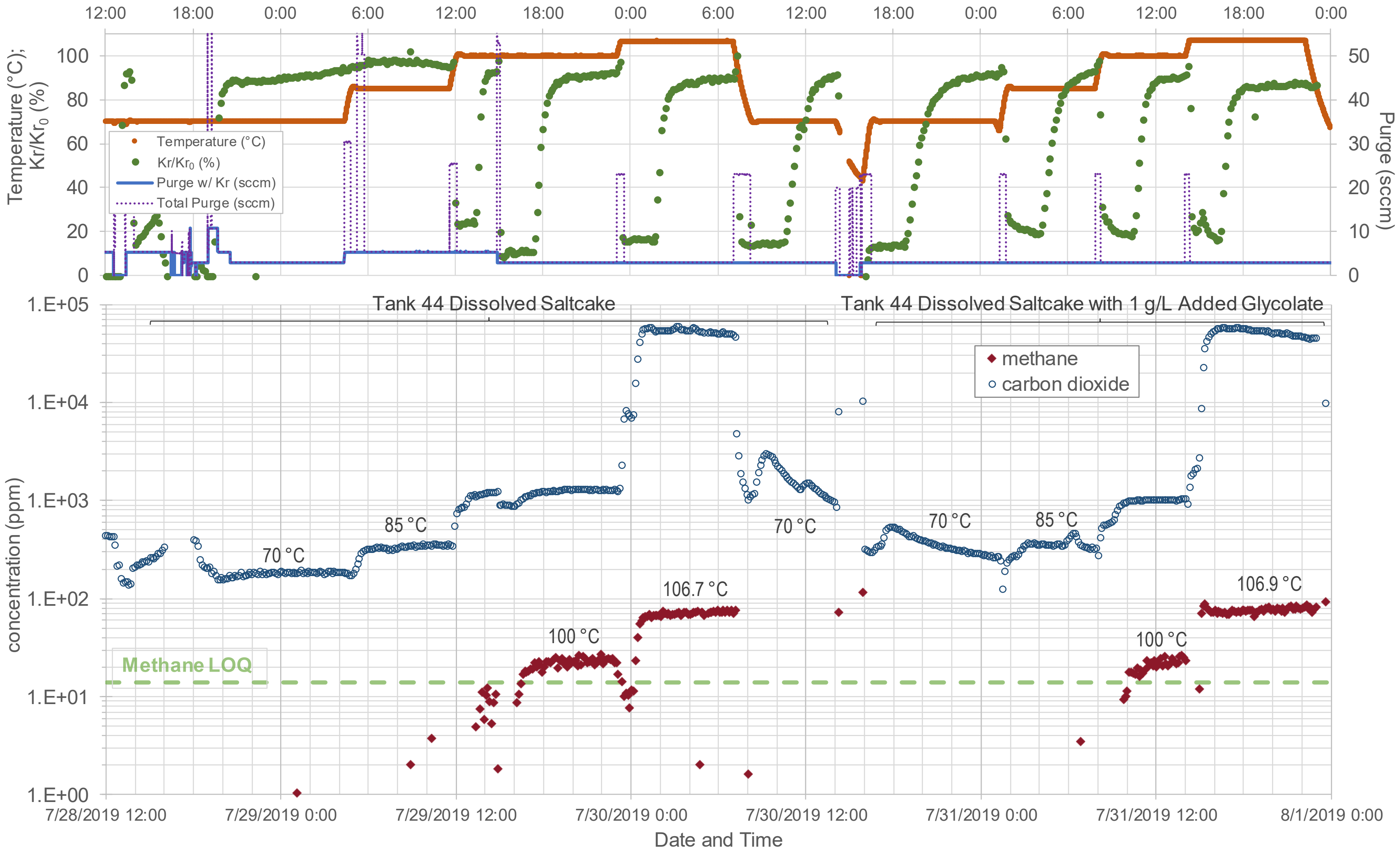


**Figure 4-1. HGR of Tank 44 dissolved saltcake without and with added glycolate**

**Figure 4-2. Generation of carbon dioxide and methane during Tank 44 dissolved saltcake HGR testing**



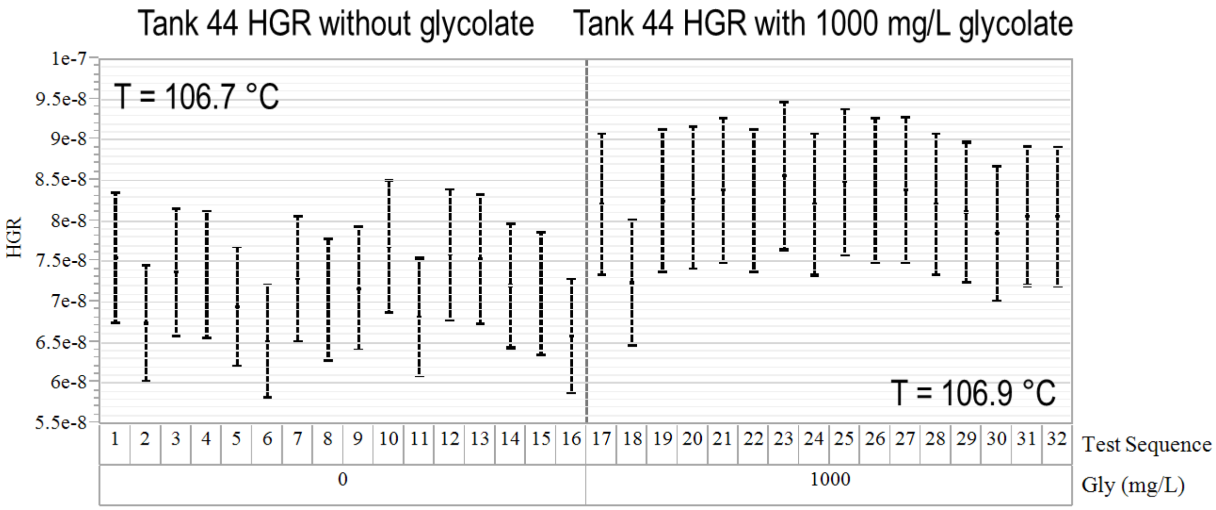


**Figure 4-3. Comparison of individual measurements and uncertainties for Tank 44 dissolved saltcake HGR without (left) and with (right) 1000 mg/L added glycolate**

Several models developed during simulant testing[16] could be useful comparison points for radioactive waste thermolytic HGR data. Because all of the models developed for HGR involve hydroxide as an important parameter, however, they might not be directly applicable for comparison to Tank 44 dissolved saltcake results. Due to the low amount of hydroxide in the Tank 44 sample (resulting in inaccurate hydroxide measurements) and the high uncertainty in the TOC measurement, comparison of the Tank 44 HGR data to the simulant models and global TOC model it is not recommended.[16]

## 5.0 Conclusions

The following are key results from the Tank 44 saltcake characterization.

- The Tank 44 Upper Saltcake Composite, corresponding to the 171 to 285 inch tank level, contained by mass approximately 69% sodium nitrate, 11% sodium carbonate, 8% sodium nitrite, smaller amounts of other salts and components, and 9% unquantified (which includes water, water of hydration, oxygen/hydrogen content of oxides and hydroxides, and uncertainty).
- The Tank 44 Lower Saltcake Composite, corresponding to the 76 to 114 inch tank level, contained by mass approximately 49% sodium carbonate, 18% sodium nitrate, smaller amounts of other salts, at least 8% sludge, and 9% unquantified (see above).
- The dissolved saltcake contained free hydroxide less than quantifiable (<0.01 M) due to the limited quantity of material that could be removed from the Shielded Cells based on the sample radioactivity. Measurement by pH paper provided an approximate pH of 12.

The following are key results from the Tank 44 HGR testing.

- During boiling at 106.7 °C, HGR for Tank 44 dissolved saltcake without added glycolate was $7.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$.
- During boiling at 106.9 °C, HGR for Tank 44 dissolved saltcake with 1000 mg/L of added glycolate was $8.2\times10^{-8}$ $ft^3$ $h^{-1}$ $gal^{-1}$.

- For the test without added glycolate, the first several HGR measurements at 70, 85, and 100 °C gave indication of the release of dissolved hydrogen and should not be used to represent the sustained thermolytic HGR for those temperatures. The measurements at boiling are the best representation of thermolysis in this testing.
- Carbon dioxide was observed at concentrations up to 6 vol% in the flow-system offgas for the test at boiling.
- Methane generation was observed at 100 °C and boiling. Methane concentration in the total gas generated during testing remained well below the lower flammability limit for methane in air.
- The addition of 1000 mg/L of glycolate did not have a significant impact on the hydrogen generation rates measured during this testing.
- The low hydroxide concentration in the Tank 44 dissolved saltcake likely influenced the relatively low thermolytic HGR and high carbon dioxide release observations in this testing.

## 6.0 Recommendations

Based on the limited applicability of the Tank 44 HGR results to the modelling of Tank Farm organics thermolysis, it is not recommended that the global TOC models presented by Woodham and Martino be updated to include this data.[16] Likewise, there is little applicability of the Tank 44 HGR results to the glycolate models contained in the same reference.

The HGR measurements for Tank 44 dissolved saltcake and several previous samples revealed that small quantities of methane can also be generated or released upon heating SRS radioactive waste samples to 100 °C and above. Although this appears to fall within current facility controls, it may be warranted to develop a better mechanistic and quantitative understanding of methane generation in CSTF. The report on simulant HGR testing also recommended additional investigations into the generation rates of methane from organic molecules in the CSTF, such as methylsiloxanes and methylmercury.[16]

We recommend an additional review of the literature applicable to the possible methane generating species in the SRS CSTF and any thermolytic methane generation mechanisms of such methyl-containing species. This review will likely result in developing a plan for simulant tests with methylated siloxanes and other applicable compounds in order to gain a better mechanistic understanding of methane generation. This task will also involve improve the GC LOQ for methane analysis.

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# Appendix A. Test Process

The HGR testing process for Tank 44 sample supernate with no added glycolate followed by 1000 mg/L of added glycolate is as follows:

1. Load the system with approximately 1.1 L (1430 g) of Tank 44 dissolved saltcake.
2. Agitate sample and initiate purge gas flow
3. Heat to 70 °C
4. Adjust purge gas flow to the measurement purge rate
5. Allow the system to equilibrate and measure the HGR at 70 °C
6. Increase purge and heat to 85 °C
7. Adjust purge gas flow to the measurement purge rate
8. Allow the system to equilibrate and measure the HGR at 85 °C
9. Increase purge and heat to 100 °C
10. Adjust purge gas flow to the measurement purge rate
11. Allow the system to equilibrate and measure the HGR at 100 °C
12. Increase purge and heat to the atmospheric pressure boiling point of the mixture
13. Adjust purge gas flow to the measurement purge rate
14. Allow the system to equilibrate and measure the HGR at boiling
15. Increase purge and allow the system to cool to 70 °C, control temperature (heat) to 70 °C
16. Adjust purge gas flow to the measurement purge rate
17. Allow the system to equilibrate and measure the HGR at 70 °C
18. Shutdown the system
19. Add 1.45 g of 99.1 wt% sodium glycolate (corresponding to 1.10 g or 1.00 g/L ofglycolate)
20. Agitate sample and initiate purge at an increased rate
21. Heat to 70 °C
22. Collect an approximately 20-gram sample from the system. At this point, the sample volume remaining in the system will be approximately 1.08 L (1420 g).
23. Reestablish agitation and purge gas flow, if necessary, and heat to 70 °C
24. Adjust purge gas flow to the measurement purge rate
25. Allow the system to equilibrate and measure the HGR at 70 °C
26. Increase purge and heat to 85 °C
27. Adjust purge gas flow to the measurement purge rate
28. Allow the system to equilibrate and measure the HGR at 85 °C
29. Increase purge and heat to 100 °C
30. Adjust purge gas flow to the measurement purge rate
31. Allow the system to equilibrate and measure the HGR at 100 °C
32. Increase purge and heat to the atmospheric pressure boiling point of the mixture, which is expected to be between 105 and 115 °C
33. Adjust purge gas flow to the measurement purge rate
34. Allow the system to equilibrate and measure the HGR at boiling
35. Increase purge and allow the system to cool to below 50 °C
36. Shutdown the system and unload the Tank 44 material
37. Subsample the Tank 44 material for post-HGR chemical analysis
38. Clean and reassemble the system

# Appendix B. Additional Analytical Results

## Table B-1. Below detection limit values for Tank 44 dissolved saltcake supernate IC and ICP-ES analysis

| analyte | method | units | Tank 44 Upper Composite Supernate | | Tank 44 Lower Composite Supernate | | Tank 44 Composite Pre-HGR | | Tank 44 Composite Post-HGR | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | average | RSD | average | RSD | average | RSD | average | RSD |
| $Br^-$ | IC | M | <2.8E-02 | -- | <2.6E-02 | -- | <3.1E-02 | -- | <3.3E-02 | -- |
| Ag | ICP-AES | mg/L | <5.4E+00 | -- | <5.1E+00 | -- | <5.4E+00 | -- | <8.2E-01 | -- |
| Ba | ICP-AES | mg/L | <1.9E-01 | -- | <1.7E-01 | -- | <1.8E-01 | -- | <2.1E-01 | -- |
| Be | ICP-AES | mg/L | <2.3E-02 | -- | <2.2E-02 | -- | <2.3E-02 | -- | <2.6E-02 | -- |
| Ca | ICP-AES | mg/L | <4.6E+00 | -- | <4.3E+00 | -- | <4.5E+00 | -- | <5.9E-01 | -- |
| Cd | ICP-AES | mg/L | <2.5E-01 | -- | <2.4E-01 | -- | <2.5E-01 | -- | <2.8E-01 | -- |
| Ce | ICP-AES | mg/L | <2.1E+01 | -- | <2.0E+01 | -- | <2.1E+01 | -- | <3.3E+00 | -- |
| Co | ICP-AES | mg/L | <1.0E+00 | -- | <9.8E-01 | -- | <1.0E+00 | -- | <5.6E-01 | -- |
| Cu | ICP-AES | mg/L | <3.0E+00 | -- | <2.8E+00 | -- | <3.0E+00 | -- | <1.2E+00 | -- |
| Gd | ICP-AES | mg/L | <1.0E+01 | -- | <9.3E+00 | -- | <9.8E+00 | -- | <1.1E+00 | -- |
| La | ICP-AES | mg/L | <5.1E-01 | -- | <4.8E-01 | -- | <5.0E-01 | -- | <5.6E-01 | -- |
| Li | ICP-AES | mg/L | <7.2E-01 | -- | <6.7E-01 | -- | <7.1E-01 | -- | <1.4E+00 | -- |
| Ni | ICP-AES | mg/L | <5.3E+00 | -- | <5.0E+00 | -- | <5.2E+00 | -- | <2.5E+00 | -- |
| Pb | ICP-AES | mg/L | <3.4E+00 | -- | <3.2E+00 | -- | <3.4E+00 | -- | <2.5E+01 | -- |
| Sb | ICP-AES | mg/L | <4.4E+00 | -- | <4.1E+00 | -- | <4.3E+00 | -- | <4.8E+00 | -- |
| Sn | ICP-AES | mg/L | <1.4E+01 | -- | <1.3E+01 | -- | <1.4E+01 | -- | <1.5E+01 | -- |
| Sr | ICP-AES | mg/L | <3.9E-01 | -- | <3.7E-01 | -- | <3.9E-01 | -- | <5.1E-02 | -- |
| Th | ICP-AES | mg/L | <1.1E+01 | -- | <1.1E+01 | -- | <1.1E+01 | -- | <4.6E+00 | -- |
| Ti | ICP-AES | mg/L | <1.7E+00 | -- | <1.6E+00 | -- | <1.7E+00 | -- | <1.0E-01 | -- |
| V | ICP-AES | mg/L | <2.1E-01 | -- | <2.0E-01 | -- | <2.1E-01 | -- | <2.3E-01 | -- |
| Zn | ICP-AES | mg/L | <1.3E+00 | -- | <1.3E+00 | -- | <1.3E+00 | -- | <4.1E-01 | -- |
| Zr | ICP-AES | mg/L | <1.5E+00 | -- | <1.4E+00 | -- | <1.5E+00 | -- | <2.1E-01 | -- |

## Table B-2. Additional ICP-MS analysis of Tank 44 Dissolved Saltcake supernate, part 1 of 2

| m/z | method | units | Tank 44 Upper Composite Supernate | | Tank 44 Lower Composite Supernate | | Tank 44 Composite Pre-HGR | |
|---|---|---|---|---|---|---|---|---|
| | | | average | RSD | average | RSD | average | RSD |
| 82 | ICP-MS | mg/L | <2.3E-02 | -- | 2.70E-02 | 6.7% | <2.4E-02 | -- |
| 84 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 85 | ICP-MS | mg/L | 1.24E-01 | 3.7% | 6.45E-01 | 0.4% | 1.65E-01 | 2.9% |
| 86 | ICP-MS | mg/L | <1.2E-02 | -- | 1.43E-02 | 18% | <1.2E-02 | -- |
| 87 | ICP-MS | mg/L | 2.57E-01 | 4.1% | 1.27E+00 | 1.9% | 3.48E-01 | 3.3% |
| 89 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | 5.8% | <1.2E-02 | -- |
| 90 | ICP-MS | mg/L | 1.30E-02 | 12% | 9.94E-01 | 2.3% | 8.26E-02 | 1.6% |
| 91 | ICP-MS | mg/L | <1.2E-02 | -- | 4.43E-01 | 3.6% | 3.41E-02 | 1.2% |
| 92 | ICP-MS | mg/L | 9.70E-01 | 1.3% | 8.74E-01 | 1.9% | 9.70E-01 | 0.0% |
| 93 | ICP-MS | mg/L | <1.2E-02 | -- | 8.88E-01 | 2.5% | 2.45E-02 | 2.9% |
| 94 | ICP-MS | mg/L | 6.38E-01 | 1.3% | 7.86E-01 | 2.8% | 6.49E-01 | 0.1% |
| 95 | ICP-MS | mg/L | 1.16E+01 | 3.7% | 4.91E+00 | 1.7% | 1.13E+01 | 1.2% |
| 96 | ICP-MS | mg/L | 1.00E+00 | 1.2% | 6.52E-01 | 1.8% | 9.81E-01 | 0.3% |
| 97 | ICP-MS | mg/L | 1.09E+01 | 6.2% | 4.62E+00 | 2.2% | 1.06E+01 | 2.0% |
| 98 | ICP-MS | mg/L | 1.16E+01 | 4.6% | 4.90E+00 | 2.0% | 1.13E+01 | 0.2% |
| 100 | ICP-MS | mg/L | 1.20E+01 | 2.6% | 4.71E+00 | 2.0% | 1.12E+01 | 1.0% |
| 101 | ICP-MS | mg/L | 2.49E-02 | 7.0% | 4.99E-01 | 1.9% | 6.22E-02 | 0.9% |
| 102 | ICP-MS | mg/L | 2.26E-02 | 0.7% | 4.51E-01 | 2.4% | 5.56E-02 | 4.0% |
| 104 | ICP-MS | mg/L | 1.90E-02 | 0.6% | 3.90E-01 | 2.8% | 3.88E-02 | 1.1% |
| 105 | ICP-MS | mg/L | 3.83E-02 | 2.8% | 9.31E-01 | 0.6% | 3.12E-02 | 8.9% |
| 106 | ICP-MS | mg/L | 3.04E-02 | 11% | 7.83E-01 | 1.0% | 2.60E-02 | 9.6% |
| 107 | ICP-MS | mg/L | <2.3E-02 | -- | 5.77E-01 | 5.6% | 4.08E-02 | 15% |
| 108 | ICP-MS | mg/L | <2.3E-02 | -- | 2.74E-01 | 7.6% | <2.4E-02 | -- |
| 109 | ICP-MS | mg/L | <2.3E-02 | -- | 7.01E-02 | 18% | <2.4E-02 | -- |
| 110 | ICP-MS | mg/L | <3.5E-02 | -- | 1.18E-01 | 3.9% | <3.6E-02 | -- |
| 111 | ICP-MS | mg/L | <3.5E-02 | -- | <3.4E-02 | -- | <3.6E-02 | -- |
| 112 | ICP-MS | mg/L | <4.6E-02 | -- | <4.5E-02 | -- | <5.0E-02 | -- |
| 113 | ICP-MS | mg/L | <4.6E-02 | -- | <4.5E-02 | -- | <4.8E-02 | -- |
| 114 | ICP-MS | mg/L | <5.8E-02 | -- | <5.7E-02 | -- | <6.2E-02 | -- |
| 116 | ICP-MS | mg/L | 6.14E-02 | 1.9% | 3.54E-02 | 13% | 3.42E-02 | 31% |
| 117 | ICP-MS | mg/L | 4.03E-02 | 2.7% | 1.13E-02 | 5.8% | 1.73E-02 | 12% |
| 118 | ICP-MS | mg/L | 1.15E-01 | 2.7% | 3.94E-02 | 4.2% | 5.07E-02 | 2.9% |
| 119 | ICP-MS | mg/L | 8.29E-01 | 0.3% | 9.74E+01 | 1.8% | 8.09E+00 | 0.2% |
| 120 | ICP-MS | mg/L | 1.56E-01 | 1.5% | 3.97E-02 | 13% | 6.89E-02 | 6.0% |
| 121 | ICP-MS | mg/L | <2.3E-02 | -- | 1.91E-01 | 3.1% | <2.4E-02 | -- |
| 122 | ICP-MS | mg/L | 3.89E-02 | 2.3% | <2.3E-02 | -- | <2.4E-02 | -- |
| 123 | ICP-MS | mg/L | <2.3E-02 | -- | 1.39E-01 | 2.0% | <2.4E-02 | -- |
| 124 | ICP-MS | mg/L | 5.53E-02 | 9.5% | 1.19E-02 | 12% | 2.60E-02 | 4.7% |
| 125 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 126 | ICP-MS | mg/L | 1.32E-01 | 0.9% | 7.31E-02 | 7.8% | 5.47E-02 | 8.7% |
| 128 | ICP-MS | mg/L | <4.6E-02 | -- | <4.5E-02 | -- | <4.8E-02 | -- |
| 130 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 134 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 135 | ICP-MS | mg/L | 8.30E-02 | 3.8% | 2.37E-01 | 3.8% | 9.08E-02 | 2.6% |
| 136 | ICP-MS | mg/L | 1.22E-02 | 7.4% | 2.05E-02 | 39% | <1.2E-02 | -- |
| 137 | ICP-MS | mg/L | 1.80E-01 | 4.6% | 5.64E-01 | 2.1% | 1.89E-01 | 2.0% |
| 138 | ICP-MS | mg/L | 6.57E-02 | 97% | 1.20E-01 | 51% | 1.37E-02 | 28% |
| 139 | ICP-MS | mg/L | <1.2E-02 | -- | 4.74E-02 | 2.1% | <1.2E-02 | -- |
| 140 | ICP-MS | mg/L | <1.2E-02 | -- | 1.34E+00 | 0.9% | 1.10E-01 | 0.0% |
| 141 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 142 | ICP-MS | mg/L | <1.2E-02 | -- | 2.03E-01 | 4.0% | 1.63E-02 | 3.3% |
| 143 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |

## Table B-3. Additional ICP-MS analysis of Tank 44 Dissolved Saltcake supernate, part 2 of 2

| m/z | method | units | Tank 44 Upper Composite Supernate | | Tank 44 Lower Composite Supernate | | Tank 44 Composite Pre-HGR | |
|---|---|---|---|---|---|---|---|---|
| | | | average | RSD | average | RSD | average | RSD |
| 144 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 145 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 146 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 147 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 148 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 149 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 150 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 151 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 152 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 153 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 154 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 155 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 156 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 157 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 158 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 159 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 160 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 161 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 162 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 163 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 164 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 165 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 166 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 167 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 168 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 169 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 170 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 171 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 172 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 173 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 174 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 175 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 176 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 177 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 178 | ICP-MS | mg/L | <1.2E-02 | -- | 1.44E-02 | 1.0% | <1.2E-02 | -- |
| 179 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 180 | ICP-MS | mg/L | 1.47E-02 | 0.9% | 1.89E-02 | 1.8% | 1.43E-02 | 1.0% |
| 181 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 182 | ICP-MS | mg/L | 2.82E+00 | 0.3% | 2.24E-01 | 1.4% | 2.63E+00 | 1.2% |
| 183 | ICP-MS | mg/L | 1.53E+00 | 1.9% | 1.23E-01 | 1.2% | 1.44E+00 | 0.5% |
| 184 | ICP-MS | mg/L | 3.29E+00 | 0.7% | 2.60E-01 | 0.9% | 3.10E+00 | 0.1% |
| 185 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 186 | ICP-MS | mg/L | 3.10E+00 | 1.3% | 2.45E-01 | 1.4% | 2.91E+00 | 0.8% |
| 187 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 191 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 193 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 194 | ICP-MS | mg/L | <1.2E-02 | -- | 1.94E-02 | 6.8% | <1.2E-02 | -- |
| 195 | ICP-MS | mg/L | <1.2E-02 | -- | 1.85E-02 | 0.2% | <1.2E-02 | -- |
| 196 | ICP-MS | mg/L | <1.2E-02 | -- | 1.33E-02 | 5.7% | <1.2E-02 | -- |
| 198 | ICP-MS | mg/L | 2.26E-02 | 5.3% | 4.59E-02 | 8.2% | 2.34E-02 | 1.2% |
| 203 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 204 | ICP-MS | mg/L | <1.2E-02 | -- | 3.44E-02 | 7.6% | <1.2E-02 | -- |
| 205 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 206 | ICP-MS | mg/L | 4.20E-02 | 102% | 5.37E-02 | 30% | <1.2E-02 | -- |
| 207 | ICP-MS | mg/L | 3.84E-02 | 99% | 4.47E-02 | 28% | <1.2E-02 | -- |
| 208 | ICP-MS | mg/L | 8.32E-02 | 122% | 1.13E-01 | 19% | <1.2E-02 | -- |
| 230 | ICP-MS | mg/L | 1.16E-02 | 0.3% | <1.1E-02 | 5.8% | <1.2E-02 | -- |
| 241 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 242 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 243 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |
| 244 | ICP-MS | mg/L | <1.2E-02 | -- | <1.1E-02 | -- | <1.2E-02 | -- |

### Table B-4. Below detection limit values for Tank 44 segment composite IC and ICP-ES analysis

| analyte | method | units | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Supernate | Remaining Solids | | Total | Supernate | Remaining Solids | | Total |
| | | | average | average | RSD | sum | average | average | RSD | sum |
| Br ⁻ | IC | wt% | <1.8E-01 | <8.3E-02 | -- | -- | <1.7E-01 | <1.2E-01 | -- | -- |
| Ag | ICP-AES | wt% | <4.2E-04 | <2.0E-03 | -- | -- | <4.2E-04 | <2.3E-03 | -- | -- |
| Be | ICP-AES | wt% | <1.8E-06 | <3.2E-05 | -- | -- | <1.8E-06 | <3.6E-05 | -- | -- |
| Cd | ICP-AES | wt% | <2.0E-05 | <2.7E-04 | -- | -- | <1.9E-05 | <3.1E-04 | -- | -- |
| Co | ICP-AES | wt% | <8.0E-05 | <1.5E-03 | -- | -- | <8.0E-05 | <1.7E-03 | -- | -- |
| Gd | ICP-AES | wt% | <7.7E-04 | <4.4E-03 | -- | -- | <7.6E-04 | <5.1E-03 | -- | -- |
| La | ICP-AES | wt% | <3.9E-05 | <2.7E-03 | -- | -- | <3.9E-05 | <3.0E-03 | -- | -- |
| Pb | ICP-AES | wt% | <2.6E-04 | <2.1E-02 | -- | -- | <2.6E-04 | <2.5E-02 | -- | -- |
| Sb | ICP-AES | wt% | <3.4E-04 | <3.1E-03 | -- | -- | <3.3E-04 | <3.6E-03 | -- | -- |
| Sn | ICP-AES | wt% | <1.1E-03 | <2.4E-03 | -- | -- | <1.1E-03 | <2.7E-03 | -- | -- |
| Sr | ICP-AES | wt% | <3.0E-05 | <4.3E-03 | -- | -- | <3.0E-05 | <5.0E-03 | -- | -- |
| Th | ICP-AES | wt% | <8.8E-04 | <5.2E-03 | -- | -- | <8.7E-04 | <6.0E-03 | -- | -- |
| V | ICP-AES | wt% | <1.6E-05 | <1.9E-04 | -- | -- | <1.6E-05 | <2.2E-04 | -- | -- |
| Zr | ICP-AES | wt% | <1.1E-04 | <1.3E-04 | -- | -- | <1.1E-04 | <1.5E-04 | -- | -- |

## Table B-5. Additional ICP-MS analysis of Tank 44 segment composites, part 1 of 2

| | | | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| m/z | method | units | Supernate average | Remaining Solids average | Remaining Solids RSD | Total sum | Supernate average | Remaining Solids average | Remaining Solids RSD | Total sum |
| 82 | ICP-MS | wt% | <1.8E-06 | <4.7E-06 | -- | -- | 2.20E-06 | <5.4E-06 | -- | 2.25E-06 |
| 84 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 8.52E-06 | 1.4% | 1.01E-05 |
| 85 | ICP-MS | wt% | 9.55E-06 | 9.15E-06 | 13% | 2.09E-05 | 5.26E-05 | 4.74E-05 | 0.7% | 1.10E-04 |
| 86 | ICP-MS | wt% | <8.9E-07 | 5.39E-05 | 17% | 2.11E-05 | 1.17E-06 | 3.42E-04 | 3.3% | 4.08E-04 |
| 87 | ICP-MS | wt% | 1.99E-05 | 5.63E-05 | 10% | 5.80E-05 | 1.04E-04 | 3.46E-04 | 2.5% | 5.18E-04 |
| 89 | ICP-MS | wt% | <8.9E-07 | 5.49E-06 | 9.0% | 2.15E-06 | 9.23E-07 | 4.82E-05 | 5.6% | 5.83E-05 |
| 90 | ICP-MS | wt% | 1.00E-06 | 1.95E-05 | 13% | 9.45E-06 | 8.10E-05 | 1.61E-04 | 6.3% | 2.74E-04 |
| 91 | ICP-MS | wt% | 8.94E-07 | 6.09E-06 | 9.0% | 2.39E-06 | 3.61E-05 | 7.19E-05 | 5.9% | 1.22E-04 |
| 92 | ICP-MS | wt% | 7.49E-05 | 7.20E-05 | 4.4% | 1.64E-04 | 7.13E-05 | 1.29E-04 | 6.9% | 2.26E-04 |
| 93 | ICP-MS | wt% | 8.94E-07 | 1.50E-05 | 17% | 5.87E-06 | 7.24E-05 | 1.18E-03 | 3.8% | 1.47E-03 |
| 94 | ICP-MS | wt% | 4.92E-05 | 4.84E-05 | 4.7% | 1.08E-04 | 6.41E-05 | 1.17E-04 | 6.2% | 2.05E-04 |
| 95 | ICP-MS | wt% | 8.94E-04 | 7.31E-04 | 4.8% | 1.91E-03 | 4.01E-04 | 4.55E-04 | 3.5% | 9.51E-04 |
| 96 | ICP-MS | wt% | 7.74E-05 | 7.14E-05 | 3.9% | 1.68E-04 | 5.31E-05 | 9.31E-05 | 6.3% | 1.65E-04 |
| 97 | ICP-MS | wt% | 8.40E-04 | 6.68E-04 | 4.0% | 1.78E-03 | 3.77E-04 | 4.06E-04 | 5.2% | 8.68E-04 |
| 98 | ICP-MS | wt% | 8.94E-04 | 7.01E-04 | 3.3% | 1.89E-03 | 4.00E-04 | 4.37E-04 | 2.6% | 9.29E-04 |
| 100 | ICP-MS | wt% | 9.26E-04 | 7.00E-04 | 3.5% | 1.95E-03 | 3.84E-04 | 4.25E-04 | 2.5% | 8.98E-04 |
| 101 | ICP-MS | wt% | 1.92E-06 | 1.45E-05 | 10% | 9.16E-06 | 4.07E-05 | 8.70E-05 | 2.2% | 1.45E-04 |
| 102 | ICP-MS | wt% | 1.74E-06 | 1.32E-05 | 7.6% | 8.32E-06 | 3.67E-05 | 7.85E-05 | 3.0% | 1.31E-04 |
| 104 | ICP-MS | wt% | 1.47E-06 | 9.61E-06 | 6.7% | 6.43E-06 | 3.18E-05 | 7.10E-05 | 3.9% | 1.17E-04 |
| 105 | ICP-MS | wt% | 2.95E-06 | 1.30E-05 | 7.2% | 1.04E-05 | 7.59E-05 | 1.75E-04 | 4.2% | 2.86E-04 |
| 106 | ICP-MS | wt% | 2.34E-06 | 1.13E-05 | 7.6% | 8.69E-06 | 6.38E-05 | 1.52E-04 | 2.7% | 2.46E-04 |
| 107 | ICP-MS | wt% | 1.79E-06 | 2.73E-05 | 8.0% | 1.07E-05 | 4.70E-05 | 1.34E-03 | 3.7% | 1.65E-03 |
| 108 | ICP-MS | wt% | <1.8E-06 | 4.24E-06 | 8.5% | 1.66E-06 | 2.23E-05 | 5.61E-05 | 2.6% | 8.96E-05 |
| 109 | ICP-MS | wt% | <1.8E-06 | 2.02E-05 | 10% | 7.91E-06 | 5.71E-06 | 1.20E-03 | 3.5% | 1.44E-03 |
| 110 | ICP-MS | wt% | <2.7E-06 | 1.37E-05 | 8.8% | 5.39E-06 | 9.65E-06 | 1.03E-04 | 9.9% | 1.32E-04 |
| 111 | ICP-MS | wt% | <2.7E-06 | 1.86E-05 | 8.0% | 7.29E-06 | <2.8E-06 | 1.23E-04 | 14% | 1.47E-04 |
| 112 | ICP-MS | wt% | 3.58E-06 | 3.44E-05 | 9.7% | 1.35E-05 | <3.7E-06 | 2.38E-04 | 13% | 2.83E-04 |
| 113 | ICP-MS | wt% | <3.6E-06 | 1.71E-05 | 12% | 6.71E-06 | <3.7E-06 | 1.15E-04 | 14% | 1.37E-04 |
| 114 | ICP-MS | wt% | 4.47E-06 | 4.07E-05 | 12% | 1.60E-05 | <4.6E-06 | 2.76E-04 | 14% | 3.28E-04 |
| 116 | ICP-MS | wt% | 4.74E-06 | 2.57E-05 | 13% | 1.87E-05 | 2.88E-06 | 2.31E-04 | 1.3% | 2.77E-04 |
| 117 | ICP-MS | wt% | 3.11E-06 | 1.09E-05 | 14% | 9.92E-06 | 9.23E-07 | 1.09E-04 | 4.6% | 1.31E-04 |
| 118 | ICP-MS | wt% | 8.85E-06 | 3.17E-05 | 14% | 2.85E-05 | 3.21E-06 | 3.18E-04 | 3.7% | 3.82E-04 |
| 119 | ICP-MS | wt% | 6.40E-05 | 2.05E-03 | 13% | 9.21E-04 | 7.94E-03 | 2.14E-02 | 12% | 3.35E-02 |
| 120 | ICP-MS | wt% | 1.21E-05 | 4.32E-05 | 16% | 3.88E-05 | 3.24E-06 | 4.27E-04 | 4.1% | 5.11E-04 |
| 121 | ICP-MS | wt% | <1.8E-06 | 1.71E-05 | 94% | 6.70E-06 | 1.56E-05 | 1.46E-04 | 3.0% | 1.90E-04 |
| 122 | ICP-MS | wt% | <3.0E-06 | 1.02E-05 | 21% | 9.45E-06 | <1.8E-06 | 1.05E-04 | 4.9% | 1.25E-04 |
| 123 | ICP-MS | wt% | <1.8E-06 | <1.4E-05 | -- | -- | 1.13E-05 | 1.06E-04 | 4.6% | 1.38E-04 |
| 124 | ICP-MS | wt% | 4.27E-06 | 1.48E-05 | 15% | 1.35E-05 | 9.66E-07 | 1.54E-04 | 2.9% | 1.84E-04 |
| 125 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 126 | ICP-MS | wt% | 1.02E-05 | 3.19E-05 | 11% | 3.10E-05 | 5.95E-06 | 3.77E-04 | 4.5% | 4.54E-04 |
| 128 | ICP-MS | wt% | <3.6E-06 | <2.3E-06 | -- | -- | <3.7E-06 | 5.88E-06 | 5.5% | 7.00E-06 |
| 130 | ICP-MS | wt% | <8.9E-07 | <4.7E-06 | -- | -- | <9.2E-07 | 1.75E-05 | 3.7% | 2.08E-05 |
| 134 | ICP-MS | wt% | <8.9E-07 | 9.69E-06 | 16% | 3.80E-06 | <9.2E-07 | 7.80E-05 | 1.9% | 9.27E-05 |
| 135 | ICP-MS | wt% | 6.40E-06 | 3.86E-05 | 12% | 2.67E-05 | 1.93E-05 | 3.01E-04 | 1.4% | 3.78E-04 |
| 136 | ICP-MS | wt% | <9.4E-07 | 3.06E-05 | 13% | 1.37E-05 | 1.67E-06 | 2.34E-04 | 1.7% | 2.80E-04 |
| 137 | ICP-MS | wt% | 1.39E-05 | 3.15E-04 | 14% | 1.49E-04 | 4.60E-05 | 3.57E-03 | 4.0% | 4.29E-03 |
| 138 | ICP-MS | wt% | 5.07E-06 | 2.82E-04 | 12% | 1.20E-04 | 9.79E-06 | 2.12E-03 | 1.5% | 2.53E-03 |
| 139 | ICP-MS | wt% | <8.9E-07 | 2.10E-05 | 15% | 8.25E-06 | 3.86E-06 | 2.32E-03 | 3.6% | 2.76E-03 |
| 140 | ICP-MS | wt% | 8.94E-07 | 4.41E-05 | 15% | 1.73E-05 | 1.09E-04 | 1.12E-03 | 2.9% | 1.45E-03 |
| 141 | ICP-MS | wt% | <8.9E-07 | 3.29E-06 | 8.8% | 1.29E-06 | <9.2E-07 | 2.47E-05 | 4.3% | 2.94E-05 |
| 142 | ICP-MS | wt% | 8.94E-07 | 1.06E-05 | 13% | 4.17E-06 | 1.65E-05 | 1.77E-04 | 2.5% | 2.28E-04 |
| 143 | ICP-MS | wt% | <8.9E-07 | 3.17E-06 | 9.2% | 1.24E-06 | <9.2E-07 | 1.62E-05 | 6.9% | 1.93E-05 |

## Table B-6. Additional ICP-MS analysis of Tank 44 segment composites, part 2 of 2

| | | | Upper Segment Composite | | | | Lower Segment Composite | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| m/z | method | units | Supernate | Remaining Solids | | Total | Supernate | Remaining Solids | | Total |
| | | | average | average | RSD | sum | average | average | RSD | sum |
| 144 | ICP-MS | wt% | <8.9E-07 | 4.51E-06 | 14% | 1.77E-06 | <9.2E-07 | 2.47E-05 | 7.2% | 2.94E-05 |
| 145 | ICP-MS | wt% | <8.9E-07 | 2.34E-06 | -- | -- | <9.2E-07 | 1.13E-05 | 9.1% | 1.34E-05 |
| 146 | ICP-MS | wt% | <8.9E-07 | 2.80E-06 | 12% | 1.10E-06 | <9.2E-07 | 1.59E-05 | 8.8% | 1.89E-05 |
| 147 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 7.14E-06 | 6.3% | 8.49E-06 |
| 148 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 1.02E-05 | 6.6% | 1.22E-05 |
| 149 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 4.33E-06 | 2.5% | 5.15E-06 |
| 150 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 8.94E-06 | 4.7% | 1.06E-05 |
| 151 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 152 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 9.94E-06 | 1.9% | 1.18E-05 |
| 153 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 3.99E-06 | 3.3% | 4.75E-06 |
| 154 | ICP-MS | wt% | <8.9E-07 | 2.99E-06 | 8.8% | 1.17E-06 | <9.2E-07 | 2.80E-05 | 2.0% | 3.33E-05 |
| 155 | ICP-MS | wt% | <8.9E-07 | 7.05E-06 | 14% | 2.77E-06 | <9.2E-07 | 3.21E-05 | 1.5% | 3.82E-05 |
| 156 | ICP-MS | wt% | <8.9E-07 | 8.05E-06 | 15% | 3.16E-06 | <9.2E-07 | 3.75E-05 | 4.7% | 4.46E-05 |
| 157 | ICP-MS | wt% | <8.9E-07 | 6.00E-06 | 17% | 2.35E-06 | <9.2E-07 | 1.84E-05 | 1.6% | 2.19E-05 |
| 158 | ICP-MS | wt% | <8.9E-07 | 9.65E-06 | 14% | 3.78E-06 | <9.2E-07 | 1.60E-05 | 4.0% | 1.91E-05 |
| 159 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 3.69E-06 | 3.1% | 4.38E-06 |
| 160 | ICP-MS | wt% | <8.9E-07 | 8.86E-06 | 16% | 3.47E-06 | <9.2E-07 | 1.34E-05 | 2.4% | 1.60E-05 |
| 161 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.8E-06 | -- | -- |
| 162 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 3.06E-06 | 5.8% | 3.64E-06 |
| 163 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 2.89E-06 | 9.9% | 3.44E-06 |
| 164 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 3.20E-06 | 5.6% | 3.81E-06 |
| 165 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 166 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 167 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 168 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 169 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 170 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 171 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 172 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 173 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 174 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 175 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 176 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 177 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 178 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 1.17E-06 | <2.7E-06 | -- | -- |
| 179 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 180 | ICP-MS | wt% | 1.13E-06 | 2.39E-06 | 7.5% | 2.99E-06 | 1.54E-06 | <2.8E-06 | 8.0% | 4.87E-06 |
| 181 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 182 | ICP-MS | wt% | 2.17E-04 | 2.84E-04 | 3.7% | 5.05E-04 | 1.82E-05 | 7.95E-05 | 2.6% | 1.13E-04 |
| 183 | ICP-MS | wt% | 1.18E-04 | 1.56E-04 | 3.5% | 2.74E-04 | 1.00E-05 | 4.40E-05 | 3.1% | 6.26E-05 |
| 184 | ICP-MS | wt% | 2.54E-04 | 3.38E-04 | 3.3% | 5.92E-04 | 2.12E-05 | 9.40E-05 | 3.5% | 1.33E-04 |
| 185 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 186 | ICP-MS | wt% | 2.39E-04 | 3.14E-04 | 3.5% | 5.56E-04 | 2.00E-05 | 8.70E-05 | 3.2% | 1.24E-04 |
| 187 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 191 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 193 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | <2.7E-06 | -- | -- |
| 194 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 1.58E-06 | <2.7E-06 | -- | 1.62E-06 |
| 195 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 1.51E-06 | <2.7E-06 | -- | 1.54E-06 |
| 196 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 1.09E-06 | <2.7E-06 | -- | 1.11E-06 |
| 198 | ICP-MS | wt% | 1.74E-06 | 6.79E-06 | 7.7% | 5.82E-06 | 3.74E-06 | 2.94E-05 | 3.8% | 3.88E-05 |
| 203 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 5.17E-06 | 4.7% | 6.15E-06 |
| 204 | ICP-MS | wt% | <8.9E-07 | 5.64E-06 | 6.7% | 2.21E-06 | 2.81E-06 | 1.26E-04 | 75% | 1.52E-04 |
| 205 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | <9.2E-07 | 1.17E-05 | 2.3% | 1.39E-05 |
| 206 | ICP-MS | wt% | <3.2E-06 | 5.42E-05 | 11% | 2.71E-05 | 4.38E-06 | 2.03E-03 | 89% | 2.42E-03 |
| 207 | ICP-MS | wt% | <3.0E-06 | 4.62E-05 | 13% | 2.35E-05 | 3.64E-06 | 1.74E-03 | 89% | 2.08E-03 |
| 208 | ICP-MS | wt% | <6.4E-06 | 1.13E-04 | 10% | 5.59E-05 | 9.23E-06 | 4.31E-03 | 86% | 5.13E-03 |
| 230 | ICP-MS | wt% | <8.9E-07 | <2.3E-06 | -- | -- | 9.23E-07 | <2.7E-06 | -- | 9.44E-07 |
| 241 | ICP-MS | wt% | -- | <2.7E-06 | -- | -- | -- | 7.77E-05 | 5.8% | 9.24E-05 |
| 242 | ICP-MS | wt% | -- | <2.3E-06 | -- | -- | -- | 6.41E-06 | 4.7% | 7.62E-06 |
| 243 | ICP-MS | wt% | -- | <2.3E-06 | -- | -- | -- | <2.7E-06 | -- | -- |
| 244 | ICP-MS | wt% | -- | <2.3E-06 | -- | -- | -- | <2.7E-06 | -- | -- |

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