Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

We put science to work.™

Savannah River
National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Low Temperature Aluminum Dissolution (LTAD) Real Waste Testing of the November 2017 Tank 51 Slurry Sample

S. H. Reboul
J. D. Newell
J. M. Pareizs
C. J. Coleman
June 2018
SRNL-STI-2018-00179, Revision 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2018-00179
Revision 0

Keywords: *LTAD, gas generation, real waste testing, Tank 51, hydrogen*

Retention: *Permanent*

Low Temperature Aluminum Dissolution (LTAD) Real Waste Testing of the November 2017 Tank 51 Slurry Sample

S. H. Reboul
J. D. Newell
J. M. Pareizs
C. J. Coleman

June 2018

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

S. H. Reboul, Advanced Characterization and Processing Date

J. D. Newell, Process Technology Programs Date

J. M. Pareizs, Process Technology Programs Date

C. J. Coleman, Analytical Development Date

TECHNICAL REVIEW:

M. S. Hay, Advanced Characterization and Processing, Reviewed per E7 2.60 Date

APPROVAL:

B. J. Wiedenman, Manager Date
Advanced Characterization and Processing

D. E. Dooley, Director, Chemical Processing Technologies Date

J. E. Occhipinti, Manager Date
SRR Tank Farm Facility Engineering

ACKNOWLEDGEMENTS

The following individuals are acknowledged for providing significant contributions to this task: R. W. Blessing, P. U. Burkhalter, J. Fawbush, M. L. Jenkins, M. C. Lee, J. B. Mixon, C. D. Nguyen, V. A. Skeens, R. J. Stanley, R. C. Sullivan, and D. J. Wheeler of SRNL's Shielded Cells Operations group; A. J. Boggess, L. W. Brown, J. F. Cartledge, L. E. Cheatham, S. L. Crump, A. A. Ekechukwu, C. D. Gaillard, S. C. Gleaton, M. A Jones, J. S. Moody, T. L. White, and J. E. Young of SRNL's Analytical Development section; and C. L. Crawford, T. B. Edwards, C. J. Martino, B. C. Miller, and K. L. Wyszynski of SRNL's Environmental Stewardship section. The assistance of each of these individuals is appreciated.

EXECUTIVE SUMMARY

Low Temperature Aluminum Dissolution (LTAD) will be performed on Tank 51 sludge prior to sending Sludge Batch 10 to the Defense Waste Processing Facility (DWPF), such that a sizable fraction of the insoluble aluminum will be dissolved and removed. During LTAD, the free hydroxide concentration and temperature of the sludge slurry are both raised, resulting in significantly increased aluminum solubility, which facilitates aluminum removal via decanting of the liquid phase. This Research and Development task will provide input information regarding the expected gas generation rates under the bounding temperature and free hydroxide conditions of the upcoming Tank 51 LTAD evolution. It will also provide information on the expected fraction of insoluble aluminum that will dissolve as a function of temperature and time, as well as the expected chemical and physical properties of the Tank 51 sludge slurry, prior to and following the LTAD operations.

Savannah River National Laboratory's LTAD testing was performed on aliquots of a three liter Tank 51 sludge slurry sample collected in November 2017. Two sets of tests were performed – baseline tests utilizing pure "as received" Tank 51 slurry material – and high caustic tests utilizing a combination of the "as received" slurry material and sufficient 50 wt% NaOH to raise the initial supernatant free hydroxide concentration to 6 M. In each test, gas generation from the respective slurry material was monitored while the slurry temperature was raised sequentially to temperatures of 50, 75, and 85 °C, and then held at those temperatures for a minimum of 12, 12, and 48 hours, respectively. Hydrogen generation rates (HGRs) and methane concentrations were both monitored continuously over the course of the testing. Characterization of pre-LTAD slurry samples, post-LTAD slurry samples, and process slurry samples collected during the course of testing provided the bases for determining the portions of insoluble aluminum dissolved over time, and the relative differences between the pre-LTAD and post-LTAD properties and compositions.

HGRs measured during the LTAD tests ranged from a low of ~2.5E-07 ft^3/hr/gal sludge to a high of ~2.5E-06 ft^3/hr/gal sludge, with HGRs in the baseline tests being somewhat higher than those in the high caustic test. Short-term HGRs peaks were observed immediately after increasing the temperature (particularly after raising the temperature to 50 °C and to 75 °C), and a short-term HGR decline was observed upon addition of the 50 wt% NaOH in the high caustic tests. In general, the HGR variations were attributed to changes in the slurry's ability to retain gas and to release retained gas, rather than to changes in the source (or sources) of the HGRs. Statistical analysis of the data indicates that the uncertainties of the HGR results fall in the range of ~4-20% (on a relative basis), with the lowest uncertainties applicable to the highest measured HGR values and the highest uncertainties applicable to the lowest measured HGR values. Radiolysis was thought to be the primary source of the HGRs, as on average, the magnitude of the HGRs was consistent with that of the theoretical estimate based on radiolysis. Other potential contributors to the HGRs may have been present, but if so, were minor compared to radiolysis.

In contrast to the majority of HGR results, all of the measured methane concentrations were below the methane limit of quantification (LOQ), which was 90 ppmv. As the methane LOQ is relatively high compared to the hydrogen LOQ, it is acknowledged that non-detection of methane does not necessarily ensure its absence.

Characterization of the "as received" sludge slurry identified the following pre-LTAD properties:

- A sludge slurry density of 1.22 g/mL
- A supernatant density of 1.17 g/mL
- A total solids content of 27.0 wt%
- An insoluble solids content of 8.3 wt%
- An aluminum content of 10.7 wt% of the total solids, with ~87% of the aluminum present in the solid phase and ~13% present in the liquid phase (a supernatant aluminum concentration of ~0.17 M)
- A supernatant free hydroxide concentration of ~0.97 M
- A supernatant sodium concentration of ~4.1 M
- A supernatant total organic carbon (TOC) concentration of 235 mg/L, primarily due to oxalate
- Undetectable supernatant volatile organic constituents including butanol and propanol (< 2.4 mg/L)
- Undetectable supernatant semi-volatile organic constituents (< 9.8 mg/L to < 98 mg/L)

Correspondingly, characterization of the post-LTAD sludge slurry (following addition of the 50 wt% NaOH and completion of the high caustic LTAD tests) identified the following properties:

- A sludge slurry density of 1.35 g/mL
- A supernatant density of 1.31 g/mL
- A total solids content of 34.7 wt%
- An insoluble solids content of 2.4 wt%
- An aluminum content of 5.58 wt% of the total solids, with ~16% of the aluminum present in the solid phase and ~82% present in the liquid phase (a supernatant aluminum concentration of ~0.81 M)
- A supernatant free hydroxide concentration of ~4.7 M
- A supernatant sodium concentration of ~7.7 M
- A supernatant TOC concentration of 105 mg/L, with less than ~28% of the TOC due to oxalate
- Undetectable supernatant volatile organic constituents including butanol and propanol (< 2.7 mg/L)
- Undetectable semi-volatile organic constituents (< 11 mg/L to < 110 mg/L)

The two primary sources of differences between the pre-LTAD and post-LTAD sludge slurry properties were: 1) the large amount of 50 wt% NaOH that was added to the slurry at the start of the high caustic LTAD tests; and 2) the partitioning of solid-phase insoluble to liquid-phase aluminum that occurred during heating in the high caustic LTAD tests. Addition of the 50 wt% NaOH had a major impact on the slurry and supernatant densities, the solids distribution, the concentrations of all elemental constituents in the total solids and the supernatant (both prior to and after heating), and the concentrations of ionic constituents in the supernatant, particularly that of free hydroxide. In contrast, the partitioning of solid-phase aluminum to liquid-phase aluminum that occurred during the high caustic LTAD tests had a major impact on the aluminum concentrations within the insoluble solids (which, in turn, had a major impact on the insoluble solids concentration) and on the aluminum concentration in the supernatant phase. In addition, it had an appreciable impact on the supernatant free hydroxide concentration (which dropped as liquid phase aluminate was formed during dissolution) and a relatively minor impact on supernatant density, dissolved solids content, and soluble solids content, which would be expected to increase slightly due to the higher liquid-phase aluminate concentrations.

A total of ~80 wt% of the insoluble aluminum in the Tank 51 slurry was found to dissolve over the course of the high caustic LTAD test. This included an insignificant amount of insoluble aluminum dissolving during the twelve hour period at 50 °C, ~25 wt% of insoluble aluminum dissolving during the twelve hour period at 75 °C, ~43 additional wt% insoluble aluminum dissolving during the first twenty-four hours at 85 °C, and ~10-14 additional wt% insoluble aluminum dissolving during the final twenty-four hours at 85 °C. Correspondingly, the insoluble solids content of the slurry dropped by ~58% over the course of the high caustic LTAD test, from 5.7 wt% insoluble solids following addition of the 50 wt%

NaOH (but prior to heating) to 2.4 wt% following completion of the 85 °C temperature regime. The relative decline in the insoluble solids content and the amount of insoluble aluminum that dissolved indicate that the primary mineral form of the insoluble aluminum was boehmite.

The supernatant TOC concentrations of the pre/post-LTAD slurries and process samples showed significant variations that were difficult to understand, thereby providing insufficient bases to make sound conclusions regarding generation or destruction of TOC compounds during LTAD. An experimental study addressing temperature and chemical effects of test slurries containing known quantities of TOC "standards" is recommended for the purpose of providing insight into the observed TOC behavior.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytical Development
AR	aqua regia
ARG	analyzed reference glass
BT	base titration
CPC	Chemical Process Cell
DAC	data acquisition and control
DWPF	Defense Waste Processing Facility
GC	gas chromatograph
GC-MS	gas chromatography-mass spectrometry
HGR	hydrogen generation rate
HM	H-Modified
IC	ion chromatography
ICP-AES	inductively coupled plasma – atomic emission spectroscopy
IS	insoluble solids
LOQ	limit of quantification
LTAD	low temperature aluminum dissolution
MDL	minimum detection limit
MW	molecular weight
n	number of determinations
%RSD	percent relative standard deviation
PID	proportional-integral-derivative
PF	peroxide fusion
SB10	Sludge Batch 10
SBQ	sludge batch qualification
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SVOA	semi-volatile organic analysis
TIC	total inorganic carbon
TOC	total organic carbon
VOA	volatile organic analysis
WTP	Waste Treatment Plant

1.0 Introduction

H-Modified (HM) sludge from Tank 15 was transferred to Savannah River Site (SRS) Tank 13, and then to Tank 51, in preparation for Sludge Batch 10 (SB10) processing. Because of the high aluminum content of the HM sludge, Low Temperature Aluminum Dissolution (LTAD) will be performed on the Tank 51 sludge prior to sending SB10 to the Defense Waste Processing Facility (DWPF). The goal of the LTAD processing is to dissolve and remove a significant portion of the insoluble aluminum. To accomplish this, the free hydroxide concentration of the sludge slurry and the temperature of the sludge slurry will both be raised, resulting in significantly increased aluminum solubility.

Based on the flowsheet,[1] the initial free hydroxide concentration will be raised to 4.3 M and the slurry temperature will be raised to a maximum temperature of 65 ºC, with the goal of dissolving 40 wt% of the insoluble aluminum. Given that the maximum expected temperature exceeds 60 °C, new gas generation rates are needed for the Waste Tank Non-Infinite Quiescent Time Program, per the direction of U-ESS-G-00007.[2] This task, the Tank 51 LTAD Real Waste Testing, will provide the input information for establishing such gas generation rates. It will also provide information on the fraction of insoluble aluminum dissolved as a function of temperature and time, and on the requested chemical and physical properties of the Tank 51 slurry, prior to and following the LTAD process.

Because this task was performed while the flowsheet was still being developed, the exact free hydroxide concentration and temperature conditions of the Tank 51 LTAD evolution had not yet been defined, and there was still consideration of using a higher initial free hydroxide concentration and a higher maximum dissolution temperature. As such, the conditions of SRNL's LTAD testing included a maximum initial free hydroxide concentration of 6.0 M and a maximum dissolution temperature of 85 ºC, which bounded LTAD operations.

The applicable scope of work for this task is defined in Technical Task Request X-TTR-H-00075[3] and Task Technical and Quality Assurance Plan SRNL-RP-2017-00786, Revision 1.[4]

2.0 Objectives

The specific objectives of this task include:

1) Quantifying hydrogen generation rates (HGRs) and methane concentrations during:

   a) baseline LTAD tests, where unadjusted "as received" Tank 51 slurry material (in the absence of additional caustic) is heated and held at temperatures ranging from ambient temperature up to 85 °C; and
   b) high caustic LTAD tests, where a mixture of the "as received" Tank 51 slurry material and sufficient 50 wt% NaOH to bring the initial supernatant free hydroxide concentration to 6 M is heated and held at temperatures ranging from 50 °C to 85 °C.

2) Characterizing the pre-LTAD and post-LTAD slurry/supernatant material compositions, for the purposes of quantifying:

   a) the fraction of insoluble aluminum that partitioned to the liquid phase during LTAD;
   b) the influence of LTAD on the solids distribution and the slurry/supernatant densities; and
   c) the influence of LTAD on the slurry and supernatant compositions.

3) Characterizing process samples collected during the baseline and high caustic LTAD tests, to quantify concentrations of key supernatant constituents as functions of the LTAD progress.

The overall goal of the task is to provide estimates of the range of HGRs, methane concentrations, and waste compositional changes to be expected during the upcoming Tank 51 LTAD operations.

3.0 Methodology

3.1 Tank 51 Sludge Slurry Sample

The LTAD gas generation testing and characterization scope was performed on aliquots of a 3.08 liter sludge slurry sample collected from SRS Tank 51 on November 28, 2017. The applicable sample identification number is HTF-51-17-112. The slurry sample mass was 3760 g. Upon receipt into the Shielded Cell, the slurry sample was transferred to a four liter polybottle, as shown in Figure 3-1.

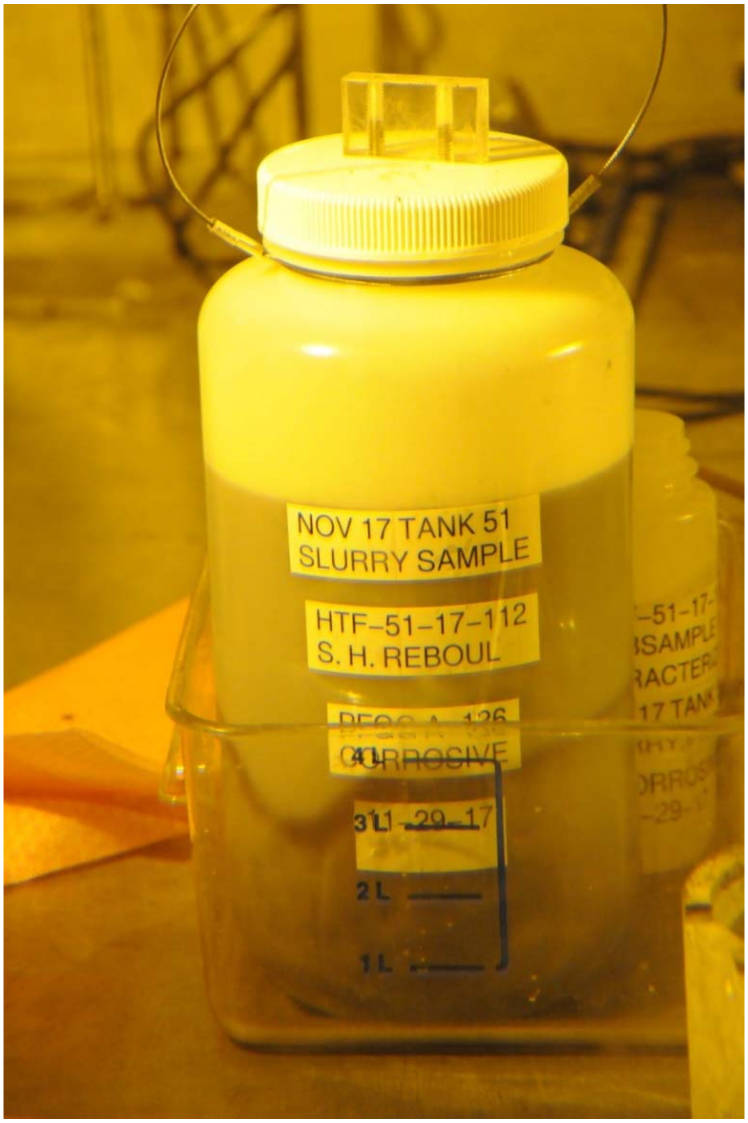


Figure 3-1. November 2017 Tank 51 Slurry Sample in the Shielded Cell Polybottle

3.2 LTAD Gas Generation Testing

Shielded Cells Real Waste LTAD Test Rig

Design elements from equipment used for previous one liter and four liter sludge batch qualification Chemical Process Cell (CPC) testing were combined to create the real waste LTAD measurement rig.[5,6] The vessel holding the real waste sample and assuring capture of gases during testing was made of 304L stainless steel, with an active volume of approximately 1.2 liters and a sealing Teflon lid. The exterior of the vessel was insulated with one quarter inch thick neoprene, to reduce heat loss and help maintain stable interior temperatures.

For the baseline LTAD tests, the insulated stainless steel vessel was mounted to the same type of stand designed for previous four liter Sludge Batch Qualification (SBQ) tests (this stand was already available for use in the Shielded Cell, having been fabricated and used in a previous SBQ test). In contrast, for the high caustic LTAD tests, the insulated stainless steel vessel was mounted to the same type of stand designed for previous one liter SBQ tests, which improved vessel handling convenience (this stand was fabricated while the baseline LTAD tests were being performed). Note that both stands performed equally well in maintaining stability of the LTAD test components. A photograph of the LTAD rig utilized in the high caustic LTAD tests is given in Figure 3-2.

Heating was provided using two 0.375-inch diameter Inconel Alloy 800 heating rods powered by an automated direct current power supply (TDK-Lambda Genesys, GEN150-10). Use of a flow-through system with minimal headspace is consistent with the HGR measurement apparatus recommended and developed for qualification of actual-waste feeds at the Hanford Waste Treatment Plant (WTP).[7,8] The WTP system, however, utilizes a water-blanketed borosilicate glass vessel for holding and heating the waste (as opposed to the rod-heated stainless steel vessel of the LTAD rig), and has a significantly smaller waste sample capacity, nominally 100 mL.

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. Two 1-inch diameter, 4-blade, 45° pitched turbine stainless steel impellers were welded to the stainless-steel agitator shaft. Mixing was utilized to maintain continuous agitation of the slurry 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 back into the LTAD vessel. Offgas 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 schematic depicting integration of the primary LTAD rig measurement components is given in Figure 3-3.

Data Acquisition and Power Control

A Data Acquisition and Control (DAC) application was programmed using National Instruments LabVIEW software. The software that controlled the process parameters for the real waste LTAD tests was developed by adapting the DAC recently used in Sludge Batch 9 qualification. The DAC logged process data and controlled mixing speed, purge gas flow rate, and heating rod temperature.

A proportional-integral-derivative (PID) control algorithm governs the amount of power supplied to the heating rods by comparing the bulk process temperature to the process temperature setpoint. To prevent the rods from overheating, a control limit is defined ("rod dT limit") that prevents the heating rods from exceeding the bulk temperature by the specified amount. Given that HGR is expected to be temperature dependent, efforts were made to eliminate localized hot regions in the process vessel by minimizing the differential temperature between the heating rods and the process temperature and by insulating the process vessel. Rod dT limits for these tests were constrained to 30 ºC. The maximum dT that was observed during steady state heating was approximately 20 °C.

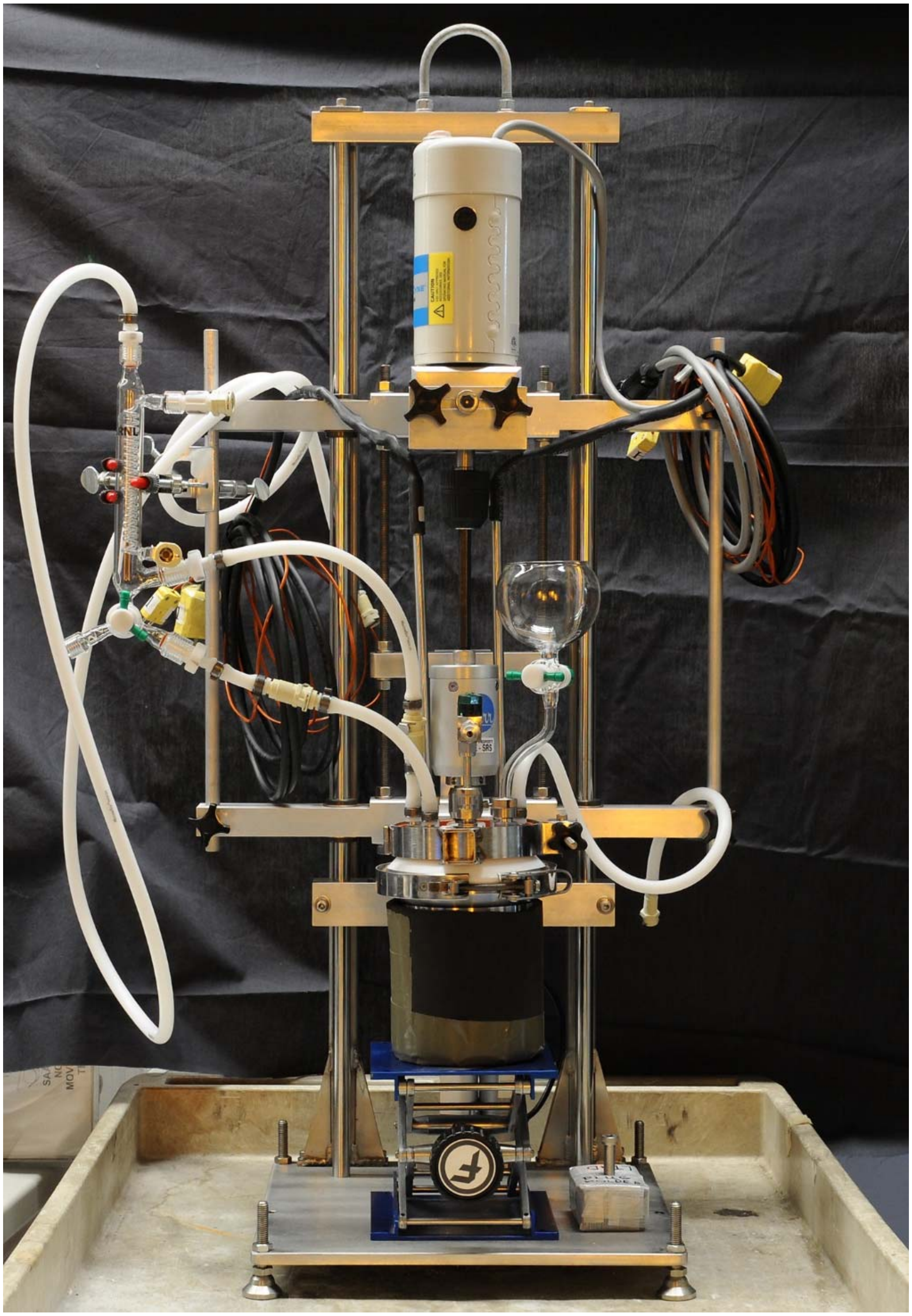


Figure 3-2. Process Equipment Used for High Caustic LTAD Real Waste Test

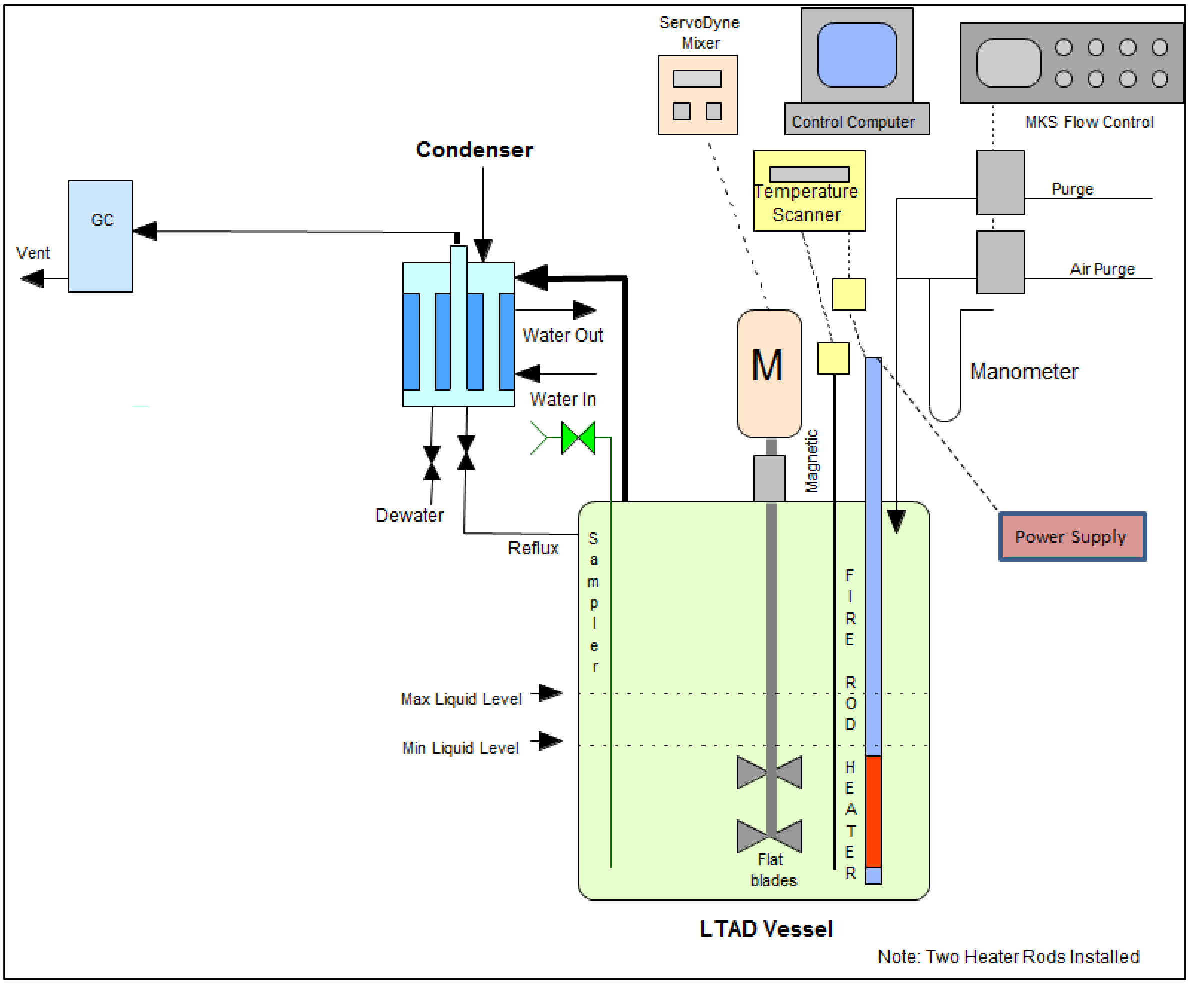


Figure 3-3. Primary LTAD Rig Measurement Components

Gas Chromatography Analyses

As identified above, offgas from the tests was characterized using an Agilent series 3000 micro GC. Column-A collected data related to He, H_2, O_2, N_2, Kr, and CH_4, while column-B collected data related to CO_2 and N_2O. Due to limited GC sensitivity, 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 has been sacrificed, although even with previous settings, the nitrogen results were of limited usefulness, due to low consistency. Raw chromatographic data were acquired by the GC from the offgas stream samples using a separate computer interfaced to the data acquisition computer (as described above). Sampling frequency was approximately one chromatogram every four minutes.

The GC was calibrated with a gas mixture containing nominally 50 ppmv hydrogen, 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.[9] Based on these data, the limit of quantification (LOQ) for hydrogen was determined to be 2.3 ppmv, which corresponds to: a) 2.1E-07 ft^3/hr per gallon of sludge slurry in the baseline LTAD tests; and b) 2.9E-07 ft^3/hr per gallon of sludge slurry in the high caustic LTAD tests. The calibrations were verified prior to and after completing each LTAD test (before and after the baseline test, and before and after the high caustic test).

A 500 ppmv methane (balance air) gas standard was analyzed on the GC, to demonstrate methane detection effectiveness and to provide input data for estimating the methane LOQ. Based on the measurement data and the methods of Taylor[10] and EPA,[11] the methane LOQ was estimated to be 90 ppmv. This LOQ value is likely conservative (high), given the relatively high methane concentration (500 ppmv) used to generate the LOQ input data. Note that the 500 ppmv methane standard was chosen for this scope based on the 500 ppmv minimum detection limit identified in the Technical Task Request.[3]

The primary purge gas contained 0.5 vol% krypton, 20.0 vol% oxygen, and 79.5 vol% nitrogen. The overall purge rate could have been significantly increased with a separate air purge to ensure the hydrogen concentration remained below the flammability limits; however, increased purge was not needed in these tests. 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, Kr was used to confirm absence of gross in-leakage or gas generation (by demonstrating that the flow rate into the vessel was equal to flow rate out of the vessel). Third, unlike air, the purge had no helium and hydrogen, which could interfere with quantification of hydrogen produced from radiolysis or thermolysis.

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. It should be noted that typical peak hydrogen generation rates (2×10^{-6} ft^3/hr per gallon of sludge slurry) are equal to approximately 0.004 cc/min, 0.04% of the 10 cc/min purge rate.

$$HGR(ft^3/hr/gal) = H_{2area} \times \frac{H_{2stdconc}}{H_{2stdarea}} \times F_{in} \times \frac{\rho_{sample}}{m_{sample}} \times 8.020\times10^{-6} \qquad \text{Eqn 1}$$

where,

H_{2area} = GC H_2 response for a gas sample
$H_{2stdconc}$ = Concentration of H_2 calibration gas, ppm
$H_{2stdarea}$ = Average of five GC responses from the H_2 calibration gas
F_{in} = flow of Kr-bearing purge gas into the reaction vessel, sccm
ρ_{sample} = density of sludge slurry sample, g/mL
m_{sample} = mass of sludge slurry sample, g
8.020×10^{-6} = conversion factor, $ft^3\cdot min\cdot mL\cdot cc^{-1}\cdot gal^{-1}\cdot ppm^{-1}$

Small aliquots of slurry material were removed from the LTAD vessel at various intervals during the tests, for purposes of characterizing key supernatant constituents as functions of LTAD progress.

Reductions in the sludge slurry mass due to these removals were taken into account when calculating the HGRs.

Gas Generation Reporting Units

HGR measurements are reported in units of ft^3/hr per gallon of the Tank 51 sludge slurry to match the units used by the SRS Tank Farm, DWPF, and Saltstone facilities. The gas volume basis (ft^3) for the reported HGR data assumes standard conditions of 1 atm pressure and 21.1 °C temperature (70 °F). In contrast, the methane measurements are reported in units of ppmv, per SRR request. Note that the purge rate during testing was 10 sccm.

Baseline LTAD Gas Generation Test Conditions

Baseline LTAD gas generation testing was performed on the "as received" slurry (in the absence of added caustic), to provide a technical basis for understanding the extent that increasing the caustic concentration of the slurry influences the gas generation rate (as compared to the baseline case). During the baseline tests, hydrogen and methane generation from a 920 mL (1122.0 g) Tank 51 sludge slurry aliquot was monitored continuously at four different temperatures and subsequently during the period while the slurry cooled-down from the final temperature, for a total monitoring duration of ~96 hours. Sequentially, the four temperatures of the baseline tests were 23 °C (ambient temperature), 50 °C, 75 °C, and 85 °C, with gas generation being continuously monitored over the durations identified in Table 3-1.

At the end of each temperature cycle (23, 50, 75, and 85 °C), a 20-30 mL process slurry sample was collected from the vessel of the LTAD rig, and the supernatant phase of the sample was analyzed for aluminum, free hydroxide, and total organic carbon (TOC). The density of each supernatant sample was also determined. (In each case, the supernatant sample was generated by processing the slurry sample through a 0.45 micron filtration membrane). Upon completion of the baseline gas generation tests, the slurry material in the LTAD vessel was removed from the vessel and transferred to a polybottle, for availability if additional slurry characterization or testing was needed. The emptied, used LTAD vessel was discarded, and then a new, unused LTAD vessel was installed, in preparation for the high caustic LTAD tests.

Table 3-1. Temperature Durations in the Baseline LTAD Gas Generation Tests

Temperature, °C	Duration, hours
23 °C (ambient temperature)	6.1
Heat-up to 50 °C	0.8
50 °C (with heating)	14.3
Heat-up to 75 °C	0.8
75 °C (with heating)	15.6
Heat-up to 85 °C	0.3
85 °C (with heating)	48.0
Cool down from 85 °C to 25 °C	10.3

High Caustic LTAD Gas Generation Test Conditions

High caustic (bounding) LTAD gas generation testing was performed similarly to the baseline LTAD testing, with the following exceptions: a) the volume of the Tank 51 sludge slurry aliquot that was used was 657 mL (a mass of 801.7 g), to accommodate the volume of caustic solution that would be added such that the headspace during the LTAD process would be similar to that of the baseline tests (note that a “fresh” unused 657 mL sludge slurry aliquot was utilized in the high caustic LTAD tests); b) 242 mL (370.0 g) of 50 wt% NaOH solution was added to the sludge slurry sample at the start of the testing to raise the initial supernatant free hydroxide concentration to 6 M; c) gas generation was monitored as the 50 wt% NaOH solution was mixed with the sludge slurry at ambient temperature and then over the temperature regimes of 50, 75, and 85 °C; and d) gas generation was not monitored during the final cool down period following the 85 °C regime. Gas generation in the high caustic LTAD testing was monitored over a total duration of ~75 hours, with the durations identified as a function of temperature in Table 3-2.

Table 3-2. Temperature Durations in the High Caustic LTAD Gas Generation Tests

Temperature, °C	Duration, hours
24 °C (ambient temperature)	1.0
24-43 °C (during NaOH addition)	0.2
Heat-up to 50 °C	0.2
50 °C (with heating)	12.0
Heat-up to 75 °C	0.5
75 °C (with heating)	12.4
Heat-up to 85 °C	0.3
85 °C (with heating)	48.1

At the end of each temperature cycle (50, 75, and 85 °C) and approximately midway through the 85 °C cycle, a 20-30 mL process slurry sample was collected and the supernatant phase of the sample was analyzed for aluminum, free hydroxide, and TOC. The density of each supernatant phase sample was also determined. (In each case, the supernatant sample was generated by processing the slurry sample through a 0.45 micron filtration membrane). Upon completion of the high caustic gas generation tests, the slurry material in the LTAD vessel was removed from the vessel and transferred to a polybottle, for availability if additional slurry characterization or testing is needed. The emptied, used LTAD vessel was then discarded.

Statistical Analysis of HGR Data

Statistical analysis of the gas monitoring data was performed to estimate uncertainties of the HGR results. GUM Workbench Version 2.4.1.411[12] was used to develop the appropriate variance propagation routine calculating uncertainties of the HGR data based upon the uncertainties of the applicable individual inputs. Subsequently, JMP Pro Version 11.2.1[13] was used to set up a parallel variance propagation routine that was checked against the GUM Workbench results and then applied to the HGR outcomes from this testing.

3.3 Pre-LTAD and Post-LTAD Slurry/Supernatant Characterization

Slurry and supernatant analyses that were performed on the pre-LTAD and post-LTAD real waste test samples are identified in Table 3-3. Summaries of the laboratory methods are given following the table. All pre-LTAD and post-LTAD analyses were performed in triplicate.

Table 3-3. Pre-LTAD and Post-LTAD Slurry/Supernatant Analyses

Analysis	Slurry	Supernatant	Method	Laboratory
Solids distribution	X	X	Gravimetric	SCO
Density	X	X	Gravimetric/volumetric	SCO
Elementals	X	X	ICP-AES	AD
TOC	X	X	TOC analyzer	AD
Free hydroxide		X	BT	AD
NO_2^-, NO_3^-, SO_4^{2-}, Cl^-, $C_2O_4^{2-}$, HCO_2^-, PO_4^{3-}		X	IC	AD
CO_3^{2-}		X	TIC analyzer	AD
Volatile organics*		X	Extraction/GC-MS	AD
Semi-volatile organics*		X	Extraction/GC-MS	AD

ICP-AES = inductively coupled plasma atomic emission spectroscopy; BT = base titration; IC = ion chromatography; TIC = total inorganic carbon; GC-MS = gas chromatography-mass spectrometry. *Total volatile organics, total semi-volatile organics, and specific volatile organics butanol and propanol will be reported.

Solids Distribution: Total solids and dissolved solids determinations were performed by driving water from slurry and supernatant aliquots (respectively) at a nominal temperature of ~110 °C. Supernatant was generated as a filtrate by processing slurry through a 0.45 micron filtration membrane (note that this generation method was utilized for all of the supernatant analyses – not just those used for dissolved solids determinations). Three individual slurry aliquots and three individual supernatant aliquots from the pre-LTAD and post-LTAD slurries were utilized in the measurements. The mass of each aliquot was ~3.0 g. Insoluble and soluble solids concentrations were calculated based on the total and dissolved solids measurements. The dissolved solids content of a 15 weight percent sodium chloride solution was determined alongside the sample determinations, to demonstrate measurement accuracy.

Densities: Density determinations were conducted at temperatures ranging from 21 °C to 25 °C, as governed by the Shielded Cells conditions at the time of the determinations (21 °C for the pre-LTAD slurry, 22 °C for the pre-LTAD supernatant, and 25 °C for the post-LTAD slurry and supernatant). Densities were determined using weight-calibrated balances in combination with: a) 8-9 mL volume-calibrated plastic test tubes for aliquoting slurry material; and b) 10.0 mL volumetric flasks for aliquoting supernatant material. Three individual slurry aliquots and three individual supernatant aliquots from the pre-LTAD and post-LTAD slurries were utilized in the determinations (triplicate determinations). Density values were calculated by dividing the measured aliquot weights by the known aliquot volumes. The density of a deionized water standard was determined alongside the slurry and supernatant densities, to demonstrate measurement accuracy.

Elemental Analysis of Slurry Solids: In preparation for the elemental analyses (prior to submittal to AD), three slurry aliquots were digested by the aqua regia (AR) dissolution method and three slurry aliquots were digested by the peroxide fusion (PF) dissolution method. This was done for both the pre-LTAD and post-LTAD slurries. The total solids mass of each sample aliquot was ~0.25 g, and the volume of each final digest solution was 100 mL. Note that the AR method utilized a sealed vessel to prevent loss of volatile constituents. Analyzed reference glass (ARG) aliquots and applicable blanks were also processed through the digestion methods and submitted for analysis alongside the digested sample aliquots, for quality assurance purposes. Similarly, a liquid-phase reference solution was submitted alongside the digested sample aliquots, although the liquid-phase reference solution was not processed through the dissolution methods.

ICP-AES was performed on both the AR and PF digest solutions, along with the applicable reference materials and blanks. The ICP-AES measurements provided quantification of all the elemental constituents reported in this document. Dilution-correction of the results was performed by AD prior to reporting.

The elemental results were based either solely on the AR digest solutions, solely on the PF digest solutions, or on both the AR and PF digest solutions, depending on the following factors: potential for interference, magnitude of "blank values," magnitude of minimum detection limits, consistency of data, ability to accurately quantify the reference materials, and/or apparent anomalies. The applicable digestion methods feeding the results are identified in the tables providing the results.

Elemental Analysis of Supernatants: In preparation for the elemental analyses (prior to submittal to AD), three pre-LTAD supernatant aliquots were each diluted by a factor of ~10 (on a volume basis), using 1.0 N nitric acid. In contrast, for the post-LTAD material, three supernatant aliquots were prepared by diluting each by a factor of 11-12 (on a volume basis), using 1.5 N nitric acid. The higher nitric acid diluent concentration and slightly higher dilution factor in the post-LTAD supernatant case was chosen to assure effective acidification, given the significantly higher supernatant hydroxide concentration. Applicable "acid blanks" were submitted alongside the acid-diluted supernatant aliquots, for quality assurance purposes. ICP-AES was used to quantify the elementals in the supernatants. Dilution-correction of the results was performed prior to reporting.

TOC Analyses: In preparation for the TOC analyses (prior to submittal to AD), three pre-LTAD slurry aliquots and three post-LTAD slurry aliquots were each diluted by a factor of ~60 (on a volume basis) with deionized water. In contrast, three pre-LTAD supernatant aliquots and three post-LTAD supernatant aliquots were prepared by diluting each by a factor of ~10 with deionized water. The higher dilution factor for the slurry aliquots was needed to reduce contact dose associated with solid-phase Sr-90/Y-90. Applicable "water blanks" were submitted alongside the water-diluted slurry and supernatant aliquots, for quality assurance purposes. TOC was quantified using a high temperature total carbon analyzer. Dilution-correction of the results was performed prior to reporting.

Other Supernatant Analyses: All other supernatant analyses were performed on triplicate aliquots that had been diluted with deionized water by a factor of ~10 (on a volume basis). This applies to both the pre-LTAD supernatant and the post-LTAD supernatant, for: a) free hydroxide analyses performed via BT; b) nitrite, nitrate, sulfate, chloride, oxalate, formate, and phosphate analyses performed via IC; c) carbonate analysis quantified as TIC through the high temperature total carbon analyzer; d) butanol, propanol, benzene, toluene, and other volatile organic constituents quantified via GC-MS/volatile organic analysis (VOA); and e) phenol, tributylphosphate, dioctylnitrosamine, and other semi-volatile organic constituents quantified via GC-MS/semi-volatile organic analysis (SVOA). Dilution-correction of the results was performed prior to reporting.

3.4 LTAD Process Sample Supernatant Characterization

Supernatant aliquots from the four process slurry samples collected during the baseline LTAD tests and the four process slurry samples collected during the high caustic LTAD tests were analyzed by the methods identified below. Due to the limited volumes of the process control samples, single aliquots of each supernatant were diluted in preparation for analyses (as opposed to triplicate aliquots being diluted in the pre-LTAD and post-LTAD characterizations), slightly higher supernatant dilution factors were employed, and significantly reduced aliquot volumes were utilized in the density determinations.

Aluminum: In preparation for the aluminum analyses (prior to submittal to AD), one supernatant aliquot from each of the eight process control samples was diluted with 1.0 N nitric acid by a factor of ~15 (on a volume basis). Subsequently, three aliquots from each acid-diluted supernatant solution were submitted for aluminum analysis by ICP-AES (triplicate analysis). Applicable "acid blanks" were submitted alongside the acid-diluted supernatants, for quality assurance purposes. Dilution-correction of the results was performed prior to reporting.

Free Hydroxide and TOC: In preparation for the free hydroxide and TOC analyses (prior to submittal to AD), one supernatant aliquot from each of the eight process control samples was diluted with deionized water by a factor of ~14 (on a volume basis). Subsequently, three aliquots from each water-diluted supernatant solution were submitted for free hydroxide quantification by BT and for TOC quantification by high temperature total carbon analysis (triplicate analyses). Applicable "water blanks" were submitted alongside the water-diluted supernatants, for quality assurance purposes. Dilution-correction of the results was performed prior to reporting.

Density: Density determinations were conducted at a temperature of ~19 °C, as governed by the Shielded Cells conditions at the time of the determinations. Densities were identified using weight-calibrated balances in combination with 2.0 mL volumetric flasks for aliquoting supernatant material. Two individual supernatant aliquots from each of the eight process control samples were utilized in the determinations (duplicate determinations). Density values were calculated by dividing the measured aliquot weights by the known aliquot volume. The density of a deionized water standard was determined alongside the supernatant determinations, to demonstrate measurement accuracy.

3.5 Format of Tabulated Results

Mean results, based on the average of all applicable analytical determinations, are reported in this document, along with the percent relative standard deviation (%RSD), and the number of determinations (n) feeding each mean. %RSD provides an indication of the measurement variation between replicate determinations, but is typically not an indicator of analytical accuracy. In general, the one sigma analytical uncertainty as reported by Analytical Development was 10%, although it was sometimes lower or higher. Specifically, the typical one sigma analytical uncertainties reported by AD were: a) ~10% for ICP-AES, TOC, BT, IC, and TIC analyses; and b) ~20% for volatile organic and semi-volatile organic analyses. As such, only one to two of the leading digits reported for the AD analysis results should be considered significant.

3.6 Assessment of Results

Multiple approaches were used to assess the validity of the analytical data being reported. The primary goal of this was to demonstrate that the reported results were both reasonable and consistent with expectations. Focus areas of the assessment included: a) densities and solids distributions; b) charge balance of the ions in the supernatant; c) dominant supernatant salts feeding the dissolved solids; d) dominant elemental constituents in the total solids; e) fraction of insoluble aluminum dissolved by LTAD; and f) fraction of insoluble solids dissolved by LTAD. Discussion of the assessment approaches and results is included in Section 4.0. Note that when characterization results were compared, percent differences were calculated as follows:

% Difference = 100 × [(absolute value of the difference between results) ÷ (the average result)]. Eqn 2

The leading three digits of each numerical result were utilized when calculating % differences, regardless of the number of digits considered significant.

3.7 Quality Assurance

Standard laboratory quality assurance protocols were used to assure analytical data quality. This includes use of blanks, reference materials, analyte standards, and replicate determinations.

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

4.0 Results and Discussion

4.1 Hydrogen Generation During the Baseline LTAD Testing

A plot of the HGRs measured from start to the finish of the 96 hour baseline LTAD test is given in Figure 4-1. At ambient temperature at the start of the test (23 °C), the measured HGRs were on the order of 1E-06 ft^3/hr per gallon of the Tank 51 sludge slurry. Upon heating to 50 °C, there was a dynamic short-term increase in the HGR, to a peak level of 2.3E-06 ft^3/hr/gal, followed by a continuous HGR decline to a level of ~2E-07 ft^3/hr/gal (which is the LOQ), after holding the temperature steady at 50 °C for approximately 14 hours. Upon heating to 75 °C, a similar trend was observed, with a dynamic short-term increase in HGR, to a peak level of 2.5E-06 ft^3/hr/gal, followed by a continuous HGR decline to a level of 8.3E-07 ft^3/hr/gal, after holding the temperature steady at 75 °C for approximately 16 hours. Based on the overall trend of the data, it is likely that the HGR would have continued to decline if the 75 °C temperature would have been sustained longer.

Upon heating to 85 °C, there was a minor short-term increase in HGR, to a peak level of 1.1E-06 ft^3/hr/gal, followed by a period of slower sporadic decline (with a couple of minor ups and downs), reaching an HGR of ~5E-07 ft^3/hr/gal after maintaining the 85 °C temperature for approximately 24 hours. Interestingly, the HGR increased somewhat as the 85 °C temperature continued, with the HGR on the order of 1E-06 ft^3/hr/gal after the 85 °C temperature had been sustained a total of 48 hours. Note that during the last 24 hours of the 85 °C temperature regime, there were two instances when purging of the sampling port was necessary to “unclog” the condensate line. The somewhat increased HGRs that were measured during the time periods just prior to, during, and immediately after purging the sampling port are annotated on Figure 4-1 and should be considered spurious, as purging of the sampling port temporarily disrupted the equilibrium of the gas sampling system.

During the 10 hour cool down period following completion of the 85 °C temperature regime, the HGRs decreased only slightly, from an average of approximately 9E-07 ft^3/hr/gal to a low of approximately 7E-07 ft^3/hr/gal. Neglecting the HGR peaks that occurred shortly after heating the slurry to 50 and 75 °C, it appears that the majority of the baseline HGRs were on the order of 5E-07 to 1E-06 ft^3/hr/gal. It is worth noting that this range is consistent with SRR’s estimate of the total volumetric radiolytic HGR for the sludge slurry material, which is ~9E-07 ft^3/hr/gal (see Attachment A).

4.2 Hydrogen Generation During the High Caustic LTAD Testing

A plot of the HGRs measured from start to finish of the 75 hour high caustic LTAD test is given in Figure 4-2. In the short duration of the test at ambient temperature (24 °C, prior to adding the caustic), the measured HGRs were approximately 6E-07 to 7E-07 ft^3/hr per gallon of the Tank 51 sludge slurry. This is 30-40% lower than the HGRs observed at ambient temperature in the baseline tests, providing an indication of the potential variability from test to test. Upon addition of the caustic and subsequent heating to 50 °C, there was a brief and minor increase in HGR (to 8.4E-07 ft^3/hr/gal), followed by a

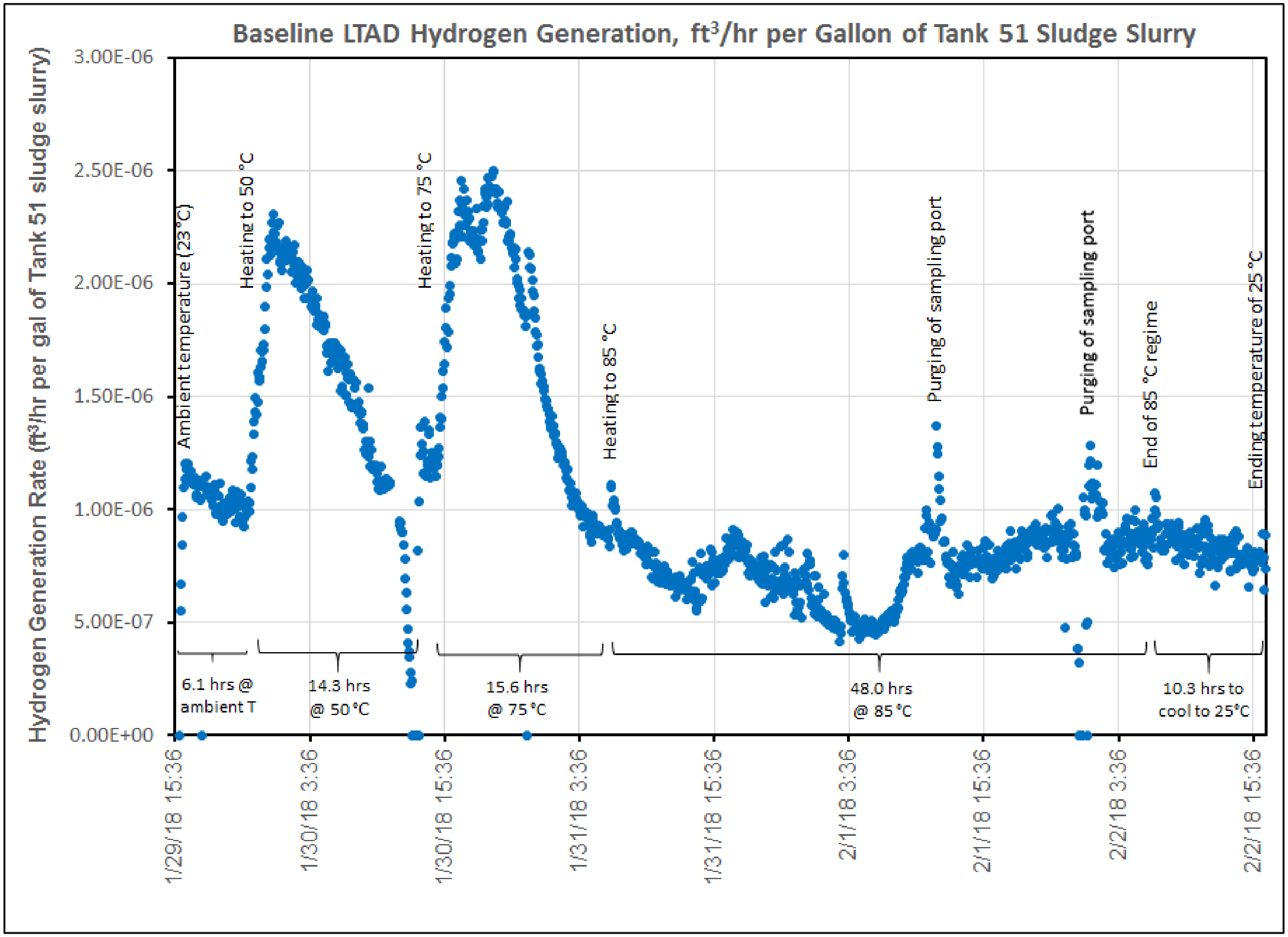


Figure 4-1. Baseline LTAD Tests: HGRs as Functions of Time and Temperature

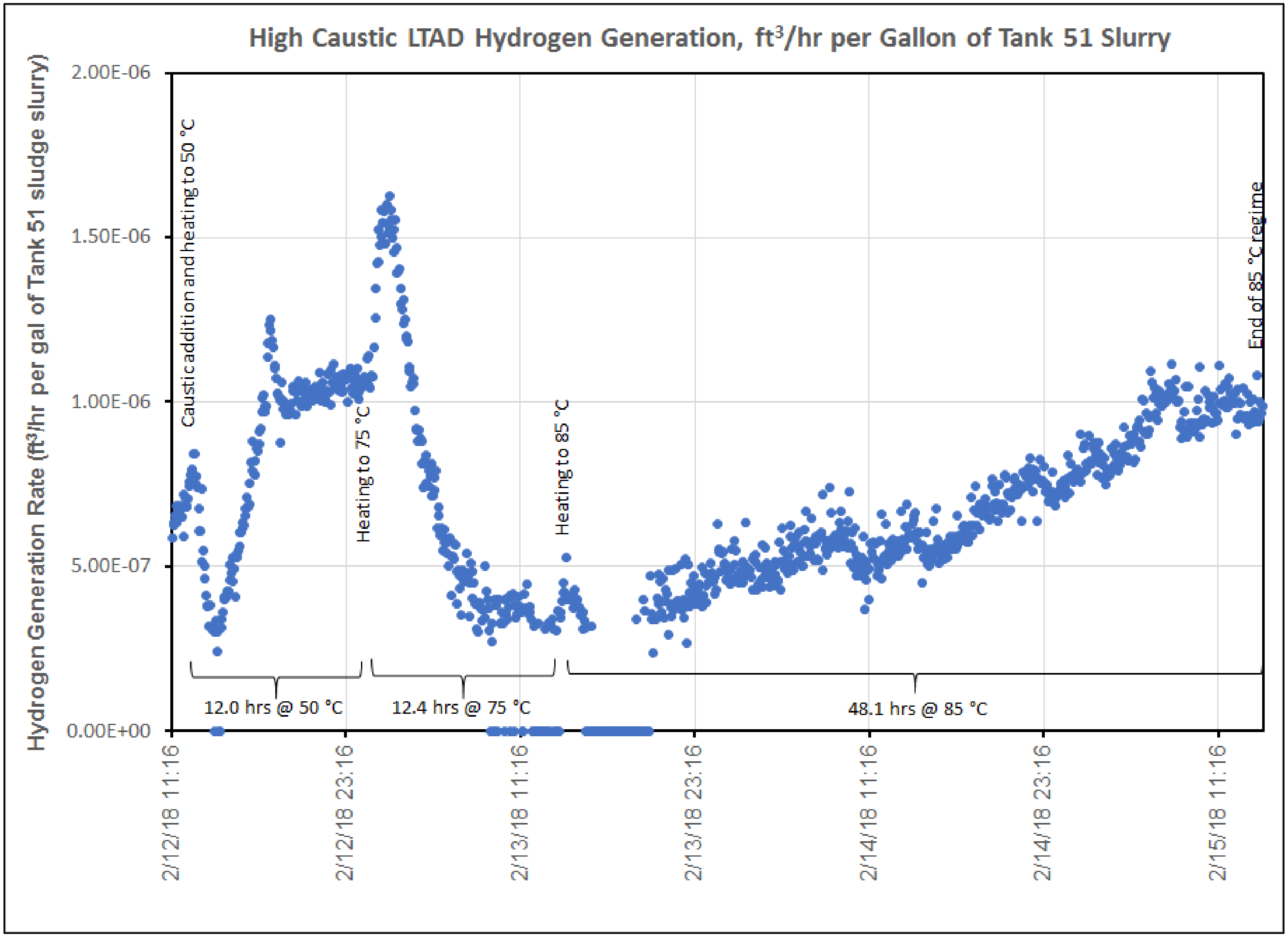


Figure 4-2. High Caustic LTAD Tests: HGRs as Functions of Time and Temperature

dynamic short-term decline to a minimum level of ~3E-07 ft^3/hr/gal, and then a four-fold dynamic increase to a peak level of ~1.3E-06 ft^3/hr/gal over the next four hours. Shortly thereafter, the HGR dropped somewhat to a level of ~1.1E-06 ft^3/hr/gal, where it stayed for the remainder of the 50 °C temperature regime.

Upon heating to 75 °C, there was a dynamic short-term increase in HGR, to a level of ~1.6E-06 ft^3/hr/gal. This was followed by a dynamic decline to a level of ~3E-07 ft^3/hr/gal over the next six to seven hours, and then a period of relative stability over the last five hours of the 75 °C temperature regime. Note that the data points identifying the HGR as zero indicate that the hydrogen signal was below the required threshold level for meaningful integration of the signal, as opposed to truly representing an HGR of zero. Correspondingly, the threshold level that is needed for a meaningful measurement is the same magnitude as the LOQ.

Raising the slurry to a temperature of 85 °C resulted in a limited short-term increase in HGR, to a level of ~5E-07 ft^3/hr/gal. Shortly thereafter, the HGR dropped back down to ~3E-07 ft^3/hr/gal, and then gradually increased to ~1E-06 ft^3/hr/gal over the next 39-40 hours of the 85 °C temperature regime. This gradual, consistent increase in HGR corresponded well with the period in which the majority of the aluminum dissolution was expected to occur (during the first 40-41 hours of the 85 °C temperature regime). Subsequently, the HGR remained relatively constant at ~1E-06 ft^3/hr/gal during the final 7-8 hours of the 85 °C temperature regime.

Implications of the HGR Results

The changes in HGRs that were observed over the course of the testing demonstrate that the quantities of hydrogen being produced and released from the slurry are impacted by many factors, including temperature, time, and solids content, as well as other potential factors associated with the caustic concentration and any caustic-related reactions. Clearly, the release rate is a function of the hydrogen generation rate, as well as the ability of the slurry material to retain hydrogen, be it through physical processes, chemical processes, and/or through gas solubility. The generation rate has multiple potential contributors, including radiolysis, which appears to dominate, as well as thermolysis, coupled with potential impacts from the chemical reactions occurring as the insoluble aluminum is converted to soluble aluminum.

In cases where the measured HGRs increased abruptly as the temperature increased, there are multiple potential mechanisms that could have effected such changes. Expansion and release of retained gas bubbles, facilitated gas release associated with temperature-diminished slurry yield stress/viscosity, and thermolysis of soluble organic compounds are a few of the possibilities. Gas retention on or within slurry particles is likely dependent on slurry characteristics including rheology, insoluble solids content, insoluble particle size, and mineralogy.

In general, the HGRs of the baseline LTAD tests were typically higher than the HGRs of the high caustic LTAD tests, although the differences were generally limited to a factor of two or less. Whereas the nominal range of HGRs in the baseline tests was 5.0E-07 to 2.5E-06 ft^3/hr/gal, the nominal range of HGRs in the high caustic tests was 2.5E-07 to 1.7E-06 ft^3/hr/gal. The exact reasons for these differences are not known, but it is clear that the lower insoluble solids content and the expected lower yield stress of the high caustic slurry (to which 50 wt% NaOH solution had been added) could have had significant impacts on gas retention and release, independent of the gas production rate. Such impacts would be expected to affect the highs and lows observed during the temperature changes, chemical reactions, and other events potentially contributing to the gas retention/release equilibria.

Despite the differences between the HGRs of the baseline and high caustic LTAD tests, there is a portion of both tests where the HGRs are relatively similar. Specifically, it occurs during the last 24 hours of the 85 °C temperature regime, where in both cases (baseline and high caustic), the measured HGR rises from a low of ~5E-07 ft^3/hr/gal to a high of ~1E-06 ft^3/hr/gal. This final HGR of ~1E-06 ft^3/hr/gal may be reflective of the HGR at equilibrium conditions, as this rate occurred after a relatively long period (~48 hours) where the temperature was held constant (85 °C). Interestingly, this HGR is reasonably consistent with SRR's estimate of the total volumetric radiolytic HGR for the sludge slurry material, ~9E-07 ft^3/hr/gal (Attachment A), suggesting that radiolysis is the primary contributor to the HGR.

Other similarities observed between the two sets of test results are the relative magnitudes of the peaks immediately following heating, with the peak after 75 °C being the highest, the peak after 50 °C being the second highest, and the peak after 85 °C being minimal in both cases.

Given the responsiveness of the HGR results to the process changes, the relative consistency between the baseline and high caustic HGR results, the stability of HGRs upon approaching equilibrium conditions, and the good agreement between stable observed HGRs and the theoretical radiolytic HGR, it is concluded that the HGRs measured in the LTAD tests are reasonable and sound.

Statistical Analysis of HGR Results

Estimated uncertainties of the measured HGR results are summarized in Table 4-1 as functions of LTAD test case and LTAD temperature. The minimum, maximum, and average estimated uncertainties are identified for each set of conditions, to provide indications of the extent that uncertainties varied over the range of conditions, and to provide insight into how the magnitude of the uncertainties corresponded to the magnitudes of the HGRs. In almost all cases, the lowest estimated uncertainties were associated with the highest measured HGRs, and the highest estimated uncertainties were associated with the lowest measured HGRs. To help illustrate this relationship, a plot summarizing the ranges of measurable HGRs as a function of the test conditions is provided in Figure 4-3.

Table 4-1. One Sigma Estimated Uncertainties of the HGR Results

LTAD Test Case	Temp, °C	Estimated Uncertainty of HGR Result, %		
		Minimum	Maximum	Average
Baseline	23	4.5	7.1	4.8
	50	3.7	15.7	4.4
	75	3.7	5.5	4.2
	85	4.3	11.9	6.2
High caustic	24	6.9	8.0	7.4
	50	5.0	17.6	6.8
	75	4.5	15.9	9.0
	85	5.5	18.6	8.2

For example, in the case of the baseline LTAD test performed at 50 °C, the minimum and maximum estimated HGR uncertainties were 3.7 and 15.7%, respectively, with an average estimated uncertainty of 4.4%. The 3.7% uncertainty applied to a measured HGR of ~2.3E-06 ft^3/hr/gal (which was the highest HGR for the 50 °C baseline case), while the 15.7% uncertainty applied to a measured HGR that was an order of magnitude lower, at ~2.3E-07 ft^3/hr/gal (the lowest HGR of the 50 °C baseline case) – see Figure 4-3 for a pictorial illustration of the range of measured HGRs for each test case and temperature regime, as well as an average HGR for each case and temperature. Note that a 95% confidence interval (green diamond) for the average HGR for each case is provided as part of the information in this plot.

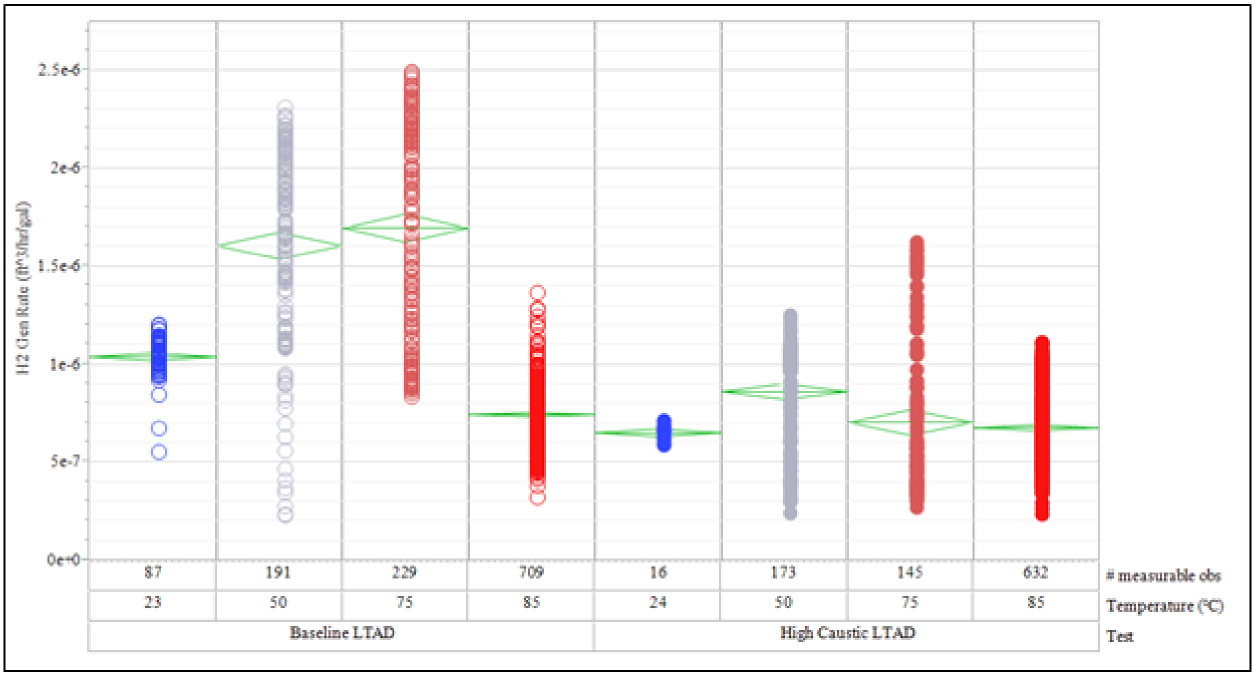


Figure 4-3. Ranges of Measurable HGRs Plotted as a Function of the LTAD Test Conditions

In contrast, in the case of the baseline LTAD test performed at 85 °C, the minimum and maximum estimated HGR uncertainties were 4.3 and 11.9%, respectively, with an average estimated uncertainty of 6.2%. The 4.3% uncertainty applied to a measured HGR of ~1.4E-06 ft^3/hr/gal (the highest HGR for the 85 °C baseline case), while the 11.9% uncertainty applied to a measured HGR of ~3.2E-07 ft^3/hr/gal (the lowest HGR for the 85 °C baseline case). The average uncertainty for the 85°C baseline case (6.2%) was a bit higher than the average uncertainty for the 50 °C baseline case (4.8%), which is consistent with expectations given that the average HGR for the 85 °C baseline case (~7.4E-07 ft^3/hr/gal) was lower than the average HGR for the 50 °C baseline case (~1.6E-06 ft^3/hr/gal). Based on the values presented in Table 4-1, it is clear that one sigma HGR uncertainties approaching 20% should be expected for the very lowest measured HGRs, in contrast to one sigma HGR uncertainties as low as ~4% for the highest measured HGRs.

In general, the estimated HGR uncertainties for the baseline LTAD test cases were lower than the estimated HGR uncertainties for the high caustic LTAD test cases. This is not surprising, given that the average measured HGRs of the baseline tests were higher than the average measured HGRs of the high caustic tests.

For further illustration of the HGR uncertainty expectations, estimates of the HGR standard deviations are plotted as functions of the measured HGRs in Attachments B and C, respectively, for the baseline and high caustic test cases. Consistent with the information presented in Table 4-1 and Figure 4-3, the plotted standard deviations range from ~4% to ~20% of the measured HGRs, with the relative deviations increasing with decreasing HGRs.

Also included in Attachments A and B are plots showing the relative contributions to uncertainty stemming from each of the primary input parameters (H_{2area}, $H_{2stdconc}$, $H_{2stdarea}$, F_{in}, ρ_{sample}, and m_{sample}, as defined for Equation 1). Although the magnitudes of the contributions are dependent on the HGRs, the two input parameters with the greatest potential for impacting uncertainties include H_{2area} first (with the potential for contributing 90+% of the uncertainty at low HGRs) and $H_{2stdconc}$ second (with the potential for contributing up to ~40% of the uncertainty at high HGRs).

Methane Generation During the Baseline and High Caustic LTAD Tests

Under all conditions of the LTAD tests, no clear methane peaks were detected, and the measured methane concentrations were therefore < 90 ppmv (less than the methane LOQ). Given that the methane LOQ is high relative to the hydrogen LOQ (about forty times the hydrogen LOQ), it is clear that methane concentrations would have needed to be significantly higher than the maximum measured hydrogen concentration to have been detected and fully quantified. Specifically, a methane concentration three times that of the maximum measured hydrogen concentration would have been needed for effective detection and for discrete quantification (as opposed to quantification with a "less than" value). As such, it is acknowledged that non-detection of methane does not necessarily ensure its absence.

4.3 Characterization of the Pre-LTAD Slurry and Supernatant

Density and solids distribution results for the pre-LTAD ("as received") slurry are given in Table 4-2. The relative magnitudes of the slurry and supernatant densities (1.22 and 1.17 g/mL, respectively) are consistent with expectations based on the relative magnitudes of the total solids and dissolved solids contents (27.0 and 20.1 wt%, respectively). Specifically, the amount that the density of the slurry exceeds that of water (~0.22 g/mL) is about 30% higher than the amount that the density of the supernatant exceeds that of water (~0.17 g/mL) – which closely matches the result of the total solids content being about 30% higher than the dissolved solids content (27.0 ÷ 20.4 ≈ 1.3). Based on this correlation, the density and solids distribution results certainly appear reasonable. The calculated insoluble solids (IS) content is 8.3 wt%, a quantity which has bearing on the amount of insoluble aluminum that is available for dissolution, as will be addressed below. All of the relative standard deviations (RSDs) of the density and solids content measurements were low (≤ 0.4%), demonstrating high measurement precision and lack of any apparent shielded cells processing anomalies.

Table 4-2. Densities and Solids Distribution of the Pre-LTAD Slurry, n=3

Measurement	Mean Result	%RSD
Slurry density, g/mL	1.22	0.4
Supernatant density, g/mL	1.17	<0.1
Total solids, wt% of slurry	27.0	0.3
Dissolved solids, wt% of supernatant	20.4	0.3
Insoluble solids (calculated value), wt% of slurry	8.3	N/A
Soluble solids (calculated value), wt% of slurry	18.7	N/A

Concentrations of the elemental constituents in the pre-LTAD slurry solids are given in Table 4-3, with concentrations greater than 0.1 wt% shaded for easy identification. The three most dominant constituents in the slurry solids include sodium, aluminum, and iron, at concentrations of approximately 25, 11, and 2 wt%, respectively. The high aluminum concentration is reflective of a large insoluble aluminum content and the potential for significant IS reduction through aluminum dissolution. Less dominant constituents with concentrations greater than 0.1 wt% in the slurry include thorium, manganese, uranium, silicon, potassium, and calcium, with concentrations of approximately 0.7, 0.6, 0.2, 0.2, 0.1, and 0.1 wt%, respectively. (Note that the measured silicon may be biased high, given that the quantity of silicon in the blank was elevated above normal.) Most of the RSDs for the elemental analyses were limited to ten percent or less, demonstrating typical analytical precision. In contrast, the RSDs applicable to barium, magnesium, manganese, and silicon were somewhat higher, at 15, 16, 12, and 16%, respectively. These higher RSDs give an indication that the propagated analytical uncertainties associated with these four constituents are likely higher than those of the other constituents.

Table 4-3. Elemental Constituents in the Pre-LTAD Slurry (Shading Indicates Concentrations > 0.1 wt%)

Constituent	Digestion Method	Mean Result, wt% of solids	%RSD (n)
Ag	AR	<2.0E-03	N/A
Al	AR/PF	1.06E+01	5.7 (6)
B	AR	1.01E-02	10 (3)
Ba	AR/PF	1.64E-02	15 (6)
Be	PF	<5.9E-03	N/A
Ca	AR	1.08E-01	2.6 (3)
Cd	AR	<1.9E-03	N/A
Ce	AR	5.01E-02	0.4 (3)
Co	AR	<2.1E-03	N/A
Cr	AR/PF	4.23E-02	4.8 (6)
Cu	AR	1.50E-02	1.2 (3)
Fe	AR/PF	2.35E+00	9.9 (6)
Gd	AR	1.88E-02	0.7 (3)
K	AR	1.11E-01	2.0 (3)
La	AR/PF	1.67E-02	4.3 (6)
Li	AR	<6.5E-03	N/A
Mg	AR/PF	3.69E-02	16 (6)
Mn	AR/PF	6.15E-01	12 (6)
Mo	AR	<1.1E-02	N/A
Na	AR	2.50E+01	0.9 (3)
Ni	AR/PF	9.39E-02	10 (6)
P	AR	3.75E-02	3.7 (3)
Pb	AR	<2.7E-02	N/A
S	AR	<1.7E+00	N/A
Sb	AR	<2.8E-02	N/A
Si	PF	2.13E-01*	16 (6)
Sn	AR	<1.7E-02	N/A
Sr	AR/PF	1.01E-02	2.2 (6)
Th	AR/PF	6.75E-01	8.8 (6)
Ti	AR	<6.0E-03	N/A
U	AR	2.17E-01	5.3 (3)
V	AR	<1.6E-03	N/A
Zn	AR	5.70E-03	1.3 (3)
Zr	AR	4.52E-02	1.4 (3)

*Elevated Si in blank suggests Si result may be biased high

The concentration of TOC in the pre-LTAD slurry is given in Table 4-4. The TOC concentration was less than the minimum detection limit (MDL) of 2.0E+02 mg per kg of slurry.

Table 4-4. Total Organic Carbon in the Pre-LTAD Slurry, n=3

Concentration, mg/kg slurry	%RSD
<2.0E+02	N/A

Molar concentrations of the primary supernatant ions in the pre-LTAD slurry are given in Table 4-5. Also given in Table 4-5 are the corresponding equivalence concentrations provided to allow a simple charge balance comparison of the pertinent cations and anions. The pertinent cations include sodium, with a measured concentration of 4.13 M, and potassium, with a measured concentration of approximately 0.01 M. In contrast, the measurable anions include free hydroxide, nitrate, nitrite, carbonate, aluminate, sulfate, oxalate, and chloride, with concentrations of approximately 0.97, 0.93, 0.82, 0.29, 0.17, 0.034, 0.0098, and 0.0061 M, respectively. RSDs for the measurable ions were all low (≤ 3.5%), indicating high measurement precision. Other anions, including bromide, fluoride, formate, and phosphate, were less than the MDLs, which ranged from approximately 1E-03 to 6E-03 M.

Table 4-5. Primary Ions and Charge Balance for the Pre-LTAD Supernatant, n=3

Ion	Mean Concentration, Molarity	%RSD	Corresponding eq/L		Difference
			Cationic	Anionic	
Na^+	4.13E+00	0.8	4.13	N/A	
K^+	1.03E-02	3.5	0.0103	N/A	
Free OH^-	9.73E-01	1.0	N/A	0.973	
NO_3^-	9.27E-01	1.4	N/A	0.927	
NO_2^-	8.20E-01	1.8	N/A	0.820	
CO_3^{2-}	2.87E-01	3.5	N/A	0.574	
$Al(OH)_4^-$	1.73E-01	0.7	N/A	0.173	
SO_4^{2-}	3.40E-02	2.2	N/A	0.0680	
$C_2O_4^{2-}$	9.78E-03	2.1	N/A	0.0196	
Cl^-	6.14E-03	2.7	N/A	0.00614	
Br^-	<6.1E-03	N/A	N/A	N/A	
F^-	<5.2E-03	N/A	N/A	N/A	
CHO_2^-	<2.2E-03	N/A	N/A	N/A	
PO_4^{3-}	<1.0E-03	N/A	N/A	N/A	
			Σ = 4.14	Σ = 3.56	15%

For the charge balance comparison, the molar ion concentrations were converted to equivalence concentrations based upon the applicable ionic charges – one for the measurable monovalent ions including sodium, potassium, free hydroxide, nitrate, nitrite, aluminate, and chloride – and two for the measurable divalent ions including carbonate, sulfate, and oxalate. Note that the ions with concentrations below the MDLs were not included in the charge balance assessment, as they were assumed to have an insignificant impact on the total charge balance.

As shown in Table 4-5, the sum of the pertinent cations was 4.14 eq/L, while the sum of the pertinent anions was 3.56 eq/L. The difference between these values is ~15%, a value which indicates good data consistency, as it is below the anticipated, unpropagated two sigma analytical uncertainty of ~20%.

A separate assessment utilizing the measured ion concentrations was performed to gauge consistency between the primary supernatant constituent concentrations and the measured dissolved solids content. Projected wt% values were calculated based on the molar concentrations of the known sodium salts (assuming that the contribution of the potassium salts is insignificant), the molecular weights (MWs) of the sodium salts, and the measured density of the supernatant phase (1.17 g/mL). Results of these calculations are presented in Table 4-6, which shows that the projected dissolved solids content based on the ion data is 19.8 wt%, which is about 3% lower than the dissolved solids content measured in the Shielded Cells. A three percent difference is considered extremely good, as it is significantly less than the expected one sigma analytical uncertainty for a single ion determination (10%) and much lower than the anticipated, propagated analytical uncertainty associated with the eight constituents that were summed.

Table 4-6. Projected Dissolved Solids Content for the Pre-LTAD Supernatant

Constituent	Molarity	MW, g	Projected wt%	Measured wt%	Difference
NaOH	0.973	40	3.33		
$NaNO_3$	0.927	85	6.73		
$NaNO_2$	0.820	69	4.84		
Na_2CO_3	0.287	106	2.60		
$NaAl(OH)_4$	0.173	118	1.74		
Na_2SO_4	0.0340	142	0.41		
$Na_2C_2O_4$	0.00978	134	0.11		
NaCl	0.00614	58	0.03		
			$\Sigma = 19.8$	20.4	3%

Concentrations of the elemental constituents in the pre-LTAD supernatant are given in units of mg/L in Table 4-7. The most dominant supernatant elements were sodium and aluminum, at concentrations of approximately 95,000 and 4700 mg/L, respectively. Other measurable supernatant constituents include potassium, chromium, boron, copper, and molybdenum, at concentrations of approximately 400, 80, 40, 40, and 30 mg/L, respectively. RSDs for the measurable supernatant elements were all low (≤ 3.5%), indicating high measurement precision. Other elemental supernatant concentrations were below the MDLs, which ranged from a low of approximately 0.2 mg/L (for barium, beryllium, and strontium) to a high of approximately 2,600 mg/L (for sulfur).

Based on the concentrations of aluminum found in the slurry solids and the supernatant (10.6 wt% of slurry solids and 4670 mg per liter of supernatant), and on the solids distribution of the slurry (27.0 wt% total solids and 91.7 wt% supernatant), ~87 wt% of the pre-LTAD aluminum is expected to be insoluble and ~13 wt% of the pre-LTAD aluminum is expected to be soluble. Under the assumption that insoluble aluminum is present in the form of boehmite [AlO(OH)], ~67 wt% of the pre-LTAD insoluble solids is expected to be boehmite. In contrast, under the assumption that insoluble aluminum is present in the form of gibbsite [$Al(OH)_3$], ~87 wt% of the pre-LTAD insoluble solids is expected to be gibbsite. These figures give an indication of the maximum potential fractions of IS that could be eliminated through LTAD, depending on the extent of dissolution that is targeted. The projected insoluble/soluble aluminum fractions and the IS aluminum mineral distributions are captured in Table 4-8, for ease of identification.

Table 4-7. Elemental Constituents in the Pre-LTAD Supernatant

Constituent	Mean Result, mg/L	%RSD (n)
Ag	<3.0E+00	N/A
Al	4.67E+03	0.7
B	4.05E+01	1.0
Ba	<2.3E-01	N/A
Be	<1.7E-01	N/A
Ca	<2.4E+00	N/A
Cd	<3.0E+00	N/A
Ce	<7.9E+00	N/A
Co	<3.2E+00	N/A
Cr	8.42E+01	1.1
Cu	3.63E+01	1.0
Fe	<4.0E+00	N/A
Gd	<2.3E+00	N/A
K	4.03E+02	3.5
La	<1.8E+00	N/A
Li	<3.1E+00	N/A
Mg	<4.7E-01	N/A
Mn	<4.2E-01	N/A
Mo	3.00E+01	2.8
Na	9.50E+04	0.8
Ni	<5.1E+00	N/A
P	<4.1E+01	N/A
Pb	<4.1E+01	N/A
S	<2.6E+03	N/A
Sb	<4.3E+01	N/A
Si	<1.5E+01	N/A
Sn	<2.6E+01	N/A
Sr	<2.1E-01	N/A
Th	<3.0E+00	N/A
Ti	<9.2E+00	N/A
U	<4.2E+01	N/A
V	<1.4E+00	N/A
Zn	<1.2E+00	N/A
Zr	<1.4E+00	N/A

Table 4-8. Pre-LTAD Insoluble/Soluble Al Fractions and Boehmite/Gibbsite Distribution

	wt%
Insoluble fraction of Al in the slurry	~87
Soluble fraction of Al in the slurry	~13
Fraction of IS, if Al form is boehmite	~67
Fraction of IS, if Al form is gibbsite	~87

Concentrations of organic constituents in the pre-LTAD supernatant are given in units of mg/L in Table 4-9. The TOC concentration was 235 mg/L, while all volatile organic and semi-volatile organic constituents were less than the MDLs. This includes volatile organic constituents butanol and propanol, with concentrations less than 2.4 mg/L, and semi-volatile organic constituents phenol and tributylphosphate, with concentrations less than 98 and 9.8 mg/L, respectively. Concentrations of other volatile organic and other semi-volatile organic analytes were <2.4 mg/L and <9.8 mg/L, respectively.

Table 4-9. Organic Constituents in the Pre-LTAD Supernatant, n=3

Constituent	Mean Concentration, mg/L	%RSD
TOC	2.35E+02	1.1
n-butanol and i-butanol	<2.4E+00	N/A
Isopropanol	<2.4E+00	N/A
Benzene	<2.4E+00	N/A
Toluene	<2.4E+00	N/A
Other volatile organic analytes	<2.4E+00	N/A
Phenol	<9.8E+01	N/A
Tributylphosphate	<9.8E+00	N/A
N, N - dioctylnitrosamine	<9.8E+00	N/A
Other semi-volatile organic analytes	<9.8E+00	N/A

Interestingly, the TOC concentration (235 mg/L) is identical to the organic carbon concentration that is calculated by converting the oxalate concentration from units of molarity (Table 4-5) to units of mg carbon per liter. As such, it is clear that oxalate is the primary source of the pre-LTAD TOC. Converting the TOC concentration from a supernatant volume basis (mg TOC per liter of supernatant) to a slurry mass basis (mg TOC per kg of slurry) yields a value of 184 mg per kg slurry. This value is consistent with the TOC concentration measured for the pre-LTAD slurry (<200 mg/kg as identified in Table 4-4), suggesting that all (or essentially all) of the TOC is associated with the liquid phase.

The RSD for the pre-LTAD supernatant TOC result is very low (1.1%), indicating high measurement precision.

4.4 Characterization of the Post-LTAD Slurry and Supernatant

Density and solids distribution results for the post-LTAD slurry (following the high caustic LTAD tests) are given in Table 4-10. As expected, the post-LTAD slurry and supernatant densities, at 1.35 and 1.31 g/mL, respectively, were higher than those of the pre-LTAD slurry due to the large quantity of NaOH solids that were added to facilitate the aluminum dissolution processing. Correspondingly, the total solids and dissolved solids concentrations, at 34.7 and 33.1 wt%, respectively, were also higher than those of the pre-LTAD slurry. Given the expectation that essentially all of the added NaOH remained soluble, it is not surprising that the supernatant density and the dissolved solids content were affected to a greater extent than the slurry density and the total solids content. RSDs for the post-LTAD densities and solids distribution measurements were very low (≤ 1.7%), indicating high measurement precision.

The calculated insoluble solids content of the post-LTAD slurry, 2.4 wt%, was significantly lower than that of the pre-LTAD slurry, which was anticipated. The two primary reasons for this are: 1) addition of the 50 wt% NaOH diluted the initial insoluble solids content by ~30% (from an initial insoluble solids content of 8.3 wt% to a diluted insoluble solids content of 5.7 wt%); and 2) the LTAD processing converted a significant portion of aluminum-based insoluble solids (likely present as boehmite) to aluminum-based soluble solids (likely present as sodium aluminate).

Table 4-10. Densities and Solids Distribution of the Post-LTAD Slurry, n=3

Measurement	Mean Result	%RSD
Slurry density, g/mL	1.35	0.5
Supernatant density, g/mL	1.31	<0.1
Total solids, wt% of slurry	34.7	0.9
Dissolved solids, wt% of supernatant	33.1	1.7
Insoluble solids (calculated value), wt% of slurry	2.4	N/A
Soluble solids (calculated value), wt% of slurry	32.3	N/A

Concentrations of elemental constituents in the post-LTAD slurry are given in Table 4-11, with concentrations greater than 0.1 wt% shaded for easy identification. The three most dominant constituents in the slurry solids include sodium, aluminum, and iron, at concentrations of 38.8, 5.58, and 1.42 wt%, respectively. These concentrations are relatively consistent with expectations, based on adjusting the pre-LTAD concentrations (Table 4-3) for the 50 wt% NaOH that was added for the LTAD. (Adjustment of the sodium concentration was performed by multiplying the pre-LTAD sodium concentration [0.250 g Na per g of total solids] by the pre-LTAD total solids mass [216.5 g], adding the mass of sodium introduced by the 50 wt% NaOH [106.4 g], dividing the sum by the final mass of total solids [401.5 g], and then converting to a wt% basis by multiplying by 100. In contrast, adjustment of all other elemental concentrations was performed by multiplying the pre-LTAD elemental concentration [in units of g element per g of total solids] by the pre-LTAD total solids mass [216.5 g], dividing the product by the final mass of total solids [401.5 g], and then converting to a wt% basis by multiplying by 100.) When doing so, the expected post-LTAD sodium, aluminum, and iron concentrations are 40.0, 5.72, and 1.27 wt%, respectively, which vary from the measured values by 3, 2, and 11%, respectively. Given a typical one sigma analytical uncertainty of ~10%, the differences between the expected concentrations and the measured values are considered reasonable.

Less dominant constituents with concentrations greater than 0.1 wt% in the slurry include manganese, thorium, and uranium, with measured concentrations of 0.378, 0.352, and 0.147 wt%, respectively. In contrast, the expected concentrations based on adjusting the pre-LTAD values for the added 50 wt% NaOH are 0.332, 0.364, and 0.117 wt%, respectively, which vary from the measured values by ~13, 3, and 23%, respectively. Given a typical one sigma analytical uncertainty of ~10%, the differences between the expected concentrations and the measured values are considered reasonable. The somewhat greater difference between the expected post-LTAD uranium concentration and the expected post-LTAD uranium concentration is likely due to the magnitude of the uranium concentration, which at ~0.1 wt% is approaching the uranium MDL of the analytical approach. RSDs for the post-LTAD elemental measurements were all limited to ten percent or less, demonstrating typical analytical precision.

The concentration of TOC in the post-LTAD slurry is given in Table 4-12. The TOC concentration was 330 mg per kg of slurry, with an RSD of 26%, suggesting that the propagated analytical uncertainty of this measurement was slightly higher than usual, given the method's typical one sigma uncertainty of ~10%. The post-LTAD TOC (330 mg/kg) was higher than the pre-LTAD TOC (<200 mg/kg), indicating potential generation of TOC during the LTAD process. Note that the 50 wt% NaOH that was added to carry out the LTAD processing had minimal TOC content (< 4 mg/L), so existing TOC in the 50 wt% NaOH was not thought to be responsible for the increased post-LTAD TOC. A possible source of the additional TOC was carbon-related reactions facilitated by the increased NaOH concentration and elevated temperatures of the LTAD process.

Table 4-11. Elemental Constituents in the Post-LTAD Slurry (Shading Indicates Concentrations > 0.1 wt%)

Constituent	Digestion Method	Mean Result, wt% of solids	%RSD (n)
Ag	AR	<1.1E-03	N/A
Al	AR/PF	5.58E+00	2.4 (6)
B	AR	1.23E-02	2.5 (3)
Ba	AR/PF	9.93E-03	6.8 (6)
Be	AR	<3.5E-04	N/A
Ca	AR	5.57E-02	0.8 (3)
Cd	AR	<1.1E-03	N/A
Ce	AR	2.63E-02	2.9 (3)
Co	AR	<1.6E-03	N/A
Cr	AR/PF	3.41E-02	4.5 (6)
Cu	AR	7.62E-03	2.8 (3)
Fe	AR/PF	1.42E+00	1.5 (6)
Gd	AR	6.67E-03	2.2 (3)
K	AR	6.82E-02	12 (3)
La	AR	9.65E-03	0.5 (3)
Li	AR	<2.6E-03	N/A
Mg	AR/PF	2.13E-02	9.8 (6)
Mn	AR/PF	3.78E-01	2.9 (6)
Mo	AR	6.49E-03	4.6 (3)
Na	AR	3.88E+01	0.4 (3)
Ni	AR/PF	5.50E-02	4.6 (6)
P	AR	1.84E-02	6.6 (3)
Pb	AR	<1.5E-02	N/A
S	AR	<9.4E-01	N/A
Sb	AR	<1.6E-02	N/A
Si	PF	8.39E-02	7.1 (3)
Sn	AR	<9.4E-03	N/A
Sr	AR/PF	4.77E-03	10 (6)
Th	AR/PF	3.52E-01	4.6 (6)
Ti	AR	<3.3E-03	N/A
U	AR	1.47E-01	1.4 (3)
V	AR	<1.1E-03	N/A
Zn	AR	3.44E-03	2.1 (3)
Zr	AR	2.11E-02	0.5 (3)

Table 4-12. Total Organic Carbon in the Post-LTAD Slurry, n=3

Concentration, mg/kg slurry	%RSD
3.30E+02	26

Molar concentrations of the primary supernatant ions in the post-LTAD slurry are given in Table 4-13. Also given in Table 4-13 are the corresponding equivalence concentrations provided to allow a simple charge balance comparison of the pertinent cations and anions. The pertinent cations include sodium, with a measured concentration of 7.70 M, and potassium, with a measured concentration of approximately 0.01 M. In contrast, the measurable anions include free hydroxide, aluminate, nitrate, nitrite, carbonate, sulfate, and chloride, with concentrations of approximately 4.7, 0.81, 0.59, 0.56, 0.23, 0.022, and 0.0042 M, respectively. RSDs for the measurable ions were 8.0% or less, indicating good measurement precision. Other anions, including fluoride, formate, bromide, oxalate, and phosphate, were less than the MDLs, which ranged from approximately 1E-03 to 6E-03, the same range seen for the pre-LTAD ion measurement MDLs.

Table 4-13. Primary Ions and Charge Balance for the Post-LTAD Supernatant, n=3

Ion	Mean Concentration, Molarity	%RSD	Corresponding eq/L		Difference
			Cationic	Anionic	
Na^+	7.70E+00	0.6	7.70	N/A	
K^+	7.36E-03	8.0	0.00736	N/A	
Free OH^-	4.70E+00	1.0	N/A	4.70	
$Al(OH)_4^-$	8.11E-01	0.6	N/A	0.811	
NO_3^-	5.92E-01	0.5	N/A	0.592	
NO_2^-	5.58E-01	0.7	N/A	0.558	
CO_3^{2-}	2.25E-01	3.2	N/A	0.450	
SO_4^{2-}	2.17E-02	0.2	N/A	0.0434	
Cl^-	4.15E-03	1.5	N/A	0.00415	
F^-	<5.8E-03	N/A	N/A	N/A	
CHO_2^-	<2.4E-03	N/A	N/A	N/A	
Br^-	<1.4E-03	N/A	N/A	N/A	
$C_2O_4^{2-}$	<1.2E-03	N/A	N/A	N/A	
PO_4^{3-}	<1.2E-03	N/A	N/A	N/A	
			Σ = 7.71	Σ = 7.16	7%

As shown in Table 4-13, the sum of the pertinent cations was 7.71 eq/L, while the sum of the pertinent anions was 7.16 eq/L. The difference between these two values is ~7%, a value which indicates very good data consistency, as it is significantly below the anticipated, unpropagated two sigma uncertainty of ~20%.

As in the case of the pre-LTAD analytical results, a separate assessment utilizing the measured ion concentrations was performed to gauge consistency between the primary post-LTAD supernatant constituent concentrations and the measured post-LTAD dissolved solids content. This was done in the same manner as for the pre-LTAD case, except the density that was used in the calculations was that of the post-LTAD supernatant (1.31 g/mL). Results of the calculations are given in Table 4-14, which shows that the projected dissolved solids content based on the ion data is 30.5 wt%, which is about eight percent lower than the dissolved solids content measured in the Shielded Cells. An eight percent difference is considered good, as it is less than the expected one sigma analytical uncertainty for a single ion determination (10%) and clearly lower than the anticipated, propagated analytical uncertainty associated with the seven constituents that were summed.

Table 4-14. Projected Dissolved Solids Content for the Post-LTAD Supernatant

Constituent	Molarity	MW, g	Projected wt%	Measured wt%	Difference
NaOH	4.70	40	14.35		
$NaAl(OH)_4$	0.811	118	7.31		
$NaNO_3$	0.592	85	3.84		
$NaNO_2$	0.558	69	2.94		
Na_2CO_3	0.225	106	1.82		
Na_2SO_4	0.0217	142	0.24		
NaCl	0.00415	58	0.02		
			$\Sigma = 30.5$	33.1	8%

Concentrations of the elemental constituents in the post-LTAD supernatant are given in units of mg/L in Table 4-15. As expected, the most dominant supernatant elements were sodium and aluminum (due to the large quantity of NaOH that was added to the pre-LTAD slurry, and the large fraction of insoluble aluminum that was dissolved into solution), at concentrations of approximately 180,000 and 22,000 mg/L, respectively. Other measurable supernatant elements included potassium, chromium, boron, and iron, at concentrations of approximately 290, 120, 27, and 22 mg/L, respectively. The presence of iron at a concentration higher than found in the pre-LTAD supernatant (<4.0 mg/L) suggests that the high caustic concentration of the LTAD process dissolved a portion of the insoluble iron, albeit a very small fraction. Copper and molybdenum, which were detected in the pre-LTAD supernatant, were less than the MDLs of the post-LTAD case. This is not surprising, given that the copper and molybdenum concentrations in the pre-LTAD supernatant were just slightly higher than the MDLs – but with dilution by the water content of the added 50 wt% NaOH, the post-LTAD concentrations fell below the MDLs. RSDs for the post-LTAD supernatant elemental results were 8% or less, indicating good measurement precision. Other post-LTAD elemental supernatant concentrations were below the MDLs, which ranged from a low of approximately 0.2 mg/L (for strontium) to a high of approximately 7400 mg/L (for sulfur).

Based on the concentrations of aluminum found in the post-LTAD slurry solids and the supernatant (5.58 wt% of slurry solids and 21,900 mg per liter of supernatant), and on the solids distribution of the post-LTAD slurry (34.7 wt% total solids and 97.6 wt% supernatant), ~16 wt% of the post-LTAD aluminum is expected to be insoluble and ~84% of the post-LTAD aluminum is expected to be soluble. Comparing this insoluble/soluble Al distribution to the pre-LTAD insoluble/soluble Al distribution (~87 wt% insoluble and ~13 wt% soluble) indicates that the LTAD process dissolved ~82 wt% of the pre-LTAD insoluble aluminum. The post-LTAD insoluble/soluble aluminum fractions and the LTAD effectiveness are given in Table 4-16, for ease of identification.

Based on the IS content of the slurry following addition of the 50 wt% caustic, but prior to heating (5.7 wt% IS), and on the IS content of the post-LTAD slurry (2.4 wt% IS), the fraction of IS that dissolved during LTAD was calculated to be ~58 wt%. Given the expected fractions of pre-LTAD IS associated with the aluminum mineral forms of boehmite and gibbsite (~67 and 87 wt%, respectively, as identified in Table 4-7) and the aluminum dissolution fraction that was observed (~82%), the fractions of IS that would have been expected to dissolve were ~55% for the boehmite mineral form and ~71% for the gibbsite mineral form. (This assumes that aluminum was the primary constituent dissolved during LTAD, which is supported by the available elemental characterization data). Based on the similarity between the observed fraction of IS that dissolved (~58 wt%) and the fraction expected for the boehmite aluminum mineral form (~55 wt%), it appears that the majority of the insoluble aluminum in the Tank 51 sample was present in the form of boehmite. The fraction of IS dissolved and the expectations based on aluminum mineralogy are given in Table 4-17, for ease of identification.

Table 4-15. Elemental Constituents in the Post-LTAD Supernatant

Constituent	Mean Result, mg/L	%RSD (n)
Ag	<8.7E+00	N/A
Al	2.19E+04	0.6 (3)
B	2.66E+01	0.8 (3)
Ba	<6.6E-01	N/A
Be	<2.8E-01	N/A
Ca	<7.8E+00	N/A
Cd	<8.5E+00	N/A
Ce	<2.3E+01	N/A
Co	<9.3E+00	N/A
Cr	1.23E+02	0.3 (3)
Cu	<3.1E+01	N/A
Fe	2.24E+01*	N/A (1)
Gd	<6.6E+00	N/A
K	2.88E+02	8.0 (3)
La	<5.2E+00	N/A
Li	<8.9E+00	N/A
Mg	<1.2E+00	N/A
Mn	<1.2E+00	N/A
Mo	<2.7E+01	N/A
Na	1.77E+05	0.6 (3)
Ni	<1.5E+01	N/A
P	<1.2E+02	N/A
Pb	<1.2E+02	N/A
S	<7.4E+03	N/A
Sb	<1.2E+02	N/A
Si	<2.9E+01	N/A
Sn	<7.5E+01	N/A
Sr	<2.4E-01	N/A
Th	<9.1E+00	N/A
Ti	<2.7E+01	N/A
U	<1.2E+02	N/A
V	<3.5E+00	N/A
Zn	<3.4E+00	N/A
Zr	<4.0E+00	N/A

*The reported iron concentration is based on a single determination where the measured concentration exceeded the MDL. The other two iron measurements were just slightly less than the reporting limits and therefore quantified as being less than MDLs.

Table 4-16. Post-LTAD Insoluble/Soluble Aluminum Fractions and LTAD Effectiveness

	wt%
Insoluble fraction of Al in the post-LTAD slurry	~16
Soluble fraction of Al in the post-LTAD slurry	~84
Fraction of pre-LTAD insoluble Al that was dissolved	~82

Table 4-17. Fraction of IS Dissolved and Expectations Based on Al Mineralogy

	wt%
Fraction of IS dissolved by LTAD	~58
Fraction of IS expected to dissolve assuming the boehmite Al form	~55
Fraction of IS expected to dissolve assuming the gibbsite Al form	~71

Concentrations of organic constituents in the post-LTAD supernatant are given in Table 4-18. The post-LTAD supernatant TOC concentration was 105 mg/L, which was ~40% lower than the concentration expected upon diluting the pre-LTAD slurry with the 50 wt% NaOH needed to perform the LTAD processing. (The dilution factor associated with the 50 wt% NaOH addition was 1.36 [on a volume basis], based on a pre-LTAD supernatant mass of 735 g, a pre-LTAD supernatant density of 1.17 g/mL, a post-dilution supernatant mass of 1105 g, and a post-dilution supernatant density of 1.29 g/mL). The decline in TOC occurring during LTAD may have been due to carbon-related reactions facilitated by the increased free hydroxide concentration and the elevated LTAD temperatures.

Table 4-18. Organic Constituents in the Post-LTAD Supernatant, n=3

Constituent	Mean Concentration, mg/L	%RSD
TOC	1.05E+02	16
n-butanol and i-butanol	<2.7E+00	N/A
Isopropanol	<2.7E+00	N/A
Benzene	<2.7E+00	N/A
Toluene	<2.7E+00	N/A
Other volatile organic analytes	<2.7E+00	N/A
Phenol	<1.1E+02	N/A
Tributylphosphate	<1.1E+01	N/A
N, N - dioctylnitrosamine	<1.1E+01	N/A
Other semi-volatile organic analytes	<1.1E+01	N/A

Based on the measured oxalate concentration in the post-LTAD supernatant (<1.2E-03 M, which corresponds to <29 mg carbon per liter), it is clear that oxalate does not account for the majority of the post-LTAD supernatant TOC. This is contrary to what was seen in the pre-LTAD supernatant, where the TOC was essentially all due to oxalate. The low concentration of oxalate in the post-LTAD supernatant is not a surprise, given the diminishing solubility of oxalate at high sodium concentrations. The identity of the primary organic compound(s) contributing to the post-LTAD TOC is not clear, as no volatile or semi-volatile organic compounds were detected, and concentrations of all such compounds were less than the MDLs, as shown in Table 4-18.

Converting the TOC concentration from a supernatant volume basis to a slurry mass basis yields a value of 78 mg per kg slurry. This value is significantly lower than the TOC concentration measured for the post-LTAD slurry (330 mg/kg as identified in Table 4-12), suggesting that a large fraction (~75%) of the post-LTAD TOC is associated with the solid phase. This is very different than what was observed for pre-LTAD slurry, where essentially all of the TOC was associated with the liquid phase.

The RSD for the post-LTAD supernatant TOC result is moderately high (16 %), but still indicative of normal measurement precision assuming a two sigma analytical uncertainty of 20%.

4.5 Characterization of the Baseline and High Caustic LTAD Process Sample Supernatants

Baseline LTAD Process Supernatants

Characterization results for the process supernatants collected during the baseline LTAD tests are given in Table 4-19. For purposes of comparison, corresponding results for the pre-LTAD supernatant are also identified in the table. Densities and free hydroxide concentrations were relatively consistent over the course of the baseline testing, with fluctuations in the values being consistent with expectations based on the typical analytical uncertainties, rather than being a function of the changing test conditions. For example, the density values ranged from 1.16-1.18 g/mL, varying from the pre-LTAD density value (1.17 g/mL) by a maximum of 0.01 g/mL, which is the typical analytical uncertainty for supernatant density determinations. Similarly, the measured free hydroxide concentrations ranged from ~0.93 to 1.03 M, varying from the pre-LTAD free hydroxide value (~0.97 M) by a maximum of about 6%, which is less than the expected one sigma analytical uncertainty of ~10%. As such, the differences in density and free hydroxide values are not considered to be statistically significant. This is consistent with expectations, given that only minimal aluminum dissolution was expected to occur under the elevated temperature regimes of the baseline LTAD conditions.

Table 4-19. Baseline LTAD Process Sample Supernatant Characterization

	Pre-LTAD (As Rec'd)	Baseline LTAD Process Filtrates			
		Post 23 °C	Post 50 °C	Post 75 °C	Post 85 °C
Density, g/mL	1.17	1.16	1.16	1.18	1.17
Free OH, M	0.973	0.960	0.987	0.926	1.03
Al, M	0.173	0.156	0.150	0.216	0.263
TOC, mg/L	235	352	394	396	426
wt% insol. Al dissolved	N/A	N/A	N/A	~4	~8

In contrast, the aluminum concentrations following the 75 and 85 °C temperature regimes were ~0.22 and 0.26 M, which were about 25 and 50% higher, respectively, than the pre-LTAD aluminum concentration of ~0.17 M. Given that these differences are greater than the expected two sigma analytical uncertainty of ~20%, the differences are considered to be statistically significant. Correspondingly, the portions of insoluble aluminum that dissolved during the 75 and 85 °C temperature regimes were measurable, albeit minor, at ~4 and 8 wt%, respectively. Aluminum dissolution fractions of these small magnitudes would not be expected to have a discernible impact on density or free hydroxide concentration (as was demonstrated), given the magnitudes of the analytical uncertainties.

TOC concentrations of the process samples, ranging from ~350-430 mg/L, were significantly higher than that of the pre-LTAD slurry, at ~240 mg/L. The reasons for these differences are not clear, as the post-23 °C TOC concentration (~350 mg/L) was expected to be comparable to that of the pre-LTAD supernatant (~240 mg/L), given that the slurry underwent no temperature changes or obvious chemical changes during this first temperature regime. The only potential difference between the pre-LTAD slurry and the post-23 °C slurry is the mixing that each underwent prior to sampling. The pre-LTAD slurry was mixed for a period on the order of an hour prior to sampling, while the post-23 °C slurry was mixed for a period of approximately six additional hours prior to sampling. The difference in mixing is not expected to impact TOC – however, it is the only process difference that is known and is identified for that reason. The possibility that extended mixing displaced TOC from within the pores of the insoluble solids seems unlikely, but such possibility is identified for consideration, based on the available information.

Over the course of the baseline LTAD tests, the supernatant TOC concentration increased from ~350 mg/L (following the 23 °C regime) to ~430 mg/L (following the 85 °C regime). This is an increase of approximately 20%, which is right at the dividing line of what would be expected based on analytical uncertainty and what would be considered statistically significant. If the TOC is truly increased due to the test conditions (as opposed to being an artifact of the analytical uncertainty), two primary potential sources of the increase may be: a) impacts of the extended mixing durations (as mentioned above); and b) impacts of temperature on TOC solubility and/or TOC liquid phase partitioning. Given that essentially all of the pre-LTAD TOC was oxalate, one wonders if the higher TOC concentrations of the process supernatants are indicative of greater liquid phase oxalate or of additional TOC compounds beyond oxalate.

High Caustic LTAD Process Supernatants

Characterization results for the process supernatants collected during the high caustic LTAD tests are given in Table 4-20. For purposes of comparison, the corresponding projected results for the supernatant of the original slurry following the NaOH addition (but prior to heating) are also identified in the table, along with the analytical results for the post-LTAD supernatant. Densities during the high caustic LTAD tests were all relatively high (1.29-1.31 g/mL), due to the large fraction of soluble solids contributed by the added 50 wt% NaOH. The slight difference between the density of the post-50 °C supernatant (1.29 g/mL) and the densities of the mid-85 °C and post-85 °C supernatants (1.31 g/mL) is consistent with expectations, although it is in the range that could be attributed to analytical uncertainty versus being a clear process effect. Still, given that the typical uncertainty of the Shielded Cells supernatant density determinations is ±0.01 g/mL, and that the apparent increase was continuous over the course of the LTAD testing (from the projected density prior to heating through the measured density of the post-LTAD supernatant), the increase from 1.29 to 1.31 g/mL is likely real.

Table 4-20. High Caustic LTAD Process Sample Supernatant Characterization

	Projected values after adding 50 wt% NaOH, but prior to heating	High Caustic LTAD Process Filtrates				Post-LTAD @ 25 °C
		Post 50 °C	Post 75 °C	Mid 85 °C	Post 85 °C	
Density, g/mL	1.29	1.29	1.30	1.31	1.31	1.31
Free OH, M	6.00	5.70	5.62	4.65	4.66	4.70
Al, M	0.133	0.136	0.334	0.705	0.783	0.811
TOC, mg/L	173*	164	317	329	354	105
% Insol. Al Dissolved	N/A	Insignificant	25	68	78	82

*Projected TOC content of the slurry following addition of the NaOH but prior to heating is based solely on the dilution factor associated with the 50 wt% NaOH addition, ignoring potential impacts to the TOC solubility caused by the increased free hydroxide concentration.

The measured free hydroxide concentrations dropped from ~6.0 M for the initial supernatant (prior to heating) to around 4.7 M for the mid-85 °C and post-85 °C supernatants. This is about a 22% decrease, which borders on the expected two sigma analytical uncertainty (~20%), making it of somewhat questionable statistical significance, despite being consistent with expectations. The difference between the projected free hydroxide concentration of the supernatant prior to heating (6.0 M) and the post-50 °C supernatant (~5.7 M) is attributed to analytical uncertainty, as it is only ~5%, well below the expected one sigma analytical uncertainty (~10%). Agreement between the free hydroxide concentration of the post-85 °C process supernatant (4.66 M) and the post-LTAD supernatant (4.70 M) is extremely good, given the expected analytical uncertainty of ~10%. Clearly, lowering of the free hydroxide concentration during LTAD is due to formation of soluble aluminate, $Al(OH)_4^-$, which consumes free hydroxide as insoluble aluminum is dissolved.

Aluminum concentrations in the supernatant increased by a factor of approximately six over the course of the high caustic LTAD testing, from a low of ~0.13 M prior to heating to a high of ~0.8 M following the 85 °C temperature regime. Correspondingly, the total fraction of insoluble aluminum that was dissolved by LTAD was ~80 wt%, with fractions of ~25 wt% and ~70 wt% of the insoluble aluminum dissolved at the end of the 75 °C and mid-85 °C temperature regimes, respectively. In contrast, at the end of the 50 °C temperature regime, the fraction of insoluble aluminum that was dissolved was deemed insignificant, as it was less than the expected variations associated with the analytical uncertainties.

TOC concentrations in the process samples ranged from ~160-350 mg/L, with the lowest concentration occurring in the post-50 °C process supernatant (and being comparable to the projected TOC value based solely on dilution), and with concentrations of 320-350 mg/L occurring in the post-75 °C, mid-85 °C, and post-85 °C process supernatants. Interestingly, the TOC concentration in supernatant taken from the cooled post-LTAD slurry was the lowest of all, at ~110 mg/L. As in the baseline case, the reasons for the TOC differences are not clear. Adding to the potential mixing and temperature impacts addressed in the baseline case, the potential impact of the high sodium concentration needs to be considered in the high caustic case. Clearly, the TOC solubility would be expected to drop under conditions of high sodium concentrations, if oxalate is the primary source of TOC, as found in the pre-LTAD supernatant (Section 4.3). However, the similarity between the initial projected TOC value (which ignores potential solubility effects) and the post-50 ºC TOC value, as well as the discrepancy between TOC and oxalate in the post-LTAD case (Section 4.4), suggest that an alternate form of TOC may be present post-LTAD. Alternately, the relatively high TOC concentrations measured for the post-75 °C and post-85 °C process supernatants versus the relatively low TOC concentration supernatant collected from the cooled, post-LTAD slurry suggests the possibility that the process samples were supersaturated with TOC during and after sampling, while TOC in the post-LTAD supernatant had reached saturation equilibria prior to sampling. The apparent inconsistencies between the TOC results of the various process supernatants make it difficult to reach sound conclusions regarding the TOC behavior.

5.0 Conclusions

1) The HGRs measured during the LTAD testing ranged from a low of ~2.5E-07 ft^3/hr/gal sludge to a high of ~2.5E-06 ft^3/hr/gal sludge, with dynamic short-term increases occurring immediately following significant temperature increases and a dynamic short-term decrease occurring immediately following the caustic addition. On average, the HGRs measured during the baseline tests were somewhat higher than those measured during the high caustic tests, although still the same order of magnitude. Much of the HGR variations were thought to be due to changes impacting the slurry's ability to retain gas and to release retained gas, rather than changes affecting the potential sources of the HGRs.

2) Radiolysis was a primary contributor to the HGR, as indicated by the average measured HGRs being the same order of magnitude as the theoretical estimated HGRs due to radiolysis. Other potential contributors to HGR may have been present, but if so, were thought to be minor contributors in comparison to radiolysis.

3) Methane was not detected during the LTAD tests and was quantified as being less than the LOQ (90 ppmv). Due to the high relative LOQ, methane concentrations of at least three times the highest measured hydrogen concentration would have been necessary for discrete quantification of the methane concentrations (as opposed to quantification with a "less than" value). Methane concentrations of the same magnitude as all or most of the measured hydrogen concentrations would not have been detected. As such, it is acknowledged that non-detection of methane does not ensure its absence.

4) Supernatant-phase concentrations of volatile and semi-volatile organic constituents were all less than the minimum detection limits, which ranged from 2.4E+00 to 1.1E+2 mg/L. This applies to supernatants in both the pre-LTAD and post-LTAD slurries.

5) Approximately 80 wt% of the insoluble aluminum in the Tank 51 slurry was dissolved over the course of the high caustic LTAD tests. This includes insignificant insoluble aluminum dissolved during the twelve hour period at 50 °C, ~25 wt% insoluble aluminum dissolved during the twelve hour period at 75 °C, ~43 additional wt% insoluble aluminum dissolved during the first twenty-four hours at 85 °C, and ~10-14 additional wt% insoluble aluminum dissolved during the final twenty-four hours at 85 °C. In contrast, only ~8 wt% of the insoluble aluminum was dissolved over the course of the baseline LTAD tests, with ~4 wt% dissolving during the 15-16 hour period at 75 °C and ~4 additional wt% dissolving during the 48 hour period at 85 °C. The magnitudes of dissolved aluminum in the tests were consistent with expectations based on previously-observed aluminum dissolution behavior at SRS.

6) The primary mineral form of insoluble aluminum in the Tank 51 slurry was boehmite.

7) The supernatant TOC results of the pre/post-LTAD slurries and process samples showed significant variations that were difficult to understand. Multiple potential sources of variation were considered (i.e. physical changes, temperature changes, chemical changes, TOC supersaturation/precipitation reactions), but a clear explanation of the observed TOC behavior was not obvious. An experimental study addressing temperature and chemical effects of test slurries containing known quantities of TOC "standards" would be helpful in providing insight into the observed TOC behavior.

6.0 Recommendation

Perform TOC testing quantifying impacts of physical, chemical, and temperature changes on known concentrations and sources of TOC in caustic sludge simulant slurries, with the end goal of understanding the impact of such changes on supernatant phase TOC concentrations/measurements.

7.0 References

[1] Barrowclough, E. P. and W. A. Lewitus, "*Flowsheet for Low Temperature Aluminum Dissolution for Sludge Batch 10*," X-ESR-H-00915, Revision 0, April 2018.

[2] Eigenbrot, N. J., "*Evaluation of the Safety of the Situation (ESS): Potentially Inadequate Recognition of the Effect of Organics on Hydrogen Generation Rates in the Concentration, Storage, and Transfer Facilities (PISA PI-2017-0003)*," U-ESS-G-00007, Revision 1, November 2017.

[3] Samadi, A., "*Tank 51 Low Temperature Aluminum Dissolution (LTAD) Real Waste Testing*," X-TTR-H-00075, Revision 0, November 16, 2017.

[4] Reboul, S. H., "*Task Technical and Quality Assurance Plan for Tank 51 Low Temperature Aluminum Dissolution (LTAD) Real Waste Testing*," SRNL-RP-2017-00786, Revision 1, March 13, 2018.

[5] Newell, J. D., J. M. Pareizs, C. J. Martino, S. H. Reboul, C. J. Coleman, T. B. Edwards, and F. C. Johnson, "*Actual Waste Demonstration of the Nitric-Glycolic Flowsheet for Sludge Batch 9 Qualification*," SRNL-STI-2016-00327, Revision 1, March 2017.

6 Pareizs, J. M, J. D. Newell, C. J. Martino, C. L. Crawford, and F. C. Johnson, "*Sludge Washing and Demonstration of the DWPF Nitric/Formic Flowsheet in the SRNL Shielded Cells for Sludge Batch 9 Qualification*," SRNL-STI-2016-00355, Revision 0, October 2016.

7 Stone, M. E, D. J. Adamson, D. J. Pak, and J. M. Pareizs, "*Hydrogen Generation Rate Measurement Apparatus: Final Design Package*," SRNL-RP-2014-00866, Revision 0, September 2014.

8 Stone, M. E, J. D. Newell, T. E. Smith and J. M. Pareizs, "WTP Waste Feed Qualification: Hydrogen Generation Rate Measurement Apparatus Testing Report," SRNL-STI-2016-00247, Revision 0, June 2016.

9 Martino, C. J., J. D. Newell, W. H. Woodham, J. M. Pareizs, T. B. Edwards, D. P. Lambert, and A. M. Howe, "*Investigation of Thermolytic Hydrogen Generation Rate of Tank Farm Simulated and Actual Waste,*" SRNL-STI-2017-00611, Revision 0, November 2017.

10 Taylor, J. K., Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, Michigan, 1987.

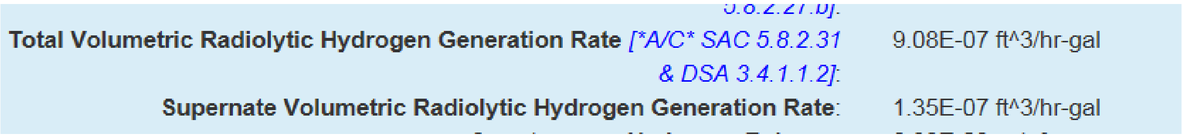
11 Environmental Protection Agency (EPA), "*Definition and Procedure for Determination of the Method Detection Limit – Revision 2*," 40 CFR 136, Appendix B, September 2017.

12 Metrodata GmbH, "GUM Workbench: User Manual for Version 1.2, 2.3, and 2.4," 2009.

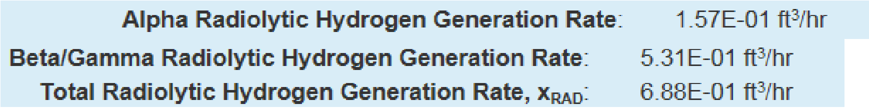
13 **JMP™ PRO, Version 11.2.1**, SAS Institute Inc., Cary, NC, 2014.

Attachment A. Estimated Radiolytic Hydrogen Generation Rates

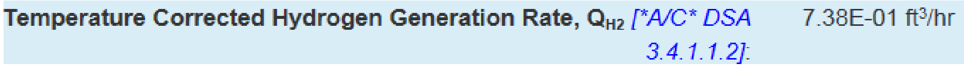
From: Christine Ridgeway <Christine.Ridgeway@srs.gov>
Date: February 28, 2018 at 3:24:33 PM EST
To: Thomas Huff <Thomas.Huff@srs.gov>, Frank Pennebaker <frank.pennebaker@srnl.doe.gov>
Subject: Tank 51 HGRs



Total Volumetric Radiolytic Hydrogen Generation Rate *[*A/C* SAC 5.8.2.31 & DSA 3.4.1.1.2]*:	9.08E-07 ft^3/hr-gal
Supernate Volumetric Radiolytic Hydrogen Generation Rate:	1.35E-07 ft^3/hr-gal



Alpha Radiolytic Hydrogen Generation Rate:	1.57E-01 ft^3/hr
Beta/Gamma Radiolytic Hydrogen Generation Rate:	5.31E-01 ft^3/hr
Total Radiolytic Hydrogen Generation Rate, x_{RAD}:	6.88E-01 ft^3/hr



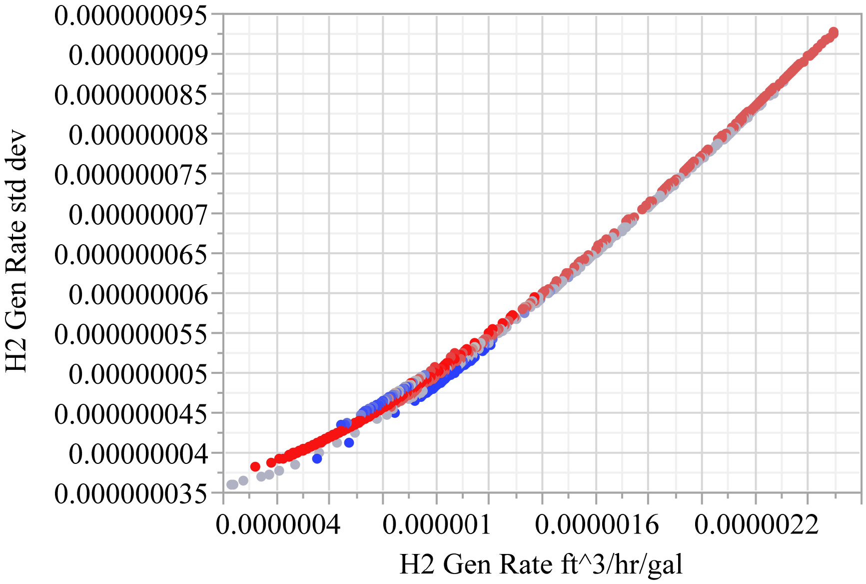
Temperature Corrected Hydrogen Generation Rate, Q_{H2} *[*A/C* DSA 3.4.1.1.2]*:	7.38E-01 ft^3/hr

Temperature Corrected is to 47C.

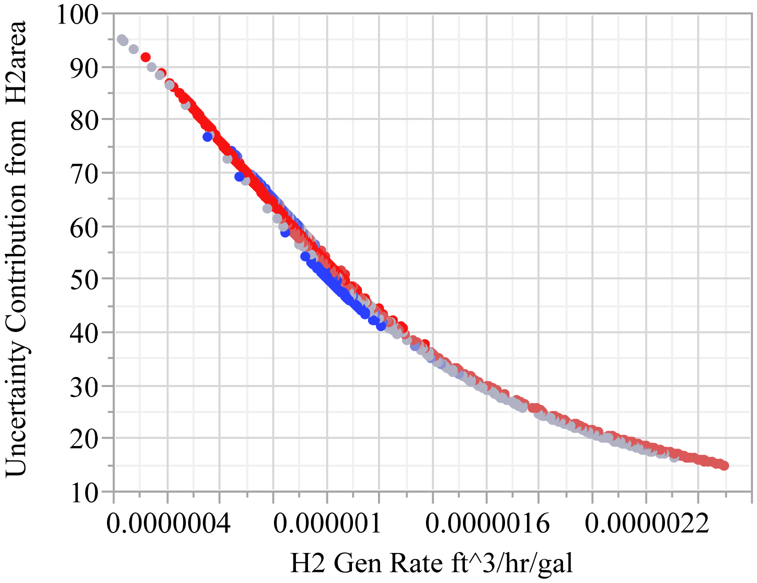
Christine Ridgeway
Process Safety and Regulatory
(803) 952-4370

Attachment B. Percent Uncertainty Contributions for Baseline LTAD HGRs

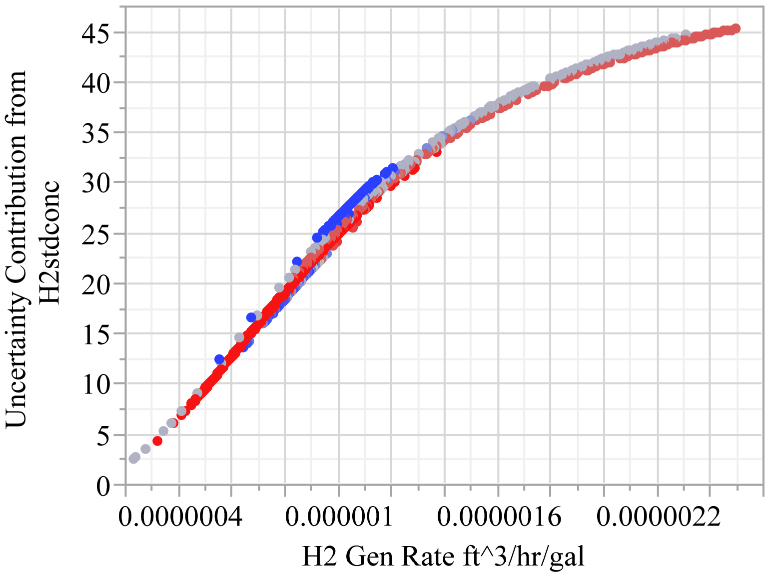
H2 Gen Rate Std Dev by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline



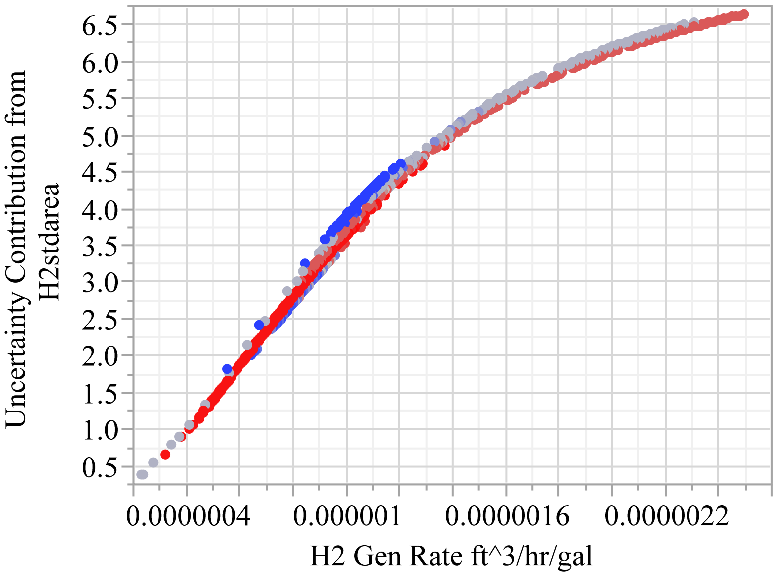
Percent Uncertainty Contribution from H2area by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline



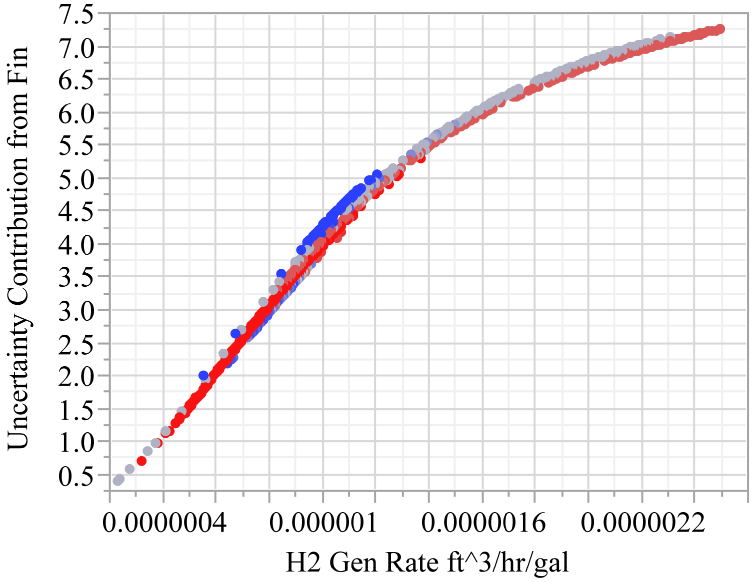
Percent Uncertainty Contribution from H2stdconc by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline



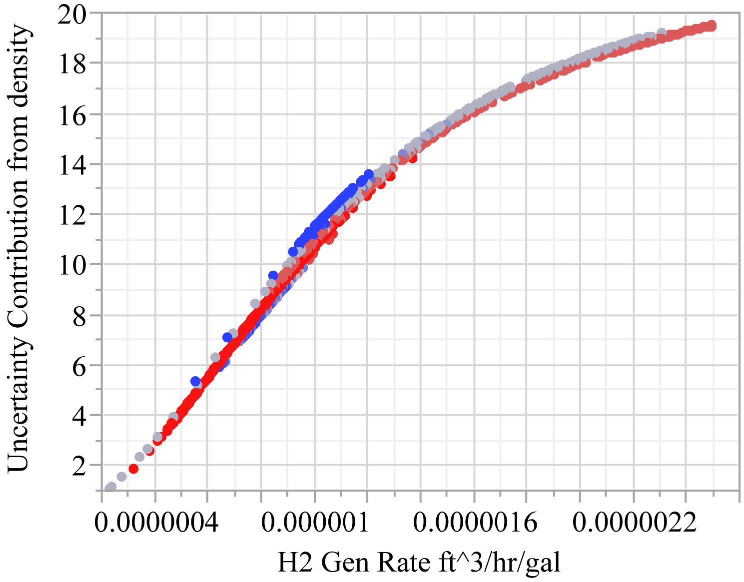
Percent Uncertainty Contribution from H2stdarea by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline



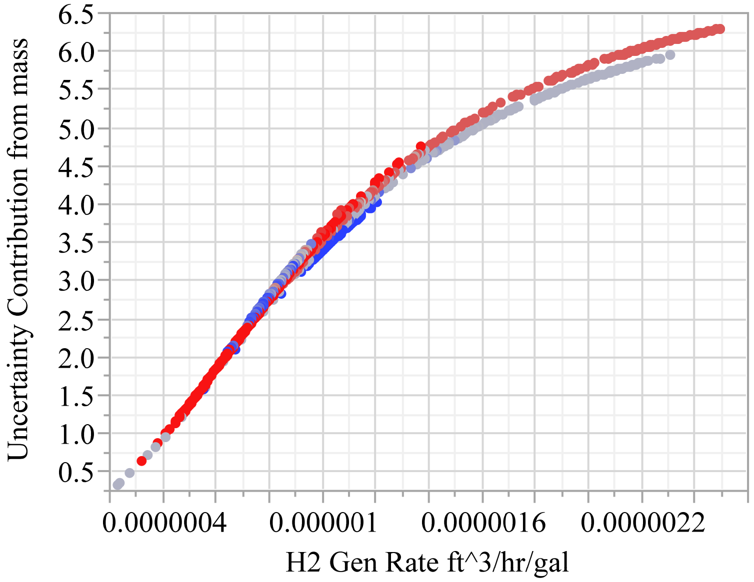
Percent Uncertainty Contribution from Fin by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline



Percent Uncertainty Contribution from Density by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline

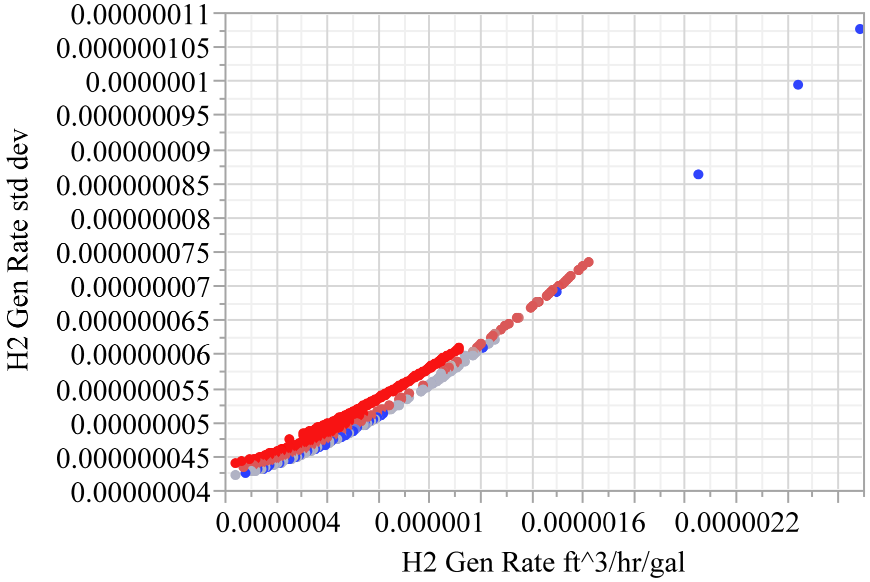


Percent Uncertainty Contribution from Mass by H2 Gen Rate ft^3/hr/gal
Test=LTAD Baseline

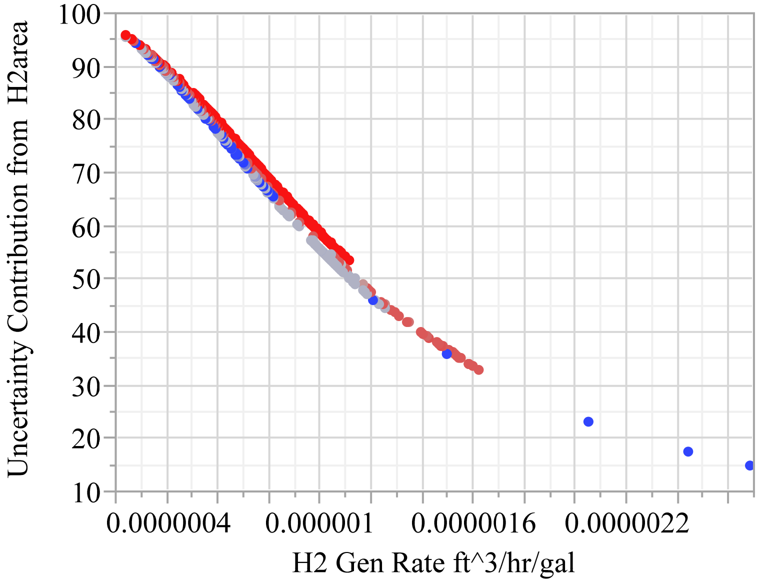


Attachment C. Percent Uncertainty Contributions for High Caustic LTAD HGRs

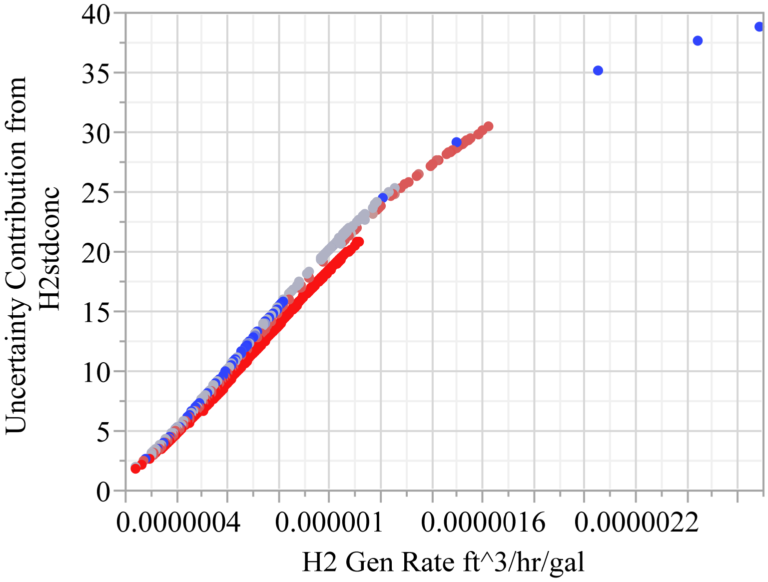
Bivariate Fit of H2 Gen Rate Std Dev by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH



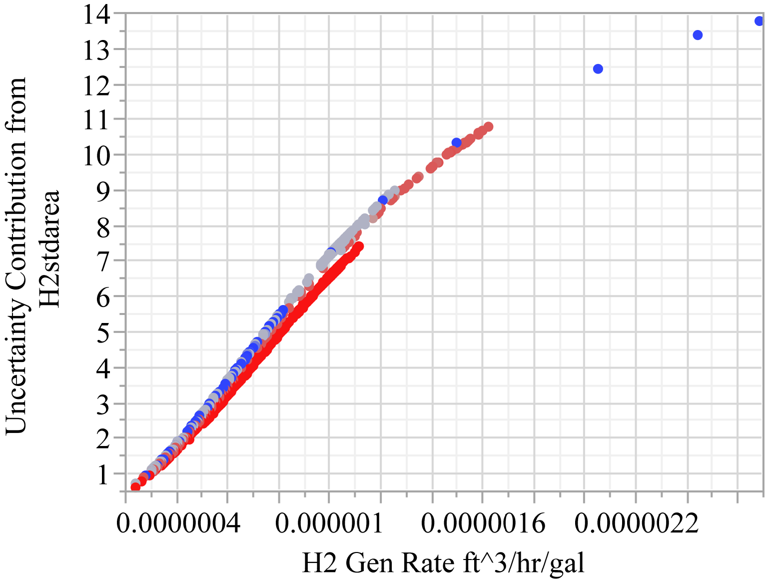
Percent Uncertainty Contribution from H2area by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH



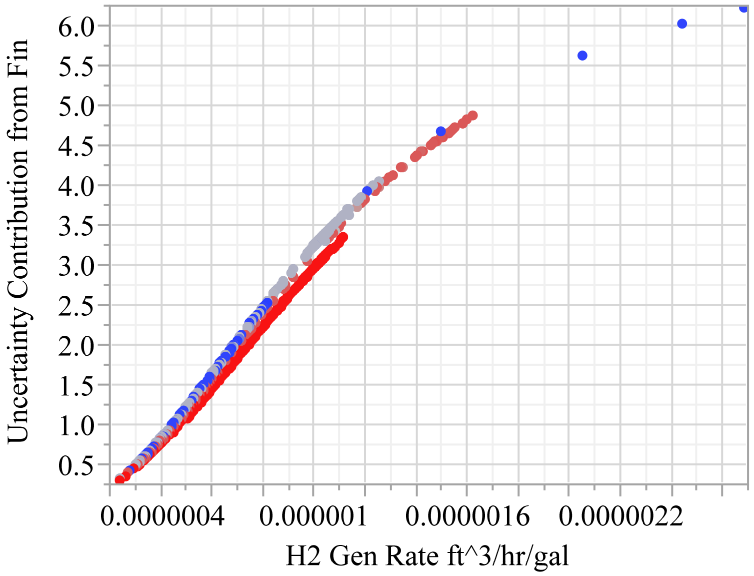
**Percent Uncertainty Contribution from H2stdconc by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH**



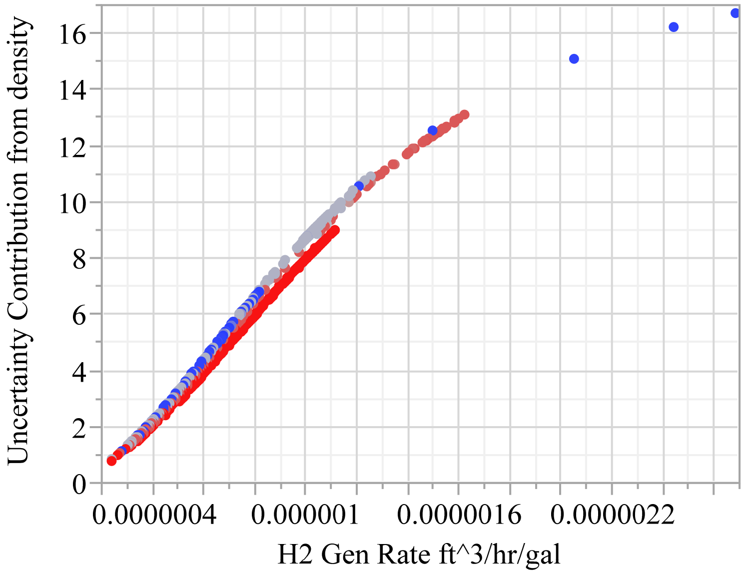
**Percent Uncertainty Contribution from H2stdarea by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH**



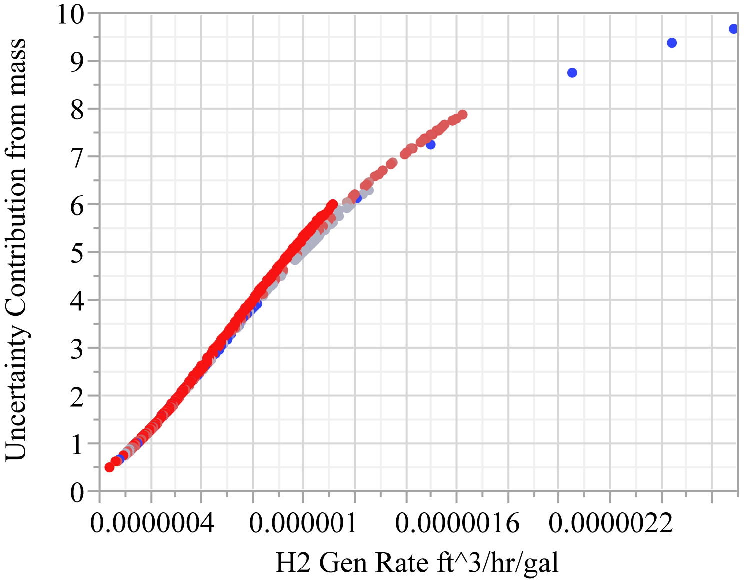
**Percent Uncertainty Contribution from Fin by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH**



**Percent Uncertainty Contribution from Density by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH**



**Percent Uncertainty Contribution from Mass by H2 Gen Rate ft^3/hr/gal
Test=LTAD w OH**



Distribution:

celia.aponte@srs.gov
eric.barrowclough@srs.gov
timothy.baughman@srs.gov
ronald.blessing@srnl.doe.gov
andrew.boggess@srnl.doe.gov
earl.brass@srs.gov
leigh.brown@srnl.doe.gov
timothy.brown@srnl.doe.gov
hilary.bui@srs.gov
phyllis.burkhalter@srnl.doe.gov
joyce.cartledge@srnl.doe.gov
lawrence.cheatham@srnl.doe.gov
charles02.coleman@srnl.doe.gov
thomas.colleran@srs.gov
alex.cozzi@srnl.doe.gov
charles.crawford@srnl.doe.gov
david.crowley@srnl.doe.gov
s.crump@srnl.doe.gov
c.diprete@srnl.doe.gov
david.dooley@srnl.doe.gov
richard.edwards@srs.gov
tommy.edwards@srnl.doe.gov
amy.ekechukwu@srnl.doe.gov
julie.fawbush@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
terry.foster@srnl.doe.gov
kevin.fox@srnl.doe.gov
eric.freed@srs.gov
chelsea.gailliard@srnl.doe.gov
sharon.gleaton@srnl.doe.gov
roberto.gonzalez@srs.gov
clint.gregory@srnl.doe.gov
nancy.halverson@srnl.doe.gov
barbara.hamm@srs.gov
erich.hansen@srnl.doe.gov
michael.hay@srnl.doe.gov
connie.herman@srnl.doe.gov
david.herman@srnl.doe.gov
bill.holtzscheiter@srs.gov
azikiwe.hooker@srs.gov
thomas.huff@srs.gov
john.iaukea@srs.gov
spencer.isom@srs.gov
vijay.jain@srs.gov
monica.jenkins@srnl.doe.gov
mark02.jones@srnl.doe.gov
victoria.kmiec@srs.gov
jocelyn.lampert@srnl.doe.gov
maurice.lee@srnl.doe.gov
craig.lewis@srs.gov
william.lewitus@srs.gov
keisha.martin@srs.gov
chris.martino@srnl.doe.gov
john.mayer@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
ryan.mcnew@srs.gov
bridget.miller@srnl.doe.gov
jeffery.mixon@srnl.doe.gov
john.moody@srnl.doe.gov
gregg.morgan@srnl.doe.gov
david.newell@srnl.doe.gov
cap.nguyen@srnl.doe.gov
john.occhipinti@srs.gov
lawrence.oji@srnl.doe.gov
john.pareizs@srnl.doe.gov
n-rao.pasala@srs.gov
frank.pennebaker@srnl.doe.gov
jeff.pike@srnl.doe.gov
michael.poirier@srnl.doe.gov
william.ramsey@srnl.doe.gov
scott.reboul@srnl.doe.gov
luke.reid@srnl.doe.gov
christine.ridgeway@srs.gov
azadeh.samadi-dezfouli@srs.gov
hasmukh.shah@srs.gov
victor.skeens@srnl.doe.gov
geoffrey.smoland@srnl.doe.gov
raenan.stanley@srnl.doe.gov
michael.stone@srnl.doe.gov
christie.sudduth@srs.gov
patricia.suggs@srs.gov
rita.sullivan@srnl.doe.gov
patrick.westover@srnl.doe.gov
denise.wheeler@srnl.doe.gov
thomas02.white@srnl.doe.gov
mary.whitehead@srs.gov
boyd.wiedenman@srnl.doe.gov
bill.wilmarth@srnl.doe.gov
kimberly.wyszynski@srnl.doe.gov
john.young@srnl.doe.gov
robin.young@srnl.doe.gov
jeffrey.zimmerly@srnl.doe.gov
Records Administration (EDWS)