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Aluminum Metal Dissolution for Mark-18A Target Processing

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REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

The Mark-18A Program was established to preserve the unique materials found in Mark-18A targets for future research and development activity within the Department of Energy or other U.S. government agencies. The Savannah River Site has 65 Mark-18A targets to be provided for the recovery of high valued isotopes. The majority of the recovery work will be performed in the Savannah River National Laboratory (SRNL) Shielded Cells due to dose concerns. The recovered product will be transported to the Oak Ridge National Laboratory (ORNL) for future research and development tasks.

The Mark-18A target material will be removed from their current configuration, dissolved, chemically separated, and calcined to a stable oxide. The baseline flowsheet is patterned after the flowsheet ORNL has previously used to process both Mark-18A and Mark-42 targets. However, it is necessary for SRNL to adapt its facility and the ORNL flowsheet to identify process improvements to successfully recover the actinide materials within the constraints of the SRNL Shielded Cells. These studies evaluated and demonstrated a chemical method for cladding removal using a mixture of sodium nitrate ($NaNO_3$) and sodium hydroxide (NaOH). Experiments provided better insights into dissolution of the Mark-18A aluminum cladding. In particular, these studies measured the effects of temperature on dissolution rate, flammable gas generation, and nitrite formation.

Using the lessons learned from batch dissolution testing at SRNL, a continuous dissolution flowsheet was successfully demonstrated using prototypic-shaped materials and chemically-conservative materials. The SRNL target dissolution flowsheet departs from the baseline ORNL flowsheet in small but significant ways as discussed in the following paragraphs. These flowsheet changes facilitate faster initial reaction rates at a given temperature, enable cladding removal at a lower process temperature, and yield a more-uniform dissolution rate throughout cladding removal.

Multiple tests indicate that the total time at the dissolution temperatures will be about six hours for one-fourth of a target. The shorter dissolution time provides the benefit of a single-shift dissolver operation. Off gas sampling determined that the quantities of flammable hydrogen (H_2) and ammonia (NH_3) expected in the process off gas will meet allowable flammable gas generation rates for the Shielded Cells Facility. The SRNL approach enables NaOH to be added at a constant rate, which simplifies operations in the shielded cells. In all six continuous dissolution tests, the process was easy to control with minimal operator interface.

Analyses of process solutions throughout the experiments provide a better understanding of system behavior. The data show consistent behavior across several similar but different test conditions. Between the batch-test and continuous-test data, if future changes to the flowsheet are required, sufficient data exist to adequately predict how the system will respond to those changes.

Future work will focus on design, fabrication, and evaluation of a system for dissolution of one-fourth of a Mark-18A target, which will be full-scale operations for SRNL. Based on these results, the process parameters are adequately understood and the system can be operated safely.

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LIST OF ABBREVIATIONS

DOE	U.S. Department of Energy
IC	ion chromatography
ICPES	inductively coupled plasma emission spectroscopy
LFL	lower flammability limit
ORNL	Oak Ridge National Laboratory
R&D	research and development
rpm	revolutions per minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 Introduction

The Mark-18A Program is being established to preserve the unique materials found in Mark-18A targets for future research and development (R&D) activity within the Department of Energy (DOE) or other U.S. government agencies.[1] Some of the unique, high valued materials include but are not limited to Plutonium-244 (^{244}Pu), heavy curium ($^{246, 248}Cm$) and Californium (Cf). Savannah River Site (SRS) has sixty-five (65) Mark-18A targets available for the recovery of high valued materials.

Detailed reactor history profile was documented during the Mark-18A irradiation cycles (1969-1979), including each target's unique rotation pattern within K-Reactor.[2] The irradiation profiles of the Mark-18A produced higher distribution of actinide isotopes than any other targets produced by the U.S. Government. The majority of the work will be performed in Savannah River National Laboratory (SRNL) E-wing Shielded Cells due to dose concerns. The sixty-five Mark-18A targets are currently stored in the L-Area Basin and will be removed one at a time and individually transported to SRNL for research tasks.

Mark-18A targets are currently stored in a double-can confinement (referred to as a "J-can"). The Mark-18A target material will be removed from the confinement, dissolved, chemically separated, and calcined to a stable oxide. The baseline flowsheet is patterned after the flowsheet Oak Ridge National Laboratory (ORNL) previously used to process both Mark-18A and Mark-42 targets.[3] However, it is necessary for SRNL to adapt the ORNL flowsheet and identify process improvements to more efficiently recover the actinide materials in the SRNL Shielded Cells. The resulting high value actinide oxide and a significant amount of the fission products will be packaged and shipped to ORNL.

This project will utilize R&D to evaluate different processing options for high burn-up material and elemental/isotopic profiles resulting from each target's unique irradiation history. Various methods of dissolution and elemental separations will be investigated with a continuous focus on process intensification and waste minimization. Analytical results collected during the SRNL R&D processes will also be used in validating and updating fundamental nuclear physics data for higher actinides to increase accuracy in reactor modeling.

These studies used continuous experiments to assess the impact of several parameters on the dissolution chemistry and process control for cladding removal using a mixture of sodium nitrate ($NaNO_3$) and sodium hydroxide (NaOH).[4] Previous batch studies were used to establish the operating parameters for these continuous experiments that will simulate cladding removal.[5] These results will provide input for safety basis calculations. An overview of this task is provided in a scope of work.[4]

2.0 Background

2.1 Process Chemistry

The first step in the chemical processing of Mark-18A target material will be the dissolution of the aluminum cladding using $NaNO_3$-NaOH mixtures. The method is well established for processing of aluminum cladding from irradiated nuclear fuel.[6][7][8] In the absence of $NaNO_3$, the dissolution of Al by NaOH generates only hydrogen gas (H_2) (Reaction 1).[7]

$$2\ Al + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_2 \quad (1)$$

When sufficient $NaNO_3$ is present with NaOH, the formation of H_2 is suppressed in favor of the formation of ammonia (NH_3) (Reaction 2).[7] Although NH_3 is also flammable, its lower flammability limit (LFL) is 15.0 vol %, which is higher than the LFL for H_2 (4.0 vol %),[9] thus allowing for faster dissolution rates while maintaining less than 25% of the LFL.

$$8\ Al + 5\ NaOH + 3\ NaNO_3 + 2\ H_2O \rightarrow 8\ NaAlO_2 + 3\ NH_3 \quad (2)$$

When a significant excess of $NaNO_3$ is present, sodium nitrite ($NaNO_2$) is also formed along with NH_3 (Reaction 3).[7]

$$2\ Al + 2\ NaOH + 3\ NaNO_3 \rightarrow 2\ NaAlO_2 + 3\ NaNO_2 + H_2O \quad (3)$$

It is has been proposed that the overall reaction in $NaNO_3$-NaOH is a combination of the three reactions which yields the empirical reaction shown in Reaction 4.[8] Reaction 4 was developed from Mark-42 target dissolution at ORNL.

$$Al + 0.63\ NaOH + 0.28\ NaNO_3 + 0.26\ H_2O \rightarrow NaAlO_2 + 0.01\ NaNO_2 + 0.37\ NH_3 + 0.02\ H_2 \quad (4)$$

Other empirical reactions have been proposed,[7] but the SRNL batch Al dissolution studies show that Reaction 4 more closely reflects the SRNL results.[5] Silicon metal, a minor component in the aluminum alloy dissolves in a solution of NaOH to yield H_2, according to Reaction 5.[10] The dissolution of silicon is the combination of (at least) two reactions. First there is the dissolution of Si by water (Reaction 6) which forms a protective silica (SiO_2) layer followed by dissolution of silica by NaOH to form sodium silicate (Na_2SiO_3), as indicated in Reaction 7.

$$Si + 2\ NaOH + H_2O \rightarrow Na_2SiO_3 + 2\ H_2 \quad (5)$$

$$Si + 2\ H_2O \rightarrow SiO_2 + 2\ H_2 \quad (6)$$

$$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O \quad (7)$$

The flowsheet used by ORNL for cladding removal from an entire Mark-18A target[3] begins with 85 L of 2.1 M $NaNO_3$ in the dissolver, to which is gradually added 10 M NaOH. The expected quantity of 10 M NaOH to be added for a full target is 36.5 L for ~4.1 kg of Al. SRNL will process one-fourth of a target at a time.

2.2 Quality Assurance

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

3.0 Experimental Procedure

3.1 Process Equipment

Aluminum alloy 6063 disk coupons, sections of alloy 6063 pipe, and alloy 4043 rods were dissolved in sodium nitrate-sodium hydroxide solutions to measure off-gas generation and aluminum dissolution rates with respect to varying solution concentrations and temperature. Alloy 6063 (0.2-0.6 wt % Si) is the principal material of construction of the Mark-18A targets. However, calculations indicate that activation products from irradiation have elevated the Si content in the Alloy 6063 to ~3.5 wt %. Alloy 4043 (4.5-6.0 wt % Si) provides a conservative simulant for the post-irradiation Alloy 6063. The dimensions of the aluminum materials for testing are contained in Table 3-1. The pipe was machined to closely reflect the dimensions of a Mark-18A target. Pictures of the samples and the holder for the disk samples are provided in Figure 3-1.

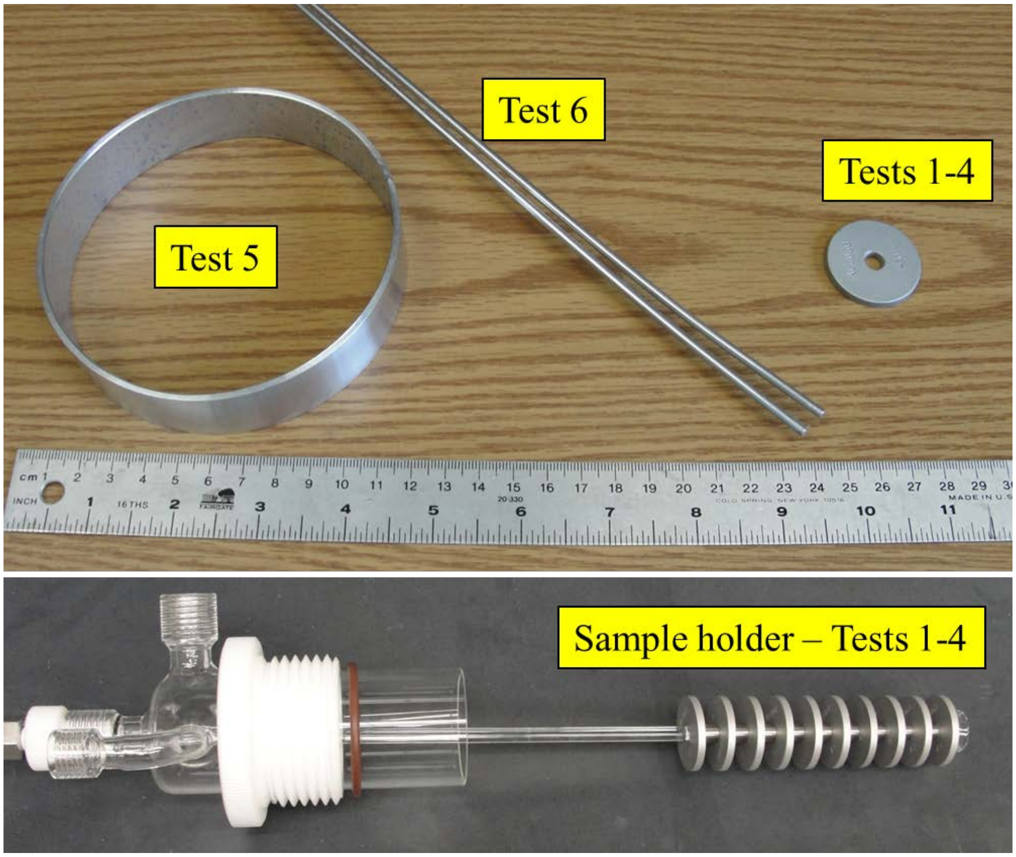
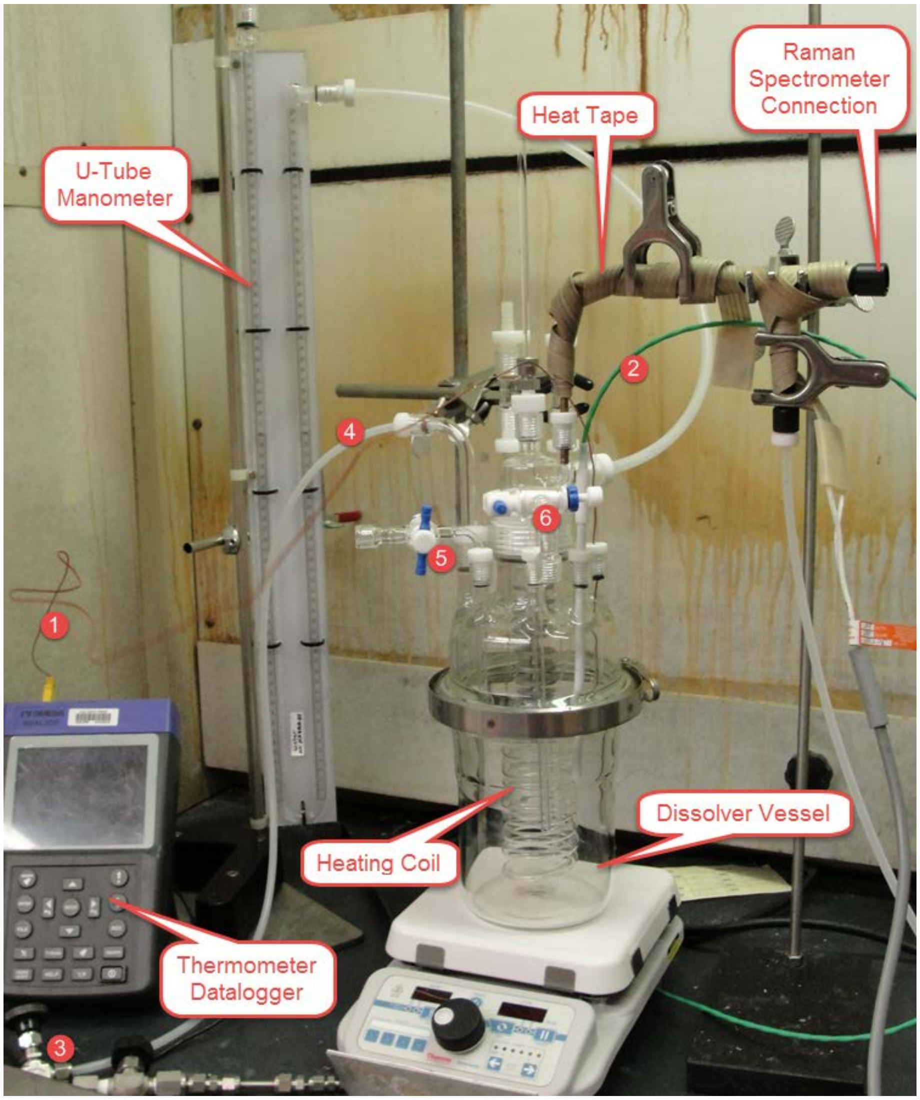


Figure 3-1. Test Samples and Holder for Disk Samples

The primary components of the dissolution apparatus are the dissolver vessel, the Gas Raman-Noch spectrometer, and the water-submerged gas collection Tedlar® bag system. Figure 3-2 and Figure 3-3 show the apparatus setup located in the chemical hood. The dissolver vessel was fabricated in the SRNL Glass Shop from borosilicate glass and was sized to accommodate the alloy 6063 coupons both while in the headspace and in solution (Table 3-1). The section of alloy 6063 pipe and the alloy 4043 rods were placed in solution at the beginning of their respective tests. The sealed glass vessel had multiple access ports through the lid to allow for a headspace gas purge stream, two thermocouples, liquid sample removal, and the sample holder. The sample holder is a 50-mm glass insert in the vessel headspace that houses the aluminum coupons as they are suspended above the solution; it also contains outlets to the u-tube manometer and the Gas Raman-Noch spectrometer probe. Each port through the lid of the dissolver vessel is sealed by a compressed Viton™ o-ring fitting.

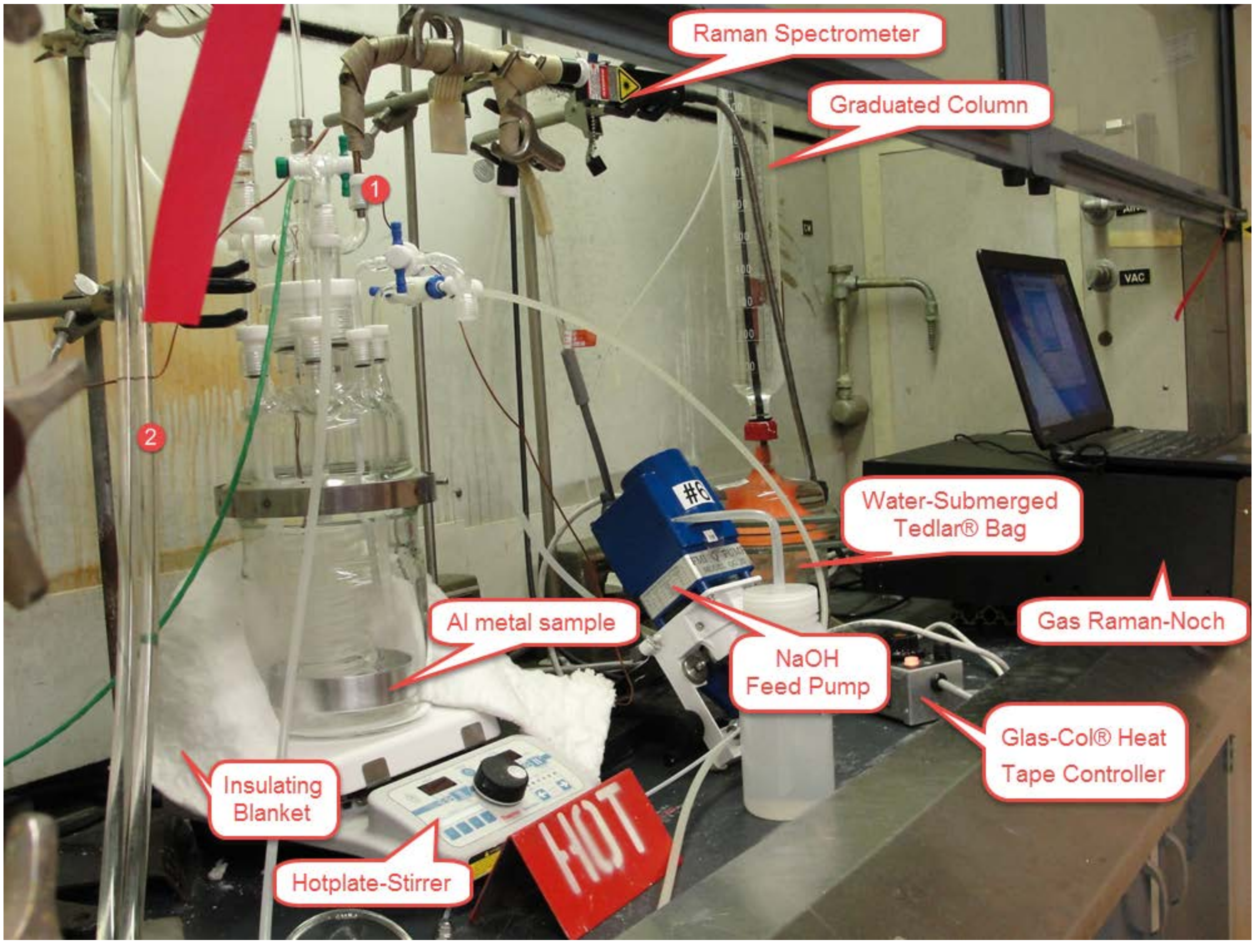


1) thermocouples to the datalogger
2) thermocouple to the hotplate
3) nitrogen gas purge valve
4) nitrogen gas purge line
5) NaOH inlet valve
6) sample collection valve

Figure 3-2. Dissolver Apparatus Setup – View 1

With 1000 mL of dissolver solution in the vessel, there was approximately 1598 mL of headspace volume to the Raman probe. For Test 5, a larger vessel was used such that with 1200 mL of dissolver solution in the vessel; there was approximately 1650 mL of headspace volume. There was an additional 30 mL of tubing volume between the Raman probe and the entrance to the gas collection bag.

The solution mixture was heated to the desired test temperature and stirred using a Thermo Scientific Super-Nuova hot plate-stirrer. The stir bar rotation was set to 250 revolutions per minute (rpm). There are three thermocouples that measure the temperature of the solution, two of which were ported through the lid of the dissolver vessel and sealed by compressed O-ring fittings. The hot plate-stirrer used the third thermocouple to control the heat of the hot plate. The two thermocouples ported through the lid were connected to an Omega Engineering RDXL 8CD Multi-Input Thermometer Datalogger that continuously measured and recorded the temperature of the solution every second.



1) gas outlet to the Raman spectrometer 2) water lines to and from heating/cooling coil

Figure 3-3. Dissolver Apparatus Setup – View 2

A stream of argon gas was continuously fed to the Raman spectrometer probe to purge the sensor of air and water vapor. The Ar gas does not become part of the stream going to the gas collection bag. The Raman probe was wrapped with 100 W, 115 V heat tape which was controlled by a 1500 W Glas-Col® heater. The heat tape prevents condensate from forming on the Raman probe window. It maintains the off gas line at 105-120 °C.

The Raman spectrometer probe measured the off-gas concentrations in the headspace (assuming perfect mixing) every minute. Raman spectra of the off-gas stream were obtained with the following components. The spectrometer is a ChemLogix GasRaman NOCH-532 (TSI, Inc., Irvine, CA) with a Charge Coupled Device detector thermoelectrically cooled to -60 °C. The spectrometer has a range of 0-4200 cm^{-1} with 8 cm^{-1} resolution. The sample is excited with a 532 nm, 50 mW DPSS laser and a fiber optic imaging probe with a 10 mm focal length coupled into a quartz gas flow cell. The cell is located downstream of a condenser but the stream is not otherwise filtered before monitoring. Spectra were obtained every 60 seconds; the spectra were automatically loaded into a Microsoft Excel spreadsheet. Peak heights are calibrated by instrumental response to calibration gases (of air, 100% CO_2, 5% NH_3 in Ar, and a series of mass spectrometry standards containing NO_2, NO, N_2O, H_2, and CO).

Table 3-1. Aluminum Test Samples

Test #	Dimensions	Mass (g)	Surface Area (cm^2)	Alloy
1-4	Disk, 31.87 mm dia, 3.22 mm thick, 6.25 mm hole, quantity = 7 (each disk weighed 6.646±0.019 g)	46.493 ±0.012	129.7	6063
5	Pipe segment, 113 mm OD, 2.32 mm thick, 25.4 mm long	56.86	192.8	6063
6	Rod, 3.21 mm dia, 910 mm long, cut to 101 mm lengths, quantity = 2	38.38	183.1	4043

A single calibration for the instrument is required to characterize the Raman cell parameters. Corrections are made for pressure and laser power fluctuations by normalizing the data. Based on subject matter experience, the estimated analytical uncertainty for the Raman spectrometer data is 20%; this is based on variability relative to calibration gases (±10%) and typical normalization (±10%). The results from the Raman spectrometer are reported in volume percent. Because Raman spectroscopy measures the total number of molecules, the magnitude of readings varies with system pressure and other transient effects. Consequently, the data must be normalized for data consistency within and between experiments.

3.2 Digestion Testing Methodology

Dissolution test conditions were selected based on results from previous batch dissolution tests.[5] It is recognized that the solution concentrations also change significantly due to dissolution of the Al metal sample, but sampling should help characterize those changes. Table 3-2 lists the test conditions. Table 3-3 compares the impurities in Alloys 4043 and 6063.

Table 3-2. Aluminum Dissolution Test Matrix

Test #	Temp (°C)*	Alloy	Sample Shape	$NaNO_3$-NaOH (mL)#	NaOH Feed (mL/min)	Total NaOH Feed (mL)	Dissolution Time (min)
1	80	6063	7 disks	1000	0.8	240	420
2	85	6063	7 disks	1000	0.9	240	305
3	80, 85, 90§	6063	7 disks	1000	0.8	240	330
4	91	6063	7 disks	1000	1.0	368	360
5	80, 85, 90†	6063	Pipe	1200	1.2	300	315
6	80, 85, 90†	4043	Rods	1000	1.0	200	285

Test 4 initial solution is 2.1 M $NaNO_3$; Tests 1 to 3, 5, and 6 initial solutions are 2.1 M $NaNO_3$- 0.425 M NaOH
* Temperatures typically held within ± 1 °C of set point
§ 90 min at 80 °C, 75 min at 85 °, and remainder at 90 °C
† 105 min at 80 °C, 60 min at 85 °, and remainder at 90 °C

Table 3-3. Comparison of Aluminum Alloys Impurities (wt %)

Alloy	Si	Fe	Cu	Mg	Mn	Cr	Zn	Ti
4043	4.5 to 6.0	0.8	0.3	0.05	0.05	---	0.1	0.2
6063	0.2 to 0.6	0.35	0.1	0.45 to 0.9	0.1	0.1	0.1	0.1
Data from Reference 10								

Based on the experimental conditions, calculated weights of sodium nitrate and sodium hydroxide solids were measured and added to deionized water to form an aqueous solution. The initial concentration of solution in the dissolver was 2.1 M $NaNO_3$-0.425 M NaOH (except for Test 4 which used 2.1 M $NaNO_3$).

The $NaNO_3$–NaOH solution mixture (1000 mL for Tests 1 to 4 and 6; 1200 mL for Test 5) was added to the dissolver vessel. To that was added 10 M NaOH at a predetermined rate. Before testing began, N_2 gas was fed into the headspace to purge the vessel headspace of air and fill the Tedlar® bag to the set point on the graduated column. Raman data were collected during this purge step to confirm that oxygen has been removed to less than 1 vol % of gas to limit oxidant due to flammability gas generation concerns.

Pre-test measurements of the temperature, gas volume, and manometer displacement were recorded. As appropriate for Tests 1 to 4, the coupons were lowered into the caustic solution once the temperature of the solution reached 4 to 5 °C below the desired test temperature. The stopwatch was started to record time, and the thermometer data logger was started to record the solution temperature. As the coupon began to dissolve in solution, off-gas was generated and filled the headspace.

The off-gas passed by the Raman spectrometer probe to a 3 way valve. The valve directs the gas to the water-submerged gas collection Tedlar® bag, and can also be turned to vent the off-gas to the atmosphere. As the off-gas filled and expanded the Tedlar® bag, the water rose in the graduated column, where measurements were obtained to calculate off-gas generation. Venting was required several times during each experiment because the u-tube reached its limiting condition without venting the headspace. The u-tube manometer filled with water was used as a pressure correction measurement, and also functioned as a pressure relief device for the system. Solution temperature, off-gas volume, off-gas concentration, and manometer displacement data were collected throughout the test.

Approximately every 30 to 45 minutes, a sample of the liquid from the dissolution vessel was collected. Due to the gas pressure in the system, samples were collected by opening a process tube whose bottom was immersed in the dissolver solution. After sufficient volume was collected for analyses, N_2 gas was injected into the process tube to clear the line of residual solution. The volume change of gas in the graduated cylinder was recorded to determine the volume of gas injected as part of the sampling in order to subtract that volume from the total gas volume collected. The liquid samples were prepared for ion chromatography (IC) anion, IC cation, inductively coupled plasma emission spectroscopy (ICPES), total base, free OH^-, and other base analyses by Analytical Development.

The off-gas generation rates and concentrations of hydrogen and ammonia were correlated with the measured change in solution concentration to examine, analyze, and better quantify the reaction of aluminum in caustic nitrate solution as a function of temperature, $NaNO_3$ concentration, NaOH concentration, and Al concentration.

The step-by-step methodology was as follows.

1) Weigh aluminum sample and record weight.
2) Load sample into the dissolution vessel, using the sample holder as appropriate.
3) Place dissolver vessel on hot plate-stirrer.
4) Connect and seal gas inlets and outlets, thermocouple connections, and the manometer connection.
5) Place the initial $NaNO_3$-NaOH solution into dissolver vessel
6) Inject N_2 gas into the system to verify system is sealed and to inflate gas sample bag to displace water into graduated cylinder to approximately 400-mL level. Stop feeding liquid and verify that system maintains gas height for about 10 minutes.
7) Begin argon purge to Raman probe head and initiate Raman sampling
8) Purge reaction vessel and headspace until Raman detects <1 vol % O_2 in the system. Vent gas from collection cylinder, as needed. Discontinue vessel purge.
9) Turn on stirrer at 250 rpm
10) Turn on heating tape to Raman probe at set point of 7.5-8.0 to maintain the Raman probe head at ~105-120 °C.

11) Set hot plate to control at test set point and begin heating the vessel. Initial heating should be toward a set point 2 to 3 °C **below** the set point.
12) Set water bath to control at set point, approximately 5 °C below the hot plate set point temperature.
13) When solution temperature is 4 to 5 °C **below** the test temperature, record the initial gas volume reading and manometer readings.
14) Begin recording temperatures using data logger.
15) Loosen the bushing that holds sample in place and lower the sample into solution. Tighten the bushing. Record this as the starting time. Record the computer start time on the provided data sheet.
16) Record time, temperature, and gas data every 1 to 10 minutes (based on gas generation rates) using the data sheet.
17) Approximately every 30 minutes, collect a 5-mL liquid sample through the metering stopcocks installed for sampling.
18) Back-purge the stopcock and sample line with N_2, recording the gas cylinder height change that occurs as a result of the purge operation. Verify that the stopcock is closed after purging.
19) If the sample bag fills enough to push liquid in the graduated cylinder to the top, release some of the gas using the 3-way valve. Record the volume (or height) of gas that is released and the time required to release it.
20) When sample dissolution is complete, turn off temperature reader data collection.
21) Discontinue heating of the dissolver solution and discontinue collection of Raman data.
22) Discontinue purge to Raman probe and turn off heating tape.
23) Exhaust the remaining contents in the gas bag to the chemical hood. Evacuate the bag using the hood vacuum service.
24) Refill the system with nitrogen gas to purge the dissolver headspace of H_2 and NH_3; vent the gases to the chemical hood.
25) Disconnect the inlets and outlets from the dissolution vessel and pour the dissolution vessel contents into a 2-liter graduated cylinder.
26) Measure the final volume of the dissolver solution.
27) Filter the dissolver solution.
28) Prepare samples of the dissolver solution for analysis by IC anion, IC cation, ICPES, and total OH^-/free OH^-/other base.

3.3 Sample Collection

The off-gas concentration was measured with the Raman spectrometer during testing as described previously. The following four types of solution analyses were conducted at the conclusion of each test.

- Ion chromatography cations for ammonium ion concentration
- Ion chromatography anions for nitrate and nitrite ion concentrations
- Total base, free base, and other base for hydroxide concentrations
- ICPES for dissolved metal concentrations, particularly Al, Si, Fe, and Mg.

For ion chromatography analyses, the Dionex RFIC-3000 Ion Chromatography system consisted of an AS-40 autosampler, a gradient pump, and a suppressed conductivity detector. Software control of the system and data acquisition was through Dionex Chromeleon v.6.8. The one sigma uncertainty of each method was ± 10%.

For ICPES, a Perkins-Elmer Optima 3000 provided multiple element analysis. A Schmidt Cross Dispenser was used in the ultraviolet range (165-375 nm) and a prism was used in the visible range (375-782 nm). Two Segmented-Array Charge-Coupled-Device Detectors were used. With the purged optics, detection of spectral wavelengths is extended from approximately 190 nm to 165 nm. The minimum reported uncertainty is assumed as 10%. Uncertainties were reported as the root mean square of the individual components when greater than 10%.

Liquid samples were analyzed for total base and free hydroxide using a Radiometer Analytical TIM870 Titration manager with auto sampler. An aliquot of sample was added to approximately 25 mL of deionized water. The total base concentration was measured using a direct inflection point titration to the inflection point closest to pH 7. Free hydroxide was determined by first removing the carbonate from the sample using a barium chloride precipitation step. The remaining supernate was titrated using a direct inflection point titration to the first inflection point between pH 9 and 10. The titrant used was standardized 0.100 N HCl (Fisher). The pH was monitored using a combination double junction glass pH electrode (Hach). Precision of duplicate analyses were nominally within +/- 10% RSD.

The liquid samples were collected in the sample bottle sent for ICPES. Essentially all samples collected from the dissolution vessel contained undissolved solids. Aliquots for other analyses were decanted the following day (to allow for solids settling) from the top of the ICPES sample. The ICPES analyst filtered the samples prior to analysis.

The solid residues from the previous batch experiments were characterized as primarily aluminum compounds which contained impurities from the Alloy 6063 material, such as Fe, Mg, and Si.[11] The solutions and residues from these tests were provided to the filtration development task.[12] The characterization of the solids and their impact on filtration will be reported as a component of that study.

4.0 Results and Discussion

All of the experiments witnessed the complete decomposition of the samples. There remained undissolved solids, but all solids were present as fine particles (discussed in Section 4.4.3). No fraction of the initial samples retained their physical integrity.

To align with the process objective, the preferred approach for data analysis would be to address Al dissolution first and then discuss the consumption of other reactants followed by the formation of products. Because the data quality of the products (e.g., NO_2^-, H_2, and NH_3) is more precise for these tests and because aluminum precipitated throughout dissolution, the order of analysis is reversed. The formation of reaction products and the consumption of reactants will be discussed individually prior to discussing them collectively in Section 4.4, “Reaction Chemistry”.

4.1 Reaction Product Measurements

As indicated in Reactions 1 to 3, there are four principal reaction products expected, three of which can be readily measured analytically – H_2 gas, NH_3 gas, and nitrite ion (NO_2^-). Hydrogen is measured solely in the gas phase, nitrite is detected solely in the aqueous phase, and NH_3 is present in both phases. The detection of each reaction product will be discussed separately before all three are discussed collectively in Section 4.4. It should be noted that none of the tests showed detectable concentrations (~0.5 vol %) of nitric oxide (NO) or nitrogen dioxide (NO_2) gases. The presence of nitrous oxide (N_2O) was readily discernible in one of the experiments and will be discussed in Section 4.1.4.

4.1.1 Ammonia Gas

Ammonia is formed during the dissolution of aluminum metal according to Reaction 2. Total gas flow rates were measured every 1 to 5 minutes depending on the overall gas flow rate. Raman spectroscopy measured the gas concentration every 60 seconds to correlate with the gas flow readings. The results from the Raman spectrometer are reported in volume percent. The gas concentrations used for calculations and graphs are five-minute averages.

Ammonia gas flow rates at each minute of the test are calculated by multiplying the average NH_3 concentration for that period by the measured gas flow rate over that duration. The calculations assume perfect mixing of the gas being generated into the headspace volume (of 1598 mL for Tests 1 to 5 and 1650 mL for Test 6). If a calculation of NH_3 flow rate exceeds that of the total gas flow rate due to limited precision and random variation of the Raman data, the total measured flow rate is assumed to be NH_3. Similarly, if a calculation of NH_3 returns a negative value, the negative value is assumed to be zero. These adjustments to the calculated values are infrequent except during the early stages of an experiment when most of the NH_3 is absorbed by the dissolver solution or the latter stages of the test when Al dissolution is complete. Adjustments are the result of fluctuations in the Raman readings which are still within the uncertainty of the instrument. The Test 5 data is contained in Table 8-3 as an example.

The NH_3 generation rate remains relatively constant (i.e., 0.1 to 2.0 mL/min over time period of 0 to 20 min) as the NaOH concentration and Al sample surface area decrease. The NH_3 concentration increases slowly and approaches steady state (i.e., near 27 vol % at 250 to 260 min) as H_2 and NH_3 displace N_2 in the vessel head space. When the concentrations reported in Appendix 8.4.1 and the volumes reported in Appendix 8.4.2 are converted to molar quantities, most (85 to 95%) of the NH_3 generated (Table 4-1) was absorbed into solution and measured as soluble NH_4^+.

A graph of the gas concentrations for Test 3 is provided in Figure 4-1. Nitrous oxide, O_2, and H_2O are plotted as five-minute averages to dampen the noise in the data which would inhibit the ability to see the other lines on the graph. The behavior of the six gases is typical for all of the experiments. Nitrogen begins near 100% and is displaced throughout the test as other gases are generated. Oxygen begins low and is also displaced during the test. Hydrogen and ammonia increase throughout the test with H_2 release being greater due to the absorption of most of the NH_3 (as NH_4^+) by the dissolver solution; NH_3 release accelerates later in the test due to reduced absorption in the dissolver solution. Water vapor is relatively constant during testing. Nitrous oxide shows a slight increase throughout the test, except for Test 6 in which there was a significant increase (as will be discussed in Section 4.1.4). The graphs for the four principle gases (N_2, H_2, NH_3, and N_2O) for all six tests are contained in Appendix 8.2.

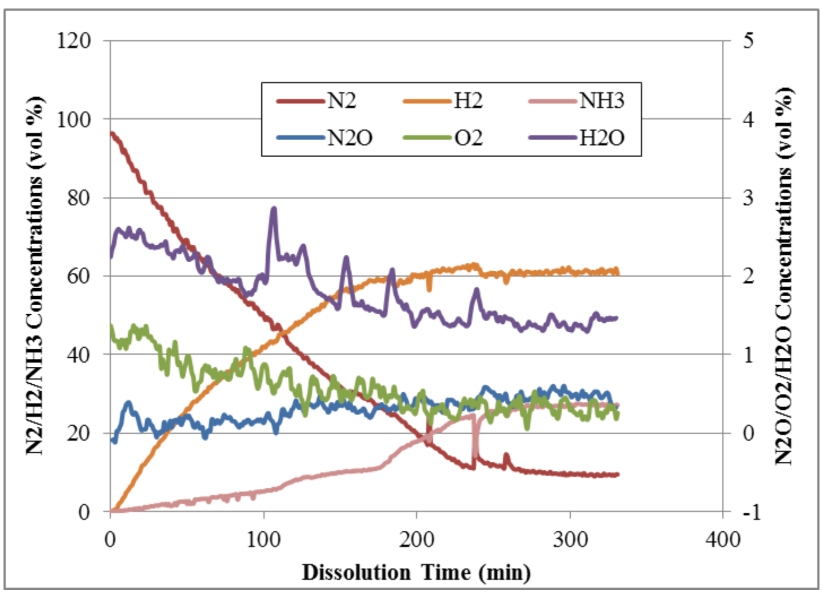


Figure 4-1. Gas Concentration Data for Test 3 (Alloy 6063 at 80, 85, 90 °C)

Two graphs comparing the NH_3 concentrations as a function of time for the six tests are shown in Figure 4-2. The NH_3 concentration increases slowly due to the absorption of NH_3 by NaOH in the dissolver solution to yield soluble NH_4^+; the NH_3 concentration approaches steady state as H_2 and NH_3 displace N_2 in the headspace. The effect of temperature on NH_3 (Tests 1, 2, and 4) is obvious as the lower temperatures allow for more absorption of NH_3 thereby resulting in less NH_3 in the off gas. Conversely, a comparison of Test 3, 5, and 6, which were all conducted using similar temperature profiles, show little difference despite the differences in materials (Alloy 4043 versus 6063) and material shapes (disks, rods, and pipe).

As will be discussed in Section 4.3, NH_3 and NH_4^+ generation are associated solely with the dissolution of Al (i.e., Reaction 4); H_2 generation is related to both Al (i.e., Reaction 4) and Si (i.e., Reaction 5) dissolution. Even after Al has dissolved, NH_3 is still observed in the off-gas stream because of soluble NH_4^+ being released from solution as NH_3. This can be observed in Table 4-1. Using the volume of NH_3 measured in the off gas (Appendix 8.4.2) at a particular sample time plus the NH_4^+ concentrations measured in solution (Appendix 8.4.1) multiplied by the solution volume (Appendix 8.4.12), the moles of NH_3 generated at each sample time can be calculated. The shaded cells in Table 4-1 identify where total NH_3 generation ceased but NH_3 was still observed in the off gas (Appendix 8.4.1) as the soluble NH_4^+ concentration decreased (Appendix 8.4.2). As will be discussed in Section 4.2.1, nitrate ion concentrations reach a constant value (cease decreasing) when Al dissolution slows or ceases and when NH_3 concentrations reach a constant value (cease increasing). This trend is expected from Reaction 2.

The data in Table 4-1 show that Tests 1 to 4, which dissolved the same mass of the same Al alloy (6063), yielded the same total amount of NH_3 (within ~4%: 0.490 versus 0.470 mol). Test 5, which used the same alloy, dissolved 22% more total Al (see Table 3-1: 56.86 g versus 46.49 g) and generated 24% more NH_3 (compared to the averages of Tests 1 to 4). Only Test 6, which used Alloy 4043, exhibited a difference. Compared to Tests 1 to 4, Test 6 dissolved 18% less Al (i.e., 38.38 g) and generated 39% less NH_3. The mechanism for this reduced quantity of NH_3 is not immediately clear, but it is likely related to the formation of a greater fraction of nitrite ion (Section 4.1.3) instead of ammonia gas.

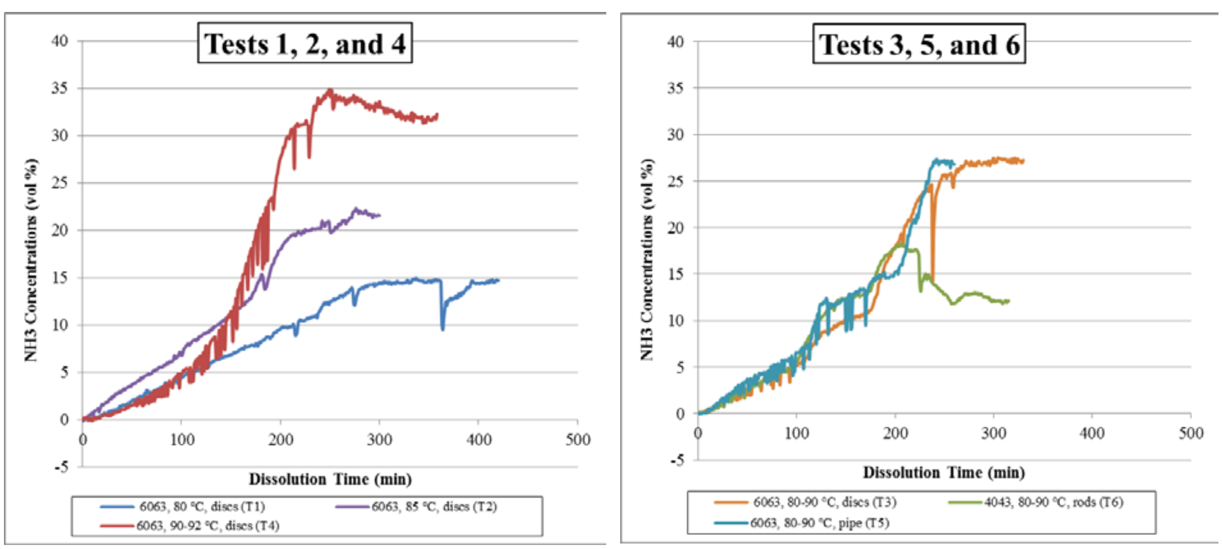


Figure 4-2. Ammonia Gas Generation Data for Tests 1 to 6

Table 4-1. Calculated Total Ammonia Quantities

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Net NH_3 (mol)	Time (min)	Net NH_3 (mol)	Time (min)	Net NH_3 (mol)	Time (min)	Net NH_3 (mol)	Time (min)	Net NH_3 (mol)	Time (min)	Net NH_3 (mol)
36	0.080	30	0.098	30	0.065	30	0.028	30	0.141	20	0.051
60	0.129	60	0.156	60	0.165	60	0.068	60	0.241	45	0.130
90	0.179	90	0.220	94	0.227	94	0.130	90	0.318	75	0.198
120	0.222	120	0.300	122	0.302	122	0.222	120	0.400	98	0.244
150	0.260	150	0.357	150	0.353	148	0.285	150	0.485	135	0.295
186	0.327	180	0.417	180	0.390	180	0.357	184	0.535	165	0.293
240	0.400	210	0.475	210	0.435	210	0.438	210	0.564	195	0.300
270	0.443	240	0.466	240	0.462	240	0.454	240	0.589	225	0.288
300	0.464	275	0.478	270	0.487	270	0.466*	270	0.606	270	0.291
330	0.478	305	0.476	300	0.485	300	0.474	285	0.591	315	0.290
360	0.468	---	---	330	0.490	330	0.470	---	---	---	---
390	0.444	---	---	---	---	360	0.478	---	---	---	---
420	0.470	---	---	---	---	---	---	---	---	---	---
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution * See Appendix 8.4.1 for a discussion of this data point											

4.1.2 Hydrogen Gas

Hydrogen gas is formed during the dissolution of aluminum metal according to Reaction 1 and by dissolution of silicon metal according to Reaction 5. Total gas flow rates were measured every 1 to 5 minutes depending on the overall gas flow rate. Raman spectroscopy measured the gas concentration every 60 seconds to correlate with the gas flow readings. The results from the Raman spectrometer are reported in volume percent. The gas concentrations used for calculations and graphs are five-minute averages.

Similar to that of NH_3, H_2 gas flow rates at each minute of the test are calculated by multiplying the average H_2 concentration during that period by the measured gas flow rate over that duration. The calculations assume perfect mixing of the gas being generated into the headspace volume (1598 mL for Tests 1 to 4 and 6; 1650 mL for Test 5). If a calculation of H_2 flow rate exceeds that of the total gas flow rate, the total measured flow rate is assumed to be H_2. If a calculation of H_2 returns a negative value, the negative value is replaced with a zero. These adjustments to the calculated values are infrequent for H_2 because it reaches relatively high concentrations compared to NH_3; adjustments are more common for NH_3, particularly when the NH_3 concentration is below 1.0 vol %. Adjustments are the result of fluctuations in the Raman readings which are still within the uncertainty of the instrument. An example from some of the Test 5 data is contained in Table 8-3.

The H_2 concentration increases rapidly and approaches steady state as H_2 and NH_3 displace N_2 in the headspace. A plot comparing the H_2 concentrations as a function of time for the six tests is shown in Figure 4-3. The data for Tests 1 to 5 with Alloy 6063 are similar with variations being a function of the heating profile. Tests 1, 2, and 4 exhibit the impact of temperature on H_2 generation rate, but the overall quantities of H_2 generation are comparable. Tests 3 and 5 are similar in response, which is to be expected since they were completed using comparable temperature profiles and sample mass-to-volume ratios.

It should be noted that an apparent "decrease" in H_2 concentration for Test 4 at about 150 min results from an increased displacement by NH_3 (Appendix 8.4.2) while the H_2 generation rate (Appendix 8.4.3) is relatively stable. Test 6 with Alloy 4043 exhibited a different behavior, possibly due to the dissolution of the higher concentration of Si in the alloy (see Reaction 5).

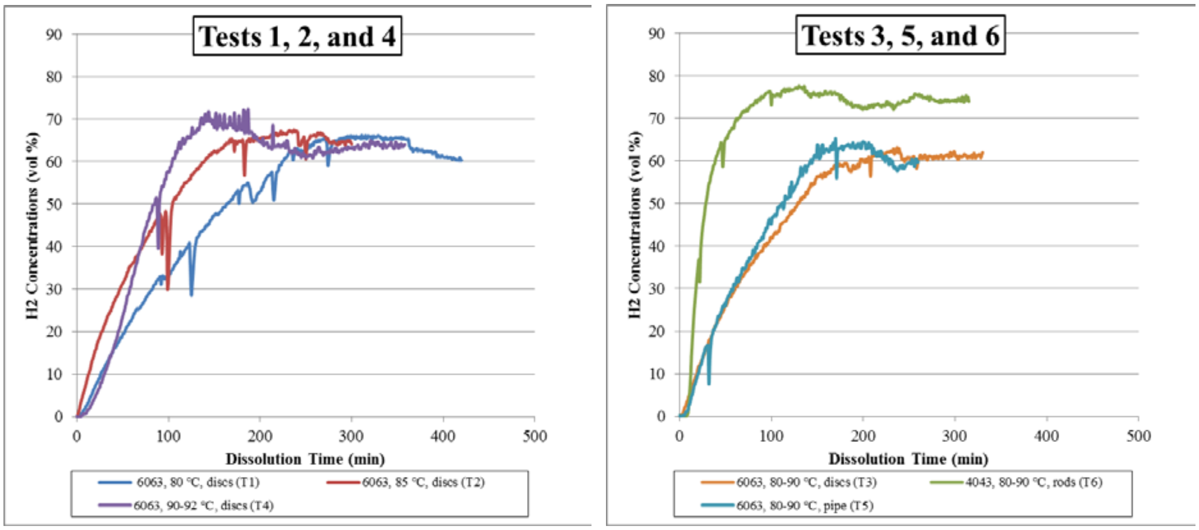


Figure 4-3. Hydrogen Gas Generation Data for Tests 1 to 6

The calculated H_2 gas generation rates are also included as graphs in Appendix 8.2 for all six experiments. In all experiments, the H_2 generation rate at a given test temperature increases for a time and then decreases as the Al dissolution rate diminishes. Even after Al dissolution is complete, H_2 generation continues due to the slower dissolution of Si. As can be seen from Appendices 8.4.3 and 8.4.10, H_2 generation continues as does Si dissolution, but Al dissolution (Table 4-11) has ceased. This behavior is particularly evident for Test 6, which dissolved the high-Si alloy 4043. For Tests 3 and 5, the effect of temperature increases can be observed in the H_2 generation rate data as localized increases in the H_2 generation rate.

The calculated flow rate of H_2 for each minute was summed to obtain a total H_2 value for a particular experiment (Table 4-2). Furthermore, the volume of H_2 collected between liquid samples (for analysis) can also be calculated. The data from Appendix 8.4.3 were converted to millimolar quantities using the ideal gas law. The quantities of H_2 generated for Tests 1 to 3 and 5 are comparable. Those four experiments were performed in a similar manner with the exception of dissolution temperature. It is surprising, however, that Test 5 dissolved 22% more Al and yet yielded the same quantity of H_2. The reason for this is unknown.

Test 4 shows an increase the quantity of H_2 released, presumably due to the NaOH addition method – starting with no NaOH in the dissolver solution and adding throughout the test. Test 6 shows a greatly increased release of H_2 due to the dissolution of an increased concentration of Si associated with Alloy 4043 (4.5-6.0% for Alloy 4043 compared to 0.2-0.6% for Alloy 6063).[11] Section 4.4.1 compares the relative contributions of Al and Si in H_2 generation. The data from Table 4-2 are displayed in Figure 4-4 on a mL/min basis. Test 6 is not included because the sample geometry yields a significantly different gas generation behavior due to the rapid decrease in sample surface area; the sample surface area is relatively constant for Tests 1 to 5. The shaded cells in Table 4-2 correspond to the cessation of both Al dissolution and NH_3 generation.

Table 4-2. Calculated Hydrogen Gas Quantities

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	H_2 (mmol)	Time (min)	H_2 (mmol)	Time (min)	H_2 (mmol)	Time (min)	H_2 (mmol)	Time (min)	H_2 (mmol)	Time (min)	H_2 (mmol)
36	10.7	30	11.7	30	10.7	30	5.6	30	12.0	20	22.8
60	7.3	60	10.0	60	8.6	60	11.3	60	10.1	45	31.3
90	7.7	90	9.7	94	8.3	94	14.2	90	10.1	75	19.1
120	6.8	120	8.6	122	10.5	122	13.8	120	14.1	98	14.0
150	7.4	150	12.3	150	9.6	148	11.6	150	13.6	135	28.4
186	10.0	180	11.7	180	9.0	180	15.9	184	8.8	165	6.3
240	19.0	210	11.4	210	13.1	210	15.2	210	6.8	195	8.2
270	10.1	240	7.0	240	11.7	240	15.6	240	8.0	225	10.4
300	4.2	275	1.0	270	4.7	270	9.4	270	3.7	270	8.1
330	2.3	305	0.22	300	2.5	300	3.7	285	0.0	315	0.54
360	0.9	---	---	330	0.50	330	0.58	---	---	---	---
390	---	---	---	---	---	360	0.17	---	---	---	---
420	---	---	---	---	---	---	---	---	---	---	---
Total = 86.4		**Total = 83.6**		**Total = 89.1**		**Total = 117.0**		**Total = 87.1**		**Total = 149.3**	
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution											

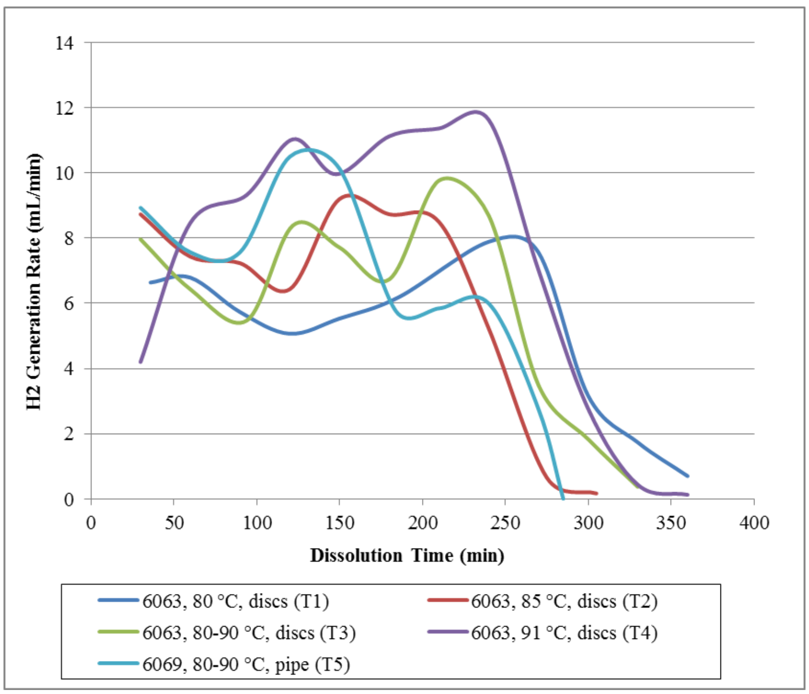


Figure 4-4. Hydrogen Generation Rates for Tests 1 to 5

The data in Figure 4-4 for Test 1 (80 °C) and Test 4 (91 °C) indicate a tendency for the H_2 generation rate to increase with time, probably due to the decreasing concentration of $NaNO_3$ in solution. Test 2 (85 °C) exhibits a spike between about 100 to 140 min which seems to correspond to a minor temperature increase (from 85 to 86 °C, see Appendix 8.5.2 for temperature profile). Experimental log sheets show no other noteworthy test variation at that time. It may be that a reaction threshold related to nitrate concentration is crossed at that time, but Tests 1 and 4 do not show similar responses at comparable nitrate concentrations. Tests 3 and 5 (80-90 °C) exhibit distinct maxima in H_2 generation due to initial dissolution at 80 °C and subsequent temperature increases to 85 and 90 °C. The above rate calculations are based on Raman spectroscopy data (20% uncertainty), headspace volume (~1 to 3% uncertainty), total gas generation rate (~5% uncertainty), and an assumption of perfect mixing. Consequently, some fluctuations of the magnitude observed in Figure 4-4 can be expected.

4.1.3 Aqueous Nitrite

The in-growth of NO_2^- into the dissolver solution occurs during the dissolution of aluminum metal according to Reaction 3. The concentration of NO_2^- was determined by IC anion. The measured solution concentrations are provided in Appendix 8.4.5 and converted to mole quantities in Table 4-3. Other than Test 6, the concentrations are statistically similar after the first few samples. This is consistent with the batch dissolution testing which showed an average formation of 0.022 to 0.038 moles of nitrite per mole of Al dissolved for solution compositions and temperatures that differed only slightly from this study.[5]

As will be discussed in Section 4.2.1, nitrate ion concentrations reach a constant value (cease decreasing, Table 4-4) when nitrite concentrations reach a constant value (cease increasing, Table 4-3). This is expected from Reaction 3. The exception to this behavior is Test 6 with Alloy 4043. For Test 6, the nitrite concentration increases steadily for the first five samples and begins to stabilize suggesting completion of Al dissolution (and NH_3 generation). The significantly higher nitrite generation rate is likely attributable to dissolution of the high-silica content in the alloy. However, the nitrite concentration declines by ~3.5% (or 0.017 mol) in the 30 minute period after the 195 minute sample. (As discussed in Section 4.1.4 nitrous oxide generation accelerates as the nitrite concentration decreases). The mechanism by which Si dissolution produces nitrite is not known.

Table 4-3. Nitrite Quantities in Solution

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Net NO_2^- (mol)	Time (min)	Net NO_2^- (mol)	Time (min)	Net NO_2^- (mol)	Time (min)	Net NO_2^- (mol)	Time (min)	Net NO_2^- (mol)	Time (min)	Net NO_2^- (mol)
36	0.015	30	0.016	30	0.012	30	0.006	30	0.022	20	0.171
60	0.020	60	0.023	60	0.023	60	0.012	60	0.033	45	0.292
90	0.025	90	0.029	94	0.029	94	0.018	90	0.041	75	0.449
120	0.028	120	0.032	122	0.032	122	0.023	120	0.050	98	0.525
150	0.030	150	0.034	150	0.035	148	0.026	150	0.064	135	0.565
186	0.031	180	0.037	180	0.035	180	0.031	184	0.074	165	0.568
240	0.033	210	0.038	210	0.039	210	0.035	210	0.076	195	0.572
270	0.034	240	0.039	240	0.040	240	0.037	240	0.081	225	0.555
300	0.034	275	0.037	270	0.040	270	0.037	270	0.082	270	0.555
330	0.034	305	0.038	300	0.040	300	0.032	285	0.084	315	0.552
360	0.033	---	---	330	0.040	330	0.034	---	---	---	---
390	0.034	---	---	---	---	360	0.034	---	---	---	---
420	0.034	---	---	---	---	---	---	---	---	---	---
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution											

4.1.4 Nitrous Oxide

During batch dissolution testing, the use of Raman spectroscopy appeared to identify another minor reaction product for some conditions but not others.[5] For some of the experiments, the Raman data exhibited a clear increasing trend in the concentration of nitrous oxide (N_2O) from zero to a range of 0.2 to 0.4 vol %. Tests 1 to 5 all showed a similar trend with the N_2O concentration gradually increasing from zero to about 0.5 vol %; Test 5 achieved a slightly higher concentration of N_2O, but the specific reason is not known. Test 6 followed a similar trend for the first 200 mins of dissolution before a large N_2O spike increased the system N_2O concentration to 4.0 vol %. The N_2O concentration continued to climb more gradually after the spike, reaching a maximum concentration of 4.5 vol %. A plot of the data for Tests 1 to 6 is provided in Figure 4-5.

The onset of the spike in Test 6 corresponds to a marked decrease (of 0.017 mol) in nitrite concentration between 195 and 225 min (Table 4-3). This correlation suggests that nitrite reached a maximum stable concentration at 195 min, decomposed between 195 and 225 min, and remained constant thereafter (within the error of the analysis) as continued nitrite production is converted to N_2O. Assuming an ideal gas, 0.017 mol of N_2O would correspond to ~380 mL of gas. After the spike, the N_2O concentration remains at ~4 vol % for the remainder of the experiment. From 225 min to the end of the test, approximately 426 mL of total gas generated, of which 4 vol % is ~17 mL. Consequently, approximately 397 mL of N_2O were generated during Test 6. Applying the same methodology to the Raman data as was used to calculate H_2 and NH_3 generation rates yields N_2O generation of 141 mL, which is of a similar order of magnitude as 397 mL. However, in the calculation, 49.2% of the calculated N_2O generation volumes are less than zero and have to be manually set to zero. In short, there is a high degree of uncertainty in the Raman N_2O data.

In Section 4.1.3, it was noted that Test 6 (with high-Si alloy) produced significantly higher concentrations of nitrite ion in solution. Consequently, the generation of N_2O may be linked to Si dissolution and precipitation. In Section 4.1.2, it was proposed that H_2 was still being generated after 195 min because of Si dissolution, but not Al dissolution (Section 4.1.1), as indicated by the discontinuation of NH_3 formation. If Si is still dissolving, as indicated by H_2 generation, it can be a source for continued nitrite production (which decomposes to N_2O). This explanation may have validity because the nitrate concentration does continue to decrease slowly after 135 min, as will be discussed in Section 4.2.1.

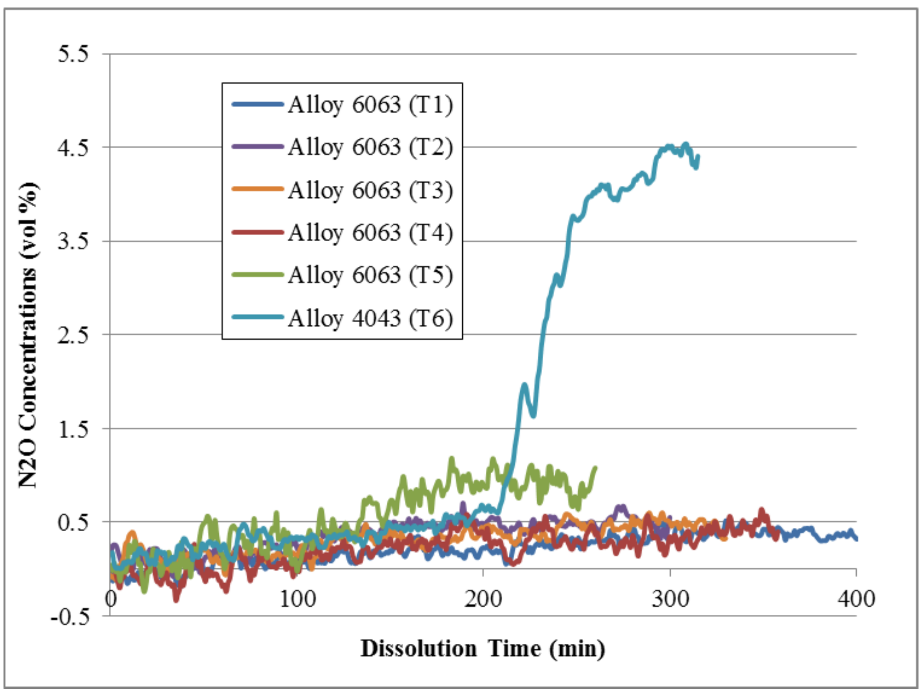


Figure 4-5. Nitrous Oxide Formation for Tests 1 to 5

One other possible mechanism involves catalytic decomposition of nitrite facilitated by impurities in the alloy, such as Fe or Cu, both of which have increased concentrations in Alloy 4043 relative to Alloy 6063. It has been demonstrated that nitrite can be reduced to nitroxyl (NOH), which decomposes to N_2O gas, at a copper cathode in aqueous solutions containing 0.01-0.5 M NaOH at 0.001-0.5 M $NaNO_2$.[13] Copper is one of the impurities (0.3 wt %) of Alloy 4043 (Table 3-3), and the release of N_2O does not occur until the nitrite concentration reaches 0.49 M (Appendix 8.4.5). The copper content of Alloy 6063 (0.1 wt %), and the nitrite concentrations of Tests 1 to 5 (0.028-0.058 M) may not have been sufficient to support the reaction. There is a decrease in nitrite concentration in Test 4 between 270 and 300 min (Table 4-3), but there is no distinctive spike in N_2O (Appendix 8.3.4).

4.2 Reactant Consumption Measurements

As indicated in Reactions 1 to 3, there are four principal reactants, two of which can be readily measured analytically – hydroxide ion (OH^-) and nitrate ion (NO_3^-); total Al metal consumption is known from the weights of the initial Al metal samples, but limited solubility prevents accurate interim measurement of Al. Nitrate and hydroxide are both detected in the aqueous phase. The detection of hydroxide and nitrate will be discussed separately before being discussed collectively with Al in Section 4.4.

4.2.1 Nitrate Ion Consumption

During the dissolution of Al metal in the presence of $NaNO_3$-NaOH, nitrate ion will be consumed according to Reactions 2 and 3. Other mechanisms may exist, but these have been specified in the literature.[7][8] Measurement of nitrate is performed using IC anion. A compilation of the measured nitrate quantities as a function of time is given in Table 4-4. The analytical data are contained in Appendix 8.4.4.

The shaded cells in Table 4-4 correspond to those in Table 4-1 which identify where total NH_3 generation ceased but NH_3 was still observed in the off gas. In general, there is good agreement between when NH_3 quantities reached a maximum and held steady and when nitrate quantities reached a minimum and held steady. The two data sets indicate that ammonia formation and nitrate depletion are closely related as suggested in Reaction 4.

Table 4-4. Nitrate Quantities in Solution

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Net NO_3^- (mol)	Time (min)	Net NO_3^- (mol)	Time (min)	Net NO_3^- (mol)	Time (min)	Net NO_3^- (mol)	Time (min)	Net NO_3^- (mol)	Time (min)	Net NO_3^- (mol)
36	1.95	30	1.92	30	2.00	30	2.09	30	2.21	20	1.87
60	1.86	60	1.90	60	1.81	60	1.95	60	2.14	45	1.52
90	1.83	90	1.82	94	1.77	94	1.90	90	2.00	75	1.43
120	1.78	120	1.73	122	1.65	122	1.84	120	1.77	98	1.29
150	1.70	150	1.64	150	1.62	148	1.66	150	1.69	135	1.16
186	1.59	180	1.55	180	1.56	180	1.59	184	1.65	165	1.14
240	1.45	210	1.47	210	1.50	210	1.51	210	1.59	195	1.11
270	1.39	240	1.44	240	1.40	240	1.40	240	1.48	225	1.11
300	1.41	275	1.36	270	1.38	270	1.34	270	1.42	270	1.10
330	1.37	305	1.40	300	1.36	300	1.26	285	1.45	315	1.10
360	1.33	---	---	330	1.34	330	1.37	---	---	---	---
390	1.37	---	---	---	---	360	1.27	---	---	---	---
420	1.37	---	---	---	---	---	---	---	---	---	---
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution											

4.2.2 Hydroxide Ion Consumption

During the dissolution of Al metal in NaOH, the hydroxide is consumed according to Reactions 1 to 3, 5, and 7. Other mechanisms may exist, but these have been specified in the literature.[7][8][10] Measurement of base is done with three measurements – total OH^-, free OH^-, and other base. For all analyses, free OH^- plus other base was approximately equal to the total OH^-. Therefore, the values used in this discussion are based on free OH^-, other base, and the sum of those two values.

At the beginning of an experiment, all hydroxide was present as free OH^-. As the reaction proceeded, free OH^- was converted to other base. Concurrently, 10 M NaOH was added to the dissolution vessel at the rates described in Table 3-2, which increased the free base concentration. The value for other base reflects the amount of OH^- consumed by the dissolution of Al and Si metals. Compilations of the total base, free OH^-, and other base concentrations during and after the dissolution of Al are provided in Appendices 8.4.6, 8.4.7, and 8.4.8, respectively.

Using the other base concentrations (Appendix 8.4.8) and calculated solution volumes (Appendix 8.4.12), the total moles of other base present at each sample time were calculated. The results are presented in Table 4-5. As before the shaded cells in Table 4-5 identify where total NH_3 generation ceased, which presumably coincides with the cessation of Al metal dissolution. The blue italicized values in Table 4-5 correspond to times when the NaOH addition had ceased for the entire sampling duration. Although the general trend for all six experiments is for the other base concentration to increase, the variability in the results complicates the interpretation of the data. The variability is more evident in looking at the change in other base concentration from one sample to the next (Table 4-6). It is assumed that the initial concentration of other base is zero.

Table 4-5. Other Base Quantities in Solution

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Other Base (mol)	Time (min)	Other Base (mol)	Time (min)	Other Base (mol)	Time (min)	Other Base (mol)	Time (min)	Other Base (mol)	Time (min)	Other Base (mol)
36	0.365	30	0.437	30	0.388	30	0.117	30	0.617	20	0.346
60	0.558	60	0.486	60	0.379	60	0.305	60	0.637	45	0.558
90	0.510	90	0.580	94	0.500	94	0.625	90	1.350	75	0.635
120	0.521	120	0.786	122	0.602	122	0.923	120	1.861	98	0.718
150	0.506	150	1.046	150	0.654	148	0.744	150	2.094	135	0.852
186	0.583	180	1.153	180	0.751	180	0.663	184	1.871	165	1.151
240	0.674	210	1.141	210	0.951	210	0.866	210	2.275	195	1.678
270	0.602	240	1.447	240	0.930	240	0.906	240	2.601	225	1.666
300	0.900	275	1.745	270	0.933	270	0.925	*270*	*1.606*	*270*	*1.694*
330	*0.932*	*305*	*1.600*	300	0.980	300	1.109	*285*	*2.663*	*315*	*1.675*
360	*0.865*	---	---	*330*	*1.030*	330	1.242	---	---	---	---
390	*0.860*	---	---	---	---	360	2.046	---	---	---	---
420	*0.897*	---	---	---	---	---	---	---	---	---	---
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution. Blue italicized numbers identify times when NaOH was not being added for the entire sample duration.											

In Test 1, which operated at a lower temperature and slower dissolution rate, the other base concentration appears to stabilize shortly after Al metal dissolution ceases. Conversely, Tests 2 to 6 exhibit increasing other base quantities after Al dissolution ceases. These data suggest that there is a continued consumption of free base even after Al metal dissolution is complete. The cause of this is presumably continued Si metal dissolution (Reaction 5). A comparison of the changes of other base with the changes of Si (Table 4-9) does not provide definitive insights because of the variability in the other base data.

Table 4-6. Change in Other Base Quantities in Solution

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Δ Other Base (mol)	Time (min)	Δ Other Base (mol)	Time (min)	Δ Other Base (mol)	Time (min)	Δ Other Base (mol)	Time (min)	Δ Other Base (mol)	Time (min)	Δ Other Base (mol)
36	0.365	30	0.437	30	0.388	30	0.117	30	0.617	20	0.346
60	0.193	60	0.049	60	-0.009	60	0.187	60	0.021	45	0.213
90	-0.048	90	0.094	94	0.121	94	0.321	90	0.713	75	0.076
120	0.011	120	0.206	122	0.103	122	0.298	120	0.511	98	0.083
150	-0.015	150	0.260	150	0.052	148	-0.179	150	0.234	135	0.134
186	0.077	180	0.107	180	0.097	180	-0.082	184	-0.224	165	0.300
240	0.091	210	-0.013	210	0.201	210	0.203	210	0.405	195	0.526
270	-0.072	240	0.306	240	-0.021	240	0.040	240	0.326	225	-0.012
300	0.298	275	0.298	270	0.002	270	0.019	*270*	*-0.995*	*270*	*0.028*
330	*0.032*	*305*	*-0.145*	300	0.047	300	0.184	*285*	*1.057*	*315*	*-0.019*
360	*-0.067*	---	---	*330*	*0.050*	330	0.132	---	---	---	---
390	*-0.005*	---	---	---	---	360	0.804	---	---	---	---
420	*0.036*	---	---	---	---	---	---	---	---	---	---

Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution.
Blue italicized numbers identify times when NaOH was not being added for the entire sample duration.

Similar to Table 4-5, the quantities of free base in each sample were calculated. These are listed in Table 4-7. However, a major difference between the two tables is that the free base continued to increase while 10 M NaOH was added. As a result, decreases in free base due to the dissolution of Al and Si metals are masked by the addition of free base.

Table 4-7. Free Base Quantities in Solution

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Free Base (mol)	Time (min)	Free Base (mol)	Time (min)	Free Base (mol)	Time (min)	Free Base (mol)	Time (min)	Free Base (mol)	Time (min)	Free Base (mol)
36	0.43	30	0.38	30	0.38	30	0.17	30	0.45	20	0.23
60	0.48	60	0.54	60	0.67	60	0.38	60	0.67	45	0.47
90	0.92	90	0.98	94	0.92	94	0.53	90	0.74	75	0.73
120	1.24	120	1.22	122	1.30	122	0.68	120	0.80	98	0.91
150	1.44	150	1.44	150	1.46	148	1.03	150	1.03	135	1.23
186	1.80	180	1.84	180	1.75	180	1.43	184	1.73	165	1.14
240	2.13	210	1.92	210	1.92	210	1.89	210	1.51	195	1.04
270	2.44	240	2.08	240	2.12	240	2.10	240	1.74	225	1.13
300	2.70	275	2.06	270	2.36	270	2.40	*270*	*1.78*	*270*	*1.18*
330	*2.78*	*305*	*2.03*	300	2.52	300	2.48	*285*	*1.80*	*315*	*1.12*
360	*2.56*	---	---	*330*	*2.56*	330	2.79	---	---	---	---
390	*2.62*	---	---	---	---	360	2.18	---	---	---	---
420	*2.67*	---	---	---	---	---	---	---	---	---	---

Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution.
Blue italicized numbers identify times when NaOH was not being added for the entire sample duration.

The general trend of Table 4-7 is that the free base increases for each sample in which 10 M NaOH is being added. Attempts to compare the total amount of free base added with the amount of free base measured did not offer any new insights.

4.3 Aluminum Dissolution

4.3.1 Dissolution Rates

A direct measurement of the Al dissolution rate for these experiments was not obtained from changing weights of coupons because once the samples were inserted into the dissolver solution; they remained in solution until the experiment finished. Liquid samples were withdrawn approximately every 30 min during the test, but almost every sample contained visible solids (Figure 4-6). The solids were submitted with the liquid portions of the samples; solid-liquid separation was performed by Analytical Development. Characterization of the solids will be reported as part of a separate technical task evaluating solids filtration.[12]

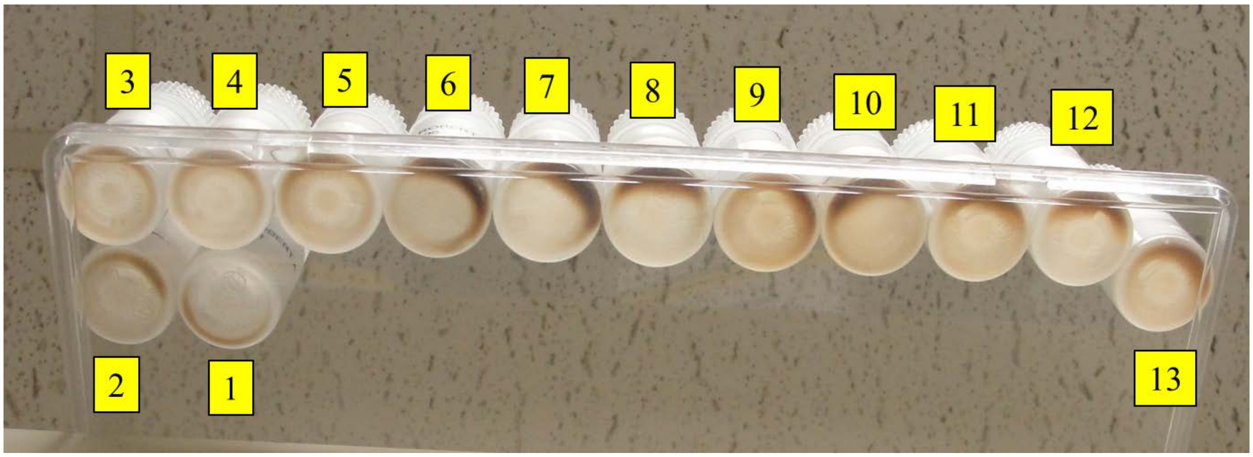


Figure 4-6. Test 1 Sample Bottles with Solids

A small amount of a 6063 disk sample was dissolved in base, acidified with HNO_3, and analyzed by ICPES. The analysis identified 99.1 wt % Al, 0.47 wt % Si, 0.078 wt% Fe, 0.33 wt % Mg, and 0.044 Zn; however, the Fe, Mg, and Zn are a little lower than expected.[11] A similar analysis was not completed with a sample of Alloy 4043. For Al:Si ratio calculations related to Test 6, mass ratios of 95.0:4.5 will be used for the maximum Si content and 93.5:6.0 will be used for the minimum Si content (see Table 3-3).[11]

The analyses are reported in Appendix 8.4.9, and converted to molar concentrations in Table 4-8. Assuming that Alloy 6063 is 99% Al, the nominal final Al concentrations for Tests 1 to 3 and 5 would be about 1.5 M, assuming all Al dissolved in the measured final volume; the nominal Al concentration for Test 4 would be about 1.3 M and Test 6 about 1.2 M [which assumes 94% Al in Alloy 4043]. All six tests fall well short of the theoretical final Al concentrations, and all tests exhibit significant fluctuations (increases followed by decreases) of the soluble Al concentrations between samples.

An alternate approach had to be identified to measure Al dissolution rates and correlate other chemical compounds with the dissolution of Al. The approach adopted involves identifying an impurity in the Al alloys which could be tracked in solution. Alloy 6063 contains the following impurities: Si, Fe, Cu, Mn, Mg, Cr, Zn, Ti; Alloy 4043 has the same impurities except for Cr. However, all of the listed impurities are insoluble in NaOH except for Si. Silicon has limited solubility in solutions containing NaOH and Al.

The ICPES data for silicon are provided in Table 4-9 (and Appendix 8.4.10). The Si concentrations for Tests 1 to 5 exhibit gradual increases throughout each test during Al dissolution (and NH_3 generation). Tests 1 to 3 and 5 also yielded similar maximum concentrations of ~6.3 mM (theoretical maximum of 6.8-6.9 mM). Test 4 was lower than Tests 1 to 3, but the data show that the Si concentration was still increasing at the conclusion of the test, indicating the presence of undissolved material when the test stopped. Test 6 achieved 24.5 mM (compared to theoretical maximum of 61.0 mM) before decreasing due to precipitation. The Si solubility for Test 6 suggests that all Si was soluble during Tests 1 to 5.

To correlate Si concentrations to dissolved Al, the ratio of Al:Si must be known. The literature indicates that the concentration limits for Si in Alloy 6063 are 0.2 to 0.6 wt % (assuming 99.0% Al), or an Al:Si mass ratio of 165 to 495. The equivalent Al:Si mole ratios are 171 to 515. For Tests 1 to 5, based on the masses of Al dissolved and the final solution volumes measured, an Al:Si mole ratio of 240 yields Al concentrations which fall within the expected Al purity range, which was used as the basis for subsequent calculations and conclusions. For Tests 1 to 5, when an Al:Si mole ratio of 240 is used to estimate the quantity of Al dissolved at a given sample time, it results in the data presented in Table 4-10. For comparison, the measured Al:Si mole ratios for Tests 1 to 6 are included in Appendix 8.4.11.

Correlating Si is much more difficult for Test 6. The literature indicates that the range of Si for Alloy 4043 is 4.5 to 6.0 wt %, which corresponds with Al concentrations of ~93.5 wt % (for 6.0 wt % Si) and ~95.0 wt % (for 4.5 wt % Si). These mass ratios yield Al:Si mole ratios of 16.2 to 22.0. However, for the measured Si concentrations to yield calculated Al concentrations, a mass ratio for Al:Si of 73.8 (equates to mole ratio of 76.9) must be used. Consequently, both Al and Si are forming precipitates during dissolution and analytical methods do not give an accurate measure of total Al dissolved.

For Test 6, the Al:Si mass ratio of 73.8 corresponds to the Al:Si mass ratio at 20 min and achieves the dissolved Al target when multiplied by the Si data. Using the data at 20 min was arbitrary. The Al:Si ratio then decreased steadily between 20 and 135 min as total Si increased steadily. However, after 165 min, Si decreased steadily (see Appendix 8.4.11). The consequence of Al:Si shifting through the test at values well above the maximum Si impurity limits is that the calculated values for dissolved Al are of poor quality and should not be used in making substantive flowsheet decisions. However, for the sake of completeness, calculations associated with Test 6 will be carried through the report. The calculations in Table 4-10 will be used in Section 4.4 to compare the moles of H_2, NH_3, and NO_2^- generated and the moles of OH^- and NO_3^- consumed per mole of Al dissolved.

Table 4-8. Aluminum Quantities in Solution - Measured

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Al (M)	Time (min)	Al (M)	Time (min)	Al (M)	Time (min)	Al (M)	Time (min)	Al (M)	Time (min)	Al (M)
36	0.224	30	0.265	30	0.211	30	0.077	30	0.282	20	0.224
60	0.347	60	0.266	60	0.415	60	0.076	60	0.201	45	0.408
90	0.493	90	0.262	94	0.368	94	0.404	90	0.203	75	0.534
120	0.331	120	0.305	122	0.389	122	0.177	120	0.285	98	0.626
150	0.355	150	0.317	150	0.441	148	0.201	150	0.378	135	0.830
186	0.445	180	0.357	180	0.456	180	0.249	184	0.415	165	1.041
240	0.471	210	0.408	210	0.537	210	0.291	210	0.471	195	1.019
270	0.482	240	0.434	240	0.545	240	0.320	240	0.526	225	0.990
300	0.537	275	0.560	270	0.574	270	0.371	270	0.563	270	1.008
330	0.586	305	0.523	300	0.619	300	0.389	285	0.556	315	1.004
360	0.560	---	---	330	0.637	330	0.419	---	---	---	---
390	0.552	---	---	---	---	360	0.460	---	---	---	---
420	0.597	---	---	---	---	---	---	---	---	---	---

Table 4-9. Silicon Quantities in Solution - Measured

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Si (mM)	Time (min)	Si (mM)	Time (min)	Si (mM)	Time (min)	Si (mM)	Time (min)	Si (mM)	Time (min)	Si (mM)
36	1.07	30	1.66	30	1.33	30	<1.22	30	1.35	20	2.91
60	1.67	60	2.20	60	2.14	60	<1.22	60	2.17	45	5.95
90	2.26	90	2.90	94	2.84	94	1.73	90	2.91	75	9.36
120	2.83	120	3.81	122	3.67	122	2.34	120	3.88	98	11.9
150	3.40	150	4.34	150	4.27	148	2.55	150	4.81	135	21.5
186	3.81	180	5.06	180	4.81	180	2.77	184	5.45	165	24.5
240	4.98	210	5.77	210	5.41	210	2.99	210	5.66	195	23.0
270	5.48	240	6.16	240	5.84	240	3.48	240	6.20	225	19.4
300	5.80	275	6.37	270	6.12	270	3.44	270	6.52	270	11.1
330	5.98	305	6.27	300	6.23	300	3.81	285	6.34	315	<7.66
360	6.23	---	---	330	6.23	330	3.99	---	---	---	---
390	5.87	---	---	---	---	360	4.59	---	---	---	---
420	6.27	---	---	---	---	---	---	---	---	---	---

Table 4-10. Aluminum Quantities Dissolved – Calculated from Silicon

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Al (mol)	Time (min)	Al (mol)	Time (min)	Time (min)	Time (min)	Al (mol)	Time (min)	Al (mol)	Time (min)	Al (mol)
36	0.263	30	0.408	30	0.326	30	<0.293	30	0.399	20	0.228
60	0.416	60	0.556	60	0.534	60	<0.293	60	0.659	45	0.475
90	0.576	90	0.747	94	0.718	94	0.450	90	0.904	75	0.766
120	0.732	120	1.001	122	0.951	122	0.620	120	1.235	98	0.989
150	0.895	150	1.165	150	1.115	148	0.687	150	1.565	135	1.343
186	1.025	180	1.382	180	1.288	180	0.766	184	1.821	165	1.343
240	1.387	210	1.607	210	1.474	210	0.846	210	1.927	195	1.343
270	1.550	240	1.749	240	1.617	240	1.003	240	2.155	225	1.343
300	1.667	275	1.823	270	1.724	270	1.012	270	2.277	270	1.343
330	1.711	305	1.778	300	1.783	300	1.145	285	2.208	315	1.343
360	1.775	---	---	330	1.787	330	1.222	---	---	---	---
390	1.667	---	---	---	---	360	1.433	---	---	---	---
420	1.770	---	---	---	---	---	---	---	---	---	---

Combining Table 4-10 with solution volume calculations (Appendix 8.4.12) yields the masses of Al dissolved at each sample time for Tests 1 to 6 (Table 4-11). The data in Table 4-10 and Table 4-11 may seem to indicate that for Test 4 not all Al is completely dissolved despite the absence of intact samples in the dissolver solution. Recall that the manner of NaOH feeding for Test 4 was different compared to the other five experiments. Test 4 began with no NaOH in solution compared to 0.425 M NaOH for the other five tests. The reduced NaOH availability may have shifted Al dissolution rates, Si dissolution rates, and Si solubility.

Table 4-11. Aluminum Masses Dissolved – Calculated from Silicon

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Al (g)	Time (min)	Al (g)	Time (min)	Al (g)	Time (min)	Al (g)	Time (min)	Al (g)	Time (min)	Al (g)
36	7.093	30	11.018	30	8.785	30	---	30	10.774	20	6.158
60	11.227	60	15.006	60	14.417	60	---	60	17.776	45	12.818
90	15.535	90	20.145	94	19.369	94	12.142	90	24.391	75	20.671
120	19.741	120	27.022	122	25.656	122	16.728	120	33.318	98	26.695
150	24.162	150	31.427	150	30.084	148	18.550	150	42.228	135	36.238
186	27.662	180	37.298	180	34.745	180	20.668	184	49.125	165	36.238
240	37.416	210	43.371	210	39.784	210	22.825	210	52.003	195	36.238
270	41.831	240	47.191	240	43.642	240	27.050	240	58.149	225	36.238
300	44.988	275	49.198	270	46.523	270	27.300	270	61.451	270	36.238
330	46.175	305	47.969	300	48.099	300	30.886	285	59.568	315	36.238
360	47.898	---	---	330	48.220	330	32.973	---	---	---	---
390	44.971	---	---	---	---	360	38.660	---	---	---	---
420	47.766	---	---	---	---	---	---	---	---	---	---

Although the data in Table 4-10 allow calculations of moles of Al dissolved per minute for Tests 1 to 5, it is not sufficient to calculate dissolution rates in mg/min/cm^2; Test 6 was omitted for reasons discussed earlier. To perform those calculations, a spreadsheet was configured to track the dissolution of Al samples. It starts with the known quantities of sample mass and surface area, and it calculates each minute how much Al dissolves at a given dissolution rate, and how much the surface area decreases for a given mass of Al dissolution. This spreadsheet enables the manual input and adjustment of an Al dissolution rate until the change in Al sample mass for a given amount of time matches the experimentally-determined masses (Table 4-11) for the same time period. The calculated dissolution rates are provided in Table 4-12 and graphed in Figure 4-7.

Table 4-12. Aluminum Dissolution Rates – Calculated

Test 1		Test 2		Test 3		Test 4		Test 5	
Time (min)	Diss. Rate	Time (min)	Diss. Rate	Time (min)	Diss. Rate	Time (min)	Diss. Rate	Time (min)	Diss. Rate
0-36	1.57	0-30	2.97	0-30	2.34	0-30	---	0-30	1.88
37-60	1.43	31-60	1.09	31-60	1.58	31-60	---	31-60	1.24
61-90	1.25	61-90	1.58	61-94	1.31	61-94	1.05	61-90	1.23
91-120	1.28	91-120	2.27	95-122	2.21	95-122	1.46	91-120	1.72
121-150	1.42	121-150	1.56	123-150	1.62	123-148	0.61	121-150	1.77
151-186	0.97	151-180	2.28	151-180	1.74	149-180	0.62	151-184	1.23
187-240	2.05	181-210	2.63	181-210	2.06	181-210	0.69	185-210	0.68
241-270	1.86	211-240	1.81	211-240	1.70	211-240	1.43	211-240	1.33
271-300	1.44	---	---	241-270	1.37	241-270	0.04	---	---
---	---	---	---	---	---	271-300	1.31	---	---
---	---	---	---	---	---	301-330	0.75	---	---
Note: Rates are reported in units of mg/min/cm^2									

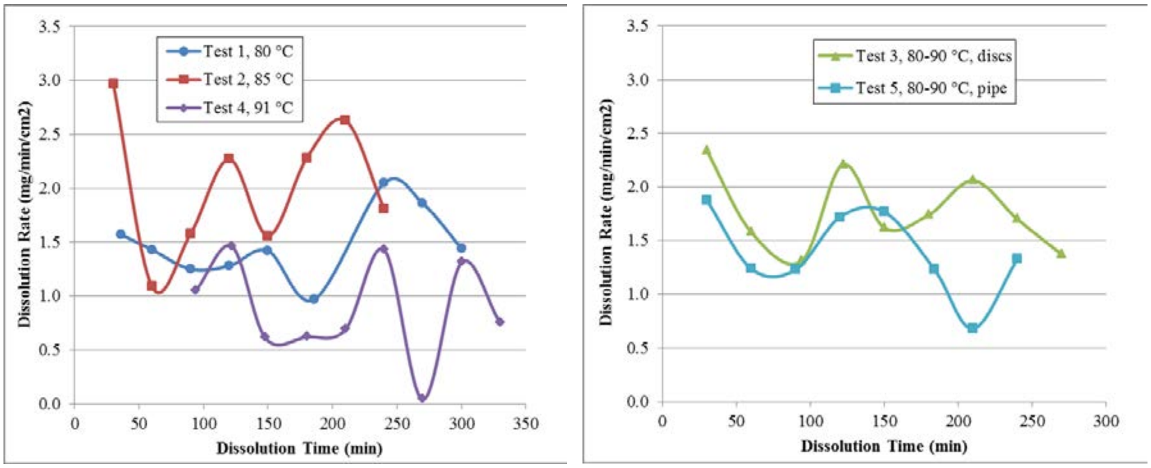


Figure 4-7. Aluminum Dissolution Rates - Calculated

In Figure 4-7, Tests 1 and 2, in general, exhibit the expected trend of higher rate due to temperature. In contrast, Test 4 rates are much lower than either Test 1 or Test 2, and this can be attributed to the NaOH addition approach. Tests 1 and 2 were initiated with 0.425 M NaOH in solution and more NaOH was added with time. Test 4 began with no NaOH and added it with time. Even though the sample shapes for Tests 3 and 5 were different, they exhibited similar dissolution rate behavior, including the effect of temperature change from 80 to 85 °C. This was expected because they were tested with the same temperature profile and sample-to-volume ratio. Test 3 also exhibited an increase in dissolution rate when the temperature was increased from 85 to 90 °C. The increase in temperature from 85 to 90 °C in Test 5 did not result in an increase in calculated dissolution rate, probably due to the degree of sample dissolution and the accumulation of reaction products in solution.

The calculation of the dissolution rates has significant limitations which become more substantial as the reaction progresses. However, without an estimate of surface are throughout the experiment, there can be no calculation of dissolution rates at various times. Due to the large amount of surface area on the samples relative to their thickness, errors in calculating the surface are likely to be relatively small during the early stages of dissolution compared to the uncertainty (10%) associated with the soluble Si measurements. Assuming uniform dissolution of the disk sample thickness and outer diameter, as the sample mass approaches zero, there is a calculated net surface area change of 52% for an entire experiment. However, periodic examinations of the disk samples showed that those samples closer to the stirrer dissolved faster and that there was more rapid dissolution along the sample edges than on the face surfaces. The method for calculating the surface areas and dissolution rates for the disks are discussed in Appendix 8.2.1.

For the pipe sample, the calculated relative change in surface area is much less (20%). Also, it was observed that the pipe retains its dominant shape (diameter and height) for a longer period of time than the disks. Pitting through the side wall occurred before the height of the sample collapsed. Consequently, the calculated error associated with the calculated surface areas for Test 5 should be less than the error of the Si analyses for a longer time than for Tests 1 to 4. The limitation of the surface area calculation assumptions can be seen in the pictures of the dissolving pipe in Figure 4-8. The sample dissolution is not uniform either from height or diameter, plus there is scale formation during at least the first 98 min (when the dissolution temperature is at 80 °C). The method for calculating the surface areas and dissolution rates for the pipe are discussed in Appendix 8.2.2. Appendix 8.2.3 shows how calculations for the rod samples could be performed if reliable Si or Al were available.

The calculated surface areas at the end of each sampling time assuming uniform dissolution are listed in Table 4-13. If complete dissolution of samples occurred (as visually indicated), their final surface area would be zero. The calculated surface areas in Table 4-13 do not reach zero and hence distort the calculated dissolution rate profile in the latter portion of the experiments. If the actual surface areas are indeed smaller, then the dissolution rates could be larger at these later times than indicated in Table 4-12 and Figure 4-7.

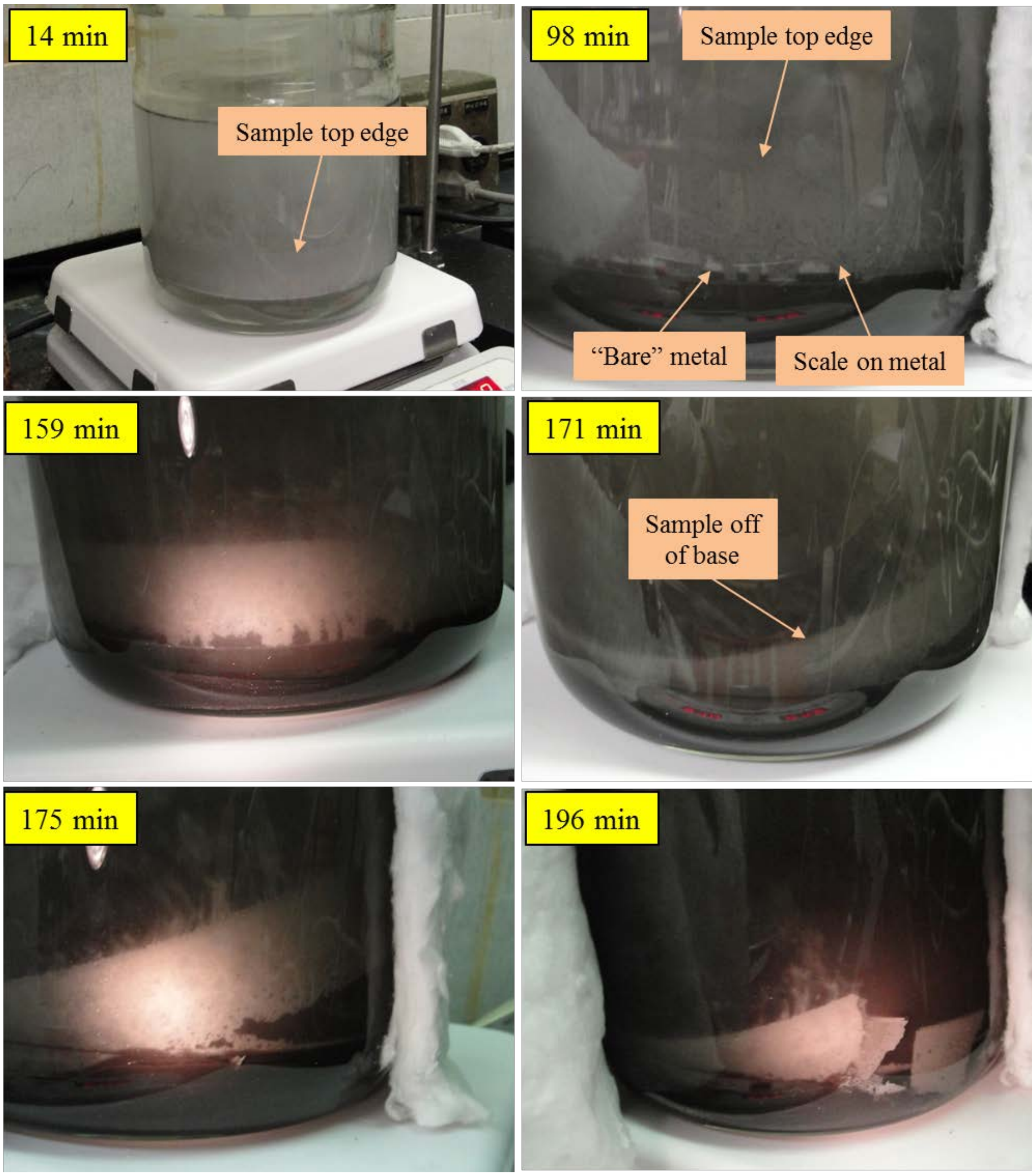


Figure 4-8. Test 5 Images of Pipe Sample Dissolution

However, as discussed above, it is recognized that the dissolution is not uniform. In particular, as the samples approach complete dissolution, the surface area will change more quickly. Nonetheless, this approach was the best available method for analyzing the data and calculating dissolution rates. Alternate approaches for calculating dissolution rates should be explored for future studies.

Table 4-13. Aluminum Sample Surface Areas – Calculated

Test 1		Test 2		Test 3		Test 4		Test 5	
Time (min)	SA (cm^2)	Time (min)	SA (cm^2)	Time (min)	SA (cm^2)	Time (min)	SA (cm^2)	Time (min)	SA (cm^2)
0	129.5	0	129.5	0	129.5	0	129.5	0	194.4
36	122.0	30	117.6	30	120.1	30	---	30	186.9
60	117.3	60	112.8	60	113.5	60	---	60	182.0
90	112.2	90	106.4	94	107.4	94	116.2	90	177.4
120	106.9	120	97.1	122	99.0	122	110.7	120	171.1
150	101.0	150	90.8	150	92.8	148	108.4	150	164.9
186	96.2	180	82.0	180	85.9	180	105.7	184	160.1
240	81.8	210	72.4	210	78.2	210	102.8	210	158.0
270	74.9	240	66.1	240	72.0	240	97.1	240	153.8
300	69.7	---	---	270	67.2	270	96.7	---	---
---	---	---	---	---	---	300	91.6	---	---
---	---	---	---	---	---	330	88.6	---	---

4.3.2 Other Metal Ion Measurements

Apart from Si (Table 4-9), Fe and Mg can be detected as impurities in solution from the aluminum alloys. Other impurities (Cu, Cr, Mn, Ti, and Zn) are also components of the alloys, but were always below the ICPES method detection limits. Sodium can also be measured. Sodium is a component of the reactant ($NaNO_3$-NaOH) added to the system. The data for Fe, Mg, and Na are provided in Appendix 8.4.13. Although Fe and Mg are occasionally above the method detection limits, their concentrations measured in solution are small compared to the expected concentration if the metals were more soluble in the dissolver dissolution. Consequently, it is suggested that the Mg and Fe have formed precipitates. Both were identified in the undissolved residues for the batch Al dissolution experiments.[5]

Sodium was part of the initial solution and added with time to each solution. Consequently, sodium increased throughout each experiment. Because Na was added at a uniform rate, the theoretical Na concentration at any point in time can be calculated. Those calculations are provided in Appendix 8.4.14. Note that due to instrument availability issues, Tests 1, 2, and 6 analyzed Na using a nonradioactive ICPES instrument and Tests 3 to 5 used one in a radioactive environment. When the measured values of Appendix 8.4.13 are compared with the calculated values of Appendix 8.4.14, there appears to be an instrument effect for Na. The comparison is shown in Appendix 8.4.15, which suggests the nonradioactive ICPES reports only ~89% of the calculated value on average. A similar effect was observed in the earlier studies.[5] Check standards used by nonradioactive ICPES confirmed that the instrument was functioning correctly.

4.4 Reaction Chemistry

As was previously presented in Reaction 4, an empirical chemical reaction for the dissolution of Al metal in $NaNO_3$- NaOH has been proposed based on ORNL processing of Mark-42 targets.[8] Batch dissolution studies yielded reasonable agreement with Reaction 4.[5] However, the data did not track the progression of the reaction as Al metal dissolved. Rather, it took a series of reaction snapshots for a range of $NaNO_3$ and NaOH concentrations as well as temperature. The significance of the difference between these experiments and the previous batch experiments has already been referenced in the discussion concerning Al metal dissolution rates (Table 4-12).

In this section, the changes in molar quantities for different chemical species provided in the tables of Sections 4.1 and 4.2 are compared with the changes in quantities for Al dissolution (Table 4-10). The molar-ratio calculations for the measured chemical species are provided throughout the processing of the Al metal samples as well as the average across the entire test. Where distinct trends are observed, graphs of the data are provided. Due to issues related to calculating the quantity of Al dissolved in any given sample for Test 6, only average values are given significant consideration, even though the Test 6 calculated values will be provided for comparison.

4.4.1 Reaction Product Measurements

Ammonia is a major product of the Al dissolution reaction (Reaction 2). As previously discussed in Section 4.1.1, NH_3 generation appears to be tied directly and solely to the dissolution of Al metal. As the Al dissolution reaction progresses, nitrate ion is consumed. Batch testing showed no correlation between NH_3 generation and $NaNO_3$ concentration (see Figure 4-6 of Reference 4). In contrast, the data from these tests indicate there is a relationship in which NH_3 generation decreases with decreasing $NaNO_3$ concentration, which would be expected based on Reaction 2.

Moles of NH_3 (Table 4-1) were divided by the corresponding moles of Al dissolved in solution (Table 4-10) to yield NH_3 generation to Al dissolution molar ratios shown in Table 4-14. Two plots of that data are provided in Figure 4-9. The figure on the left includes all of the data from Table 4-14. The figure on the right omits the data from Test 4, which was performed in different manner with regards to NaOH addition. Test 4 began with no NaOH in solution and began adding NaOH when the Al metal sample was submerged; the other five tests began with NaOH in solution and added more NaOH when the sample was submerged. The end result is that more NH_3 is generated by way of Reaction 2. The ammonium concentration data point for Test 4 at 270 min (Appendix 8.4.1) is likely the result of analytical error or mishandling of the sample as there is no good technical explanation for that point (4820 mg/L) to break from the data trend for that or any other test.

Table 4-14. Ammonia Generation to Aluminum Dissolution Molar Ratios

Test 1		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
Time (min)	NH_3-to-Al	Time (min)	NH_3-to-Al	Time (min)	NH_3-to-Al	Time (min)	NH_3-to-Al	Time (min)	NH_3-to-Al	Time (min)	NH_3-to-Al
36	0.303	30	0.240	30	0.199	30	---	30	0.352	20	0.223
60	0.320	60	0.388	60	0.478	60	---	60	0.386	45	0.321
90	0.313	90	0.339	94	0.338	94	0.139	90	0.316	75	0.235
120	0.276	120	0.313	122	0.321	122	0.542	120	0.248	98	0.205
150	0.233	150	0.350	150	0.316	148	0.929	150	0.258	135	0.143
186	0.520	180	0.276	180	0.213	180	0.917	184	0.196	165	---
240	0.201	210	0.258	210	0.241	210	1.014	210	0.268	195	---
270	0.261	240	-0.066	240	0.188	240	0.103	240	0.110	225	---
300	0.178	275	0.163	270	0.235	270	0.080*	270	0.141	270	---
330	0.342	305	0.036	300	-0.033	300	0.695	285	0.213	315	---
360	-0.157	---	---	330	1.248	330	-0.055	---	---	---	---
390	0.223	---	---	---	---	360	0.037	---	---	---	---
420	0.255	---	---	---	---	---	---	---	---	---	---
Avg = 0.266#		**Avg = 0.268#**		**Avg = 0.275#**		**Avg = 0.333#**		**Avg = 0.268#**		**Avg = 0.219#**	

Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution
* See Appendix 8.3.1 for a discussion of this data point.
# Average values calculated by dividing total number of moles of NH_3 generated (Table 4-1) by the moles (calculated from the mass) of Al in the initial samples (Table 3-1).

The data in the shaded cells, where NH_3 generation has essentially ceased, are omitted from the figure on the right because when there is little or no NH_3 generation, analytical uncertainty with the Si data (which translates into the dissolved Al calculations) can yield very high or low ratio values which break from the existing data trends without a discernible cause.

The figure on the right depicts the relationship between NH_3 generation and reaction time. Other than the data point for Test 1 at 186 min, the data show a clear trend of decreasing NH_3 generation per mole of Al dissolved as the test proceeds (and the $NaNO_3$ decreases). The data point for Test 1 at 186 min comes from a calculation where the NH_4^+ data follows the expected trend, but the Si data is significantly lower than expected based on the data trend. If the data point was increased by 10% (the analytical uncertainty), it would fit with the visible trend. The NH_3:Al molar ratio is graphed as a function of nitrate concentration in Figure 4-10. The ability to see a distinct trend is masked by uncertainty (10%) of the nitrate concentrations.

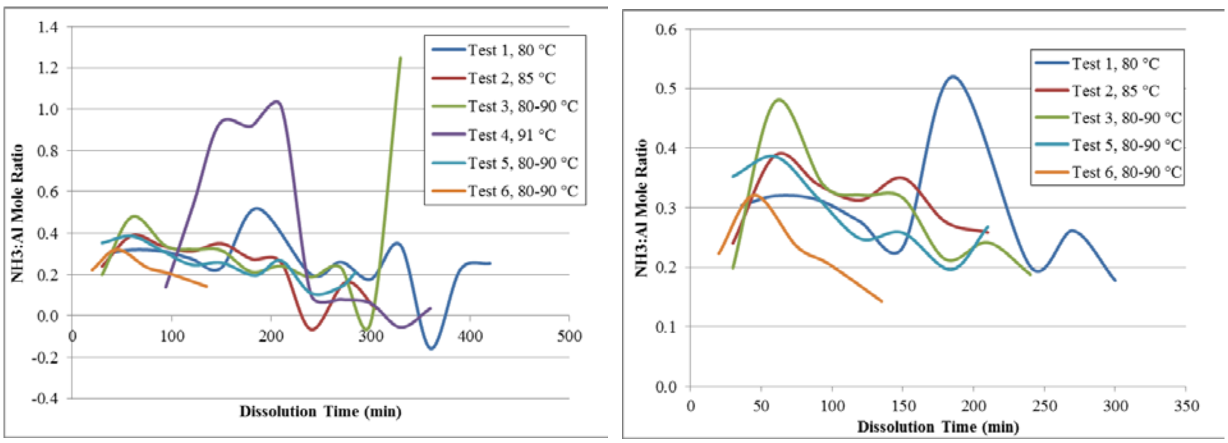


Figure 4-9. Ammonia Generation to Aluminum Dissolution Molar Ratios

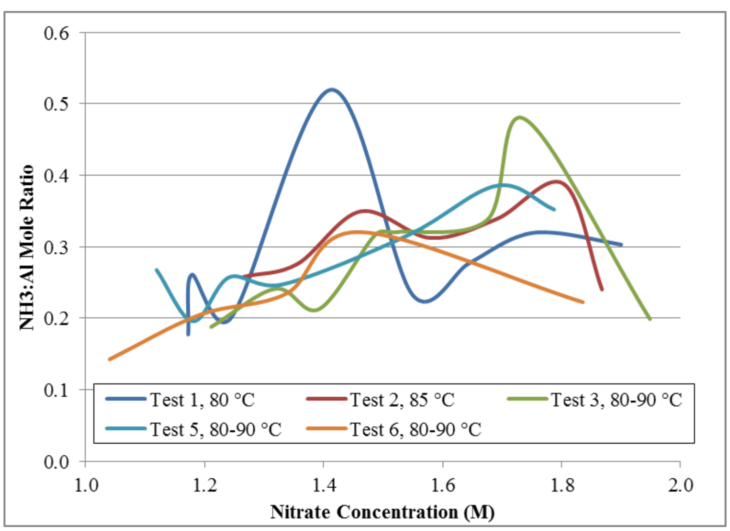


Figure 4-10. NH_3:Al Molar Ratios versus Nitrate Concentration

Because NH_3 is a flammable gas, the data indicate that the greatest releases will occur at the onset of testing when the $NaNO_3$ concentration and the dissolution rates are the highest. Expected generation rates for full-scale operations will be provided in Section 4.5.

The average moles of NH_3 generated per mole of Al dissolved was calculated by dividing the total moles of ammonia generated for the test by the aluminum in the initial sample mass; it is not an average of the values in the columns of the table. The average NH_3-to-Al ratios of 0.27 for Tests 1 to 3 and 5 are essentially the same and agree with the values reported from the batch dissolution studies. Test 4, which was performed in a manner similar to the ORNL flowsheet, yields a value rather close to the Reaction 3 value coefficient of 0.37, and it shows a 24% increase in NH_3 generation associated with the altered method of NaOH addition. Test 6 with the high-Si 4043 alloy produced 19% less flammable NH_3. However, the decrease in NH_3 generation was offset by an increase in flammable H_2 generation.

Hydrogen generation is another major product of the Al dissolution reaction (Reaction 1). As previously discussed in Section 4.1.1, NH_3 generation appears to be a product of the dissolution of both Al and Si metals. As the Al dissolution reaction progresses, $NaNO_3$ is consumed. Prior studied indicate that reduced $NaNO_3$ concentrations shift the balance of gases generated from NH_3 toward H_2.[7]

Moles of H_2 (Table 4-2) were divided by the corresponding moles of Al dissolved in solution (Table 4-10) to yield H_2 generation to Al dissolution molar ratios shown in Table 4-15. Two plots of that data are provided in Figure 4-11. The figure on the left includes all of the data from Table 4-15. The figure on the right eliminated the data from Tests 4 which was conducted in a manner different from Tests 1 to 3 and 5. Test 6 was eliminated because it used a different alloy, and because of issues with precipitation of Al and Si due to the different alloy composition. Furthermore, the final proposed flowsheet will be similar to Tests 3 and 5. The data point for Test 1 at 186 min comes from a calculation where the H_2 data follows the expected trend, but the Si data is significantly lower than expected based on the data trend. If the Si data point was increased by 10% (the analytical uncertainty), it would fit with the visible trend.

The figure on the right depicts H_2 generation as the reaction progresses. No noticeable relationship exists between H_2 generation and $NaNO_3$ concentration. This is consistent with the batch results for the $NaNO_3$ range of 1.1-1.9 M. Hydrogen is a flammable gas whose release rate will be driven by Al metal dissolution rate and, to a lesser degree, $NaNO_3$ concentration (which decreases as the reaction proceeds). Expected H_2 generation rates for full-scale operations will be provided in Section 4.5.

Batch testing (Figure 4-3 of Reference 4) showed little (if any) correlation between H_2 generation and $NaNO_3$ concentration for 1.1-1.9 M $NaNO_3$; a clear linear relationship existed between 0.75 and 1.1 M $NaNO_3$.[5] This could signal a change in the dominant reaction mechanism. However, as shown in Appendix 8.4.4, the nitrate concentrations for these experiments (converted from mass to mole basis) were almost exclusively between 1.1 and 2.1 M, the region of minimal change in H_2 as a function of $NaNO_3$ concentration. When the H_2:Al mole ratio is plotted as a function of $NaNO_3$ concentration (Figure 4-12), there is no discernible relationship, and the reason for the data variability is difficult to explain.

The average H_2-to-Al ratios for Tests 1 to 3 and 5 are essentially the same (0.046) and agree with the values reported from the batch dissolution studies. Test 4, which was performed in a manner similar to the ORNL flowsheet, shows markedly higher hydrogen than the reported 0.02 (see Reaction 4).[8] Using the average value from Tests 1 to 3 and 5 (0.046), Test 4 H_2 generation represented a 78% increase in H_2 generation when compared to tests with the currently favored method of NaOH addition. Test 6 with the high-Si 4043 alloy produced 141% more flammable H_2. The increase in H_2 was 0.065 mol/mol Al, which offsets a decrease in NH_3 of 0.051 mol/mol Al. It should be noted that H_2 has a lower flammability limit (4.0 vol %) than NH_3 (15.0 vol %) at standard conditions, but the overall system flammability is affected by temperature and the presence of two fuels.[14]

Table 4-15. Hydrogen Generation to Aluminum Dissolution Molar Ratios

Test 1		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
Time (min)	H_2-to-Al	Time (min)	H_2-to-Al	Time (min)	H_2-to-Al	Time (min)	H_2-to-Al	Time (min)	H_2-to-Al	Time (min)	H_2-to-Al
36	0.041	30	0.029	30	0.033	30	---	30	0.030	20	0.100
60	0.047	60	0.067	60	0.041	60	---	60	0.039	45	0.127
90	0.048	90	0.051	94	0.045	94	0.031	90	0.041	75	0.066
120	0.044	120	0.034	122	0.045	122	0.081	120	0.043	98	0.063
150	0.045	150	0.075	150	0.059	148	0.171	150	0.041	135	0.080
186	0.077	180	0.054	180	0.052	180	0.203	184	0.034	165	---
240	0.053	210	0.051	210	0.070	210	0.190	210	0.064	195	---
270	0.062	240	0.050	240	0.081	240	0.099	240	0.035	225	---
300	0.036	275	0.014	270	0.044	270	0.065	270	0.030	270	---
330	0.053	305	-0.005	300	0.042	300	0.028	285	0.000	315	---
360	0.015	---	---	330	0.111	330	0.008	---	---	---	---
390	0.000	---	---	---	---	360	0.001	---	---	---	---
420	---	---	---	---	---	---	---	---	---	---	---
Avg = 0.049#		**Avg = 0.047#**		**Avg = 0.050#**		**Avg = 0.082#**		**Avg = 0.039#**		**Avg = 0.111#**	
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution											
# Average values calculated by dividing total number of moles of H_2 generated (Table 4-2) by the moles (calculated from the mass) of Al in the initial samples (Table 3-1).											

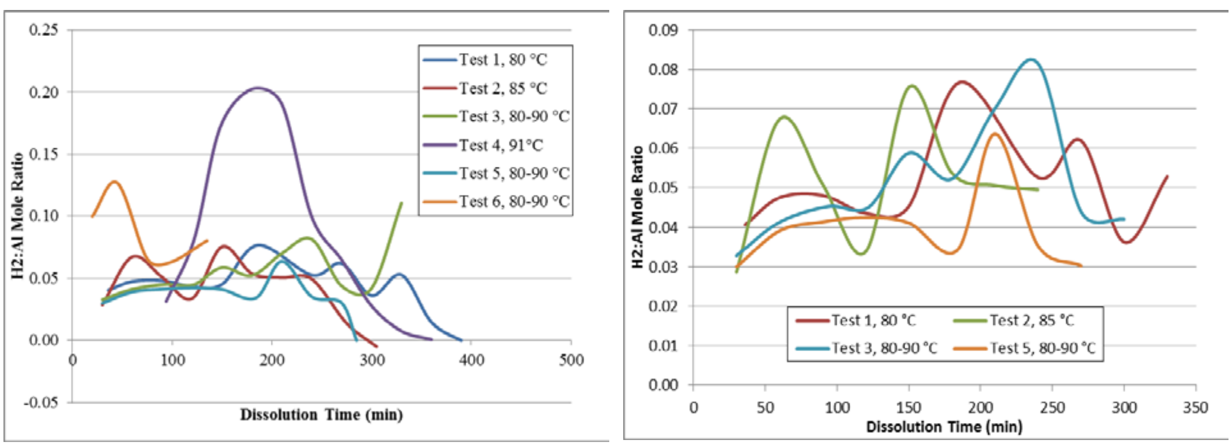


Figure 4-11. Hydrogen Generation to Aluminum Dissolution Molar Ratios

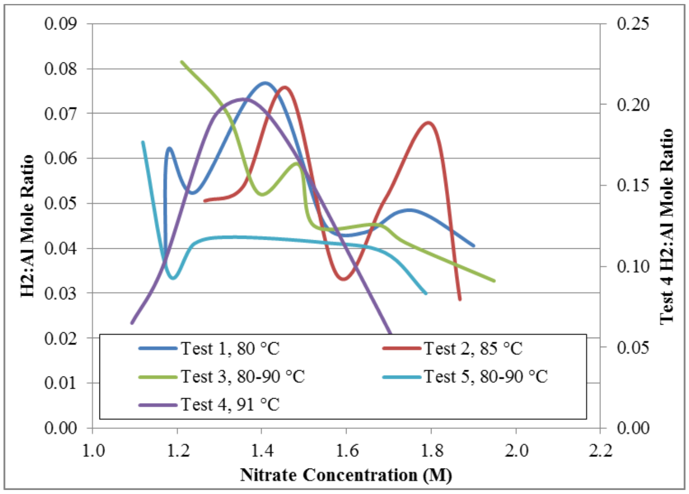


Figure 4-12. H_2:Al Molar Ratios versus Nitrate Concentration

The data in Table 4-15 provides data for an approximation of moles of H_2 generated from the dissolution of Al (Reaction 1) versus the mole of H_2 generated from the dissolution of Si (Reaction 5). A comparison of Test 3 (Alloy 6063, ~99% Al, ~0.043 Si) generation of H_2 with Test 6 (Alloy 4043, ~94% Al, ~5.0% Si) can be made by attributing the H_2 reported in Table 4-15 as being per mole of alloy instead of mole of aluminum. Tests 3 and 6 are compared because of their similar thermal profiles during dissolution. Solving the resulting equations yields 0.044 mol H_2/mol of total Al via Reaction 1 and 1.41 mol H_2/mol of Si via Reaction 5. Factoring the Al:Si mole ratio of 240 for Alloy 6063, Al dissolution accounts for about 7.6 times more H_2 gas generation than Si dissolution. For Alloy 4043 with an Al:Si mole ration of 20, Al dissolution account for about 38% of the H_2 generation. Those numbers are dependent upon other factors (as indicated by differences in average mol H_2/mol Al in Table 4-15 for Tests 3, 4, and 5), but they provide some insight into the relative quantities of H_2 gas generated by each reaction.

Nitrite is a third significant product of the Al dissolution reaction (Reaction 3). As previously discussed in Section 4.1.3, NO_2^- generation appears to be a product of the dissolution of Al metal. As the Al dissolution reaction progresses, $NaNO_3$ is consumed. The expectation is that reduced $NaNO_3$ concentrations should result in the reduction of nitrite generation. Batch testing (Figure 4-7) showed this general correlation between NO_2^- generation and $NaNO_3$ concentration for 0.8-1.9 M $NaNO_3$.[5]

Moles of NO_2^- (Table 4-3) were divided by the corresponding moles of Al dissolved in solution (Table 4-10) to yield NO_2^- generation to Al dissolution molar ratios shown in Table 4-16. Two plots of that data are provided in Figure 4-13. The figure on the left includes all of the data from Table 4-16. The figure on the right eliminated the data from Tests 4 which was conducted in a manner different from Tests 1 to 3 and 5. Test 6 was eliminated because of issues with Al and Si solubility resulting from the use of a different alloy. Furthermore, the final proposed flowsheet will be similar to Tests 3 and 5. The figure on the right depicts the nitrite generation as the reaction progresses. Nitrite generation decreases over time and hence with decreasing $NaNO_3$ concentration. This trend is consistent with the batch results. Although there are several negative values in Table 4-16, all of the negative values appear in the shaded cells, which correspond to the perceived cessation of Al dissolution. Consequently, fluctuations in the nitrite data due to analytical uncertainty result in negative values.

Table 4-16. Nitrite Generation to Aluminum Dissolution Molar Ratios

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	NO_2^--to-Al	Time (min)	NO_2^--to-Al	Time (min)	NO_2^--to-Al	Time (min)	NO_2^--to-Al	Time (min)	NO_2^--to-Al	Time (min)	NO_2^--to-Al
36	0.056	30	0.040	30	0.037	30	---	30	0.054	20	0.750
60	0.035	60	0.048	60	0.051	60	---	60	0.045	45	0.488
90	0.031	90	0.028	94	0.036	94	0.015	90	0.031	75	0.541
120	0.019	120	0.011	122	0.013	122	0.029	120	0.028	98	0.340
150	0.010	150	0.016	150	0.019	148	0.046	150	0.042	135	0.112
186	0.011	180	0.012	180	0.000	180	0.053	184	0.038	165	---
240	0.006	210	0.007	210	0.019	210	0.056	210	0.022	195	---
270	0.005	240	0.007	240	0.008	240	0.011	240	0.023	225	---
300	0.000	275	-0.024	270	0.001	270	0.003	270	0.006	270	---
330	-0.015	305	-0.021	300	0.002	300	-0.043	285	-0.032	315	---
360	-0.010	---	---	330	-0.036	330	0.033	---	---	---	---
390	-0.008	---	---	---	---	360	0.000	---	---	---	---
420	0.004	---	---	---	---	---	---	---	---	---	---
Avg = 0.019#		**Avg = 0.022#**		**Avg = 0.022#**		**Avg = 0.024#**		**Avg = 0.038#**		**Avg = 0.421#**	

Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution
Average values calculated by dividing total number of moles of NO_2^- generated by the moles (calculated from the mass) of Al in the initial samples (Table 3-1).

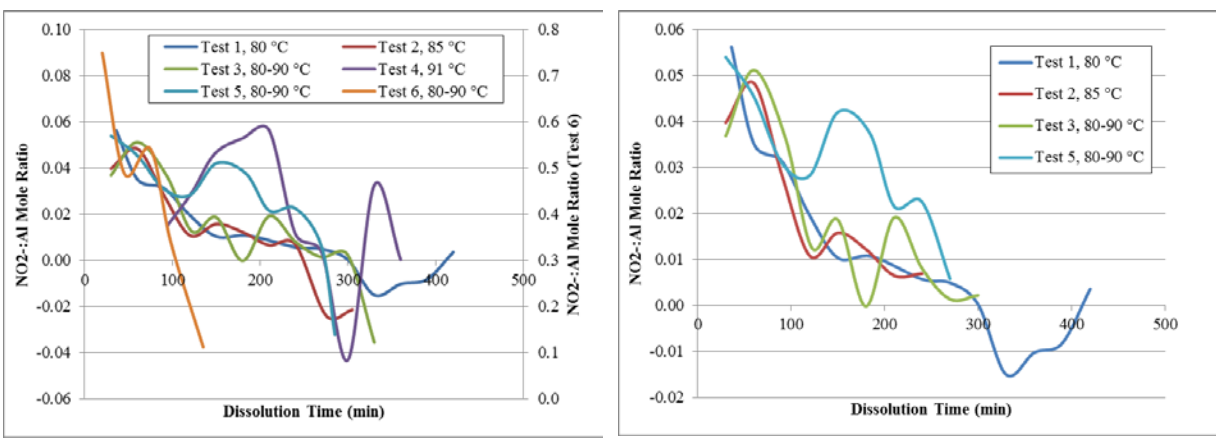


Figure 4-13. Nitrite Generation to Aluminum Dissolution Molar Ratios

When the nitrite-to-Al ratio is plotted as a function of $NaNO_3$ concentration (Figure 4-14), Tests 1 to 3 show the expected trend of nitrite generation decreasing with $NaNO_3$ concentration. Tests 4 and 5 do not show the same trends. The initial stages of Test 5 (at 0 to 120 min when $NaNO_3$ is highest) exhibit the expected decreasing behavior, but increased at 150 min and 184 min. The reason for the increase is not known and cannot be attributed to low quantities of Al dissolution. Test 4 does not follow the trend, but the different method for adding NaOH can be a significant factor.

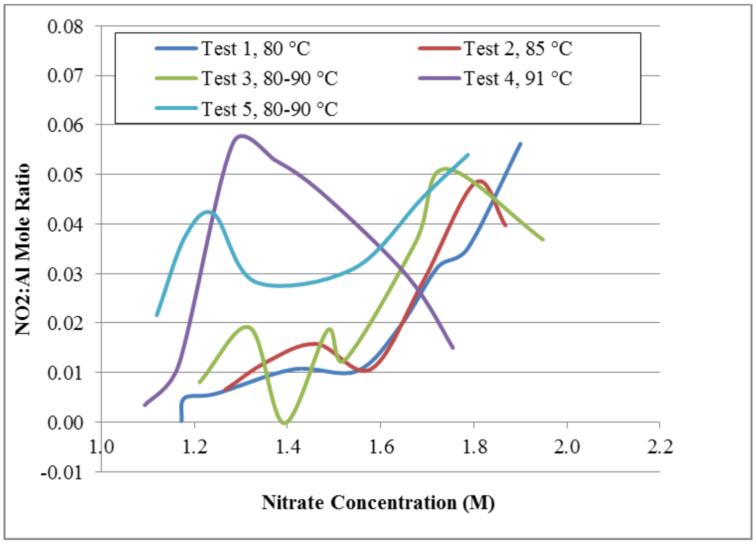


Figure 4-14. NO_2^-:Al Molar Ratios versus Nitrate Concentration

The average NO_2^--to-Al ratios for Tests 1 to 4 are essentially the same (0.022) and agree with the values reported from the batch dissolution studies. It is not understood why Test 4 performed in a manner similar to Tests 1 to 3 when this was not the case for NH_3 and H_2 generation. Test 5, which was performed with a piece of pipe rather than disks shows a 73% increase in NO_2^- generation. Although this might suggest that the pipe sample contains significantly more Si than the disk samples (Alloy 6063 contains 0.2-0.6 wt % Si, see Table 3-3), the data in Appendix 8.4.10 do not support that conclusion. Furthermore, all other Test 5 data indicate the nitrate concentrations should have been similar to Tests 1 to 3. Test 6 with the high-Si 4043 alloy produced almost 20 times more NO_2. It should be noted that Alloy 4043 contains 10-15 times more Si than Alloy 6063.

4.4.2 Reactant Consumption Measurements

Of the two primary reactants that can be tracked analytically, nitrate and hydroxide, the nitrate data is of higher quality. In addition, nitrate is an important component in that its concentration affects the generation of NH_3 and NO_2^-. However, even the nitrate analyses have their limitations because the nitrate concentrations (60,000-126,000 mg/L) and the associated uncertainty of the analyses (10%) are comparable to the magnitude of nitrate change between samples.

The data from Table 4-4 were divided by the corresponding data in Table 4-10 to yield Table 4-17. Two plots of that data are provided in Figure 4-15. The figure on the left includes all of the data from Table 4-17. The figure on the right eliminated the data from Tests 4 which was conducted in a manner different from Tests 1 to 3 and 5. Test 6 was eliminated because of issues associated with Al and Si precipitation resulting from the use of a different alloy. Furthermore, the final proposed flowsheet will be similar to Tests 3 and 5. The figure on the right shows a consistent molar ratio consumption of nitrate with aluminum dissolution throughout testing.

The average NO_3^--to-Al ratios for Tests 1 to 3 were comparable, and the average of these values (0.409) is used for comparisons. Test 5 was a 19% higher than Tests 1 to 3, but the reason is not known. Perhaps there are significant differences in the quantities of impurities present in the pipe sample compared to the disk samples. All experiments were completed at comparable $NaNO_3$ concentrations. As was seen for Test 4 nitrite generation, there was correspondingly larger nitrate consumption (42%) compared to Tests 1 to 3. During batch testing, due to magnitude of nitrate consumption being less than the method uncertainty, the nitrate consumption per mole of Al was reported based on calculation rather than analysis.

The measured data from these experiments is about 30-40% higher than the batch data calculations. Test 6 with the high-Si 4043 alloy consumed 80% more NO_3^-, which was ultimately converted to the large quantity of NO_2^- formed (Table 4-3).

Table 4-17. Nitrate Consumption to Aluminum Dissolution Molar Ratios

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	NO_3^--to-Al	Time (min)	NO_3^--to-Al	Time (min)	NO_3^--to-Al	Time (min)	NO_3^--to-Al	Time (min)	NO_3^--to-Al	Time (min)	NO_3^--to-Al
36	0.558	30	0.440	30	0.322	30	---	30	0.778	20	0.997
60	0.581	60	0.131	60	0.869	60	---	60	0.258	45	1.432
90	0.216	90	0.428	94	0.266	94	0.113	90	0.579	75	0.322
120	0.348	120	0.333	122	0.495	122	0.392	120	0.696	98	0.603
150	0.437	150	0.594	150	0.181	148	2.551	150	0.246	135	0.369
186	0.899	180	0.410	180	0.355	180	0.986	184	0.159	165	---
240	0.390	210	0.334	210	0.310	210	0.901	210	0.528	195	---
270	0.332	240	0.235	240	0.698	240	0.700	240	0.485	225	---
300	-0.125	275	1.043	270	0.210	270	0.414	270	0.480	270	---
330	0.921	305	0.839	300	0.310	300	0.616	285	0.367	315	---
360	0.570	---	---	330	3.548	330	-1.338	---	---	---	---
390	0.388	---	---	---	---	360	0.481	---	---	---	---
420	0.019	---	---	---	---	---	---	---	---	---	---
Avg = 0.412#		**Avg = 0.393#**		**Avg = 0.423#**		**Avg = 0.583#**		**Avg = 0.486#**		**Avg = 0.742#**	
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution # Average values calculated by dividing total number of moles of NO_3^- consumed by the moles (calculated from the mass) of Al in the initial samples (Table 3-1).											

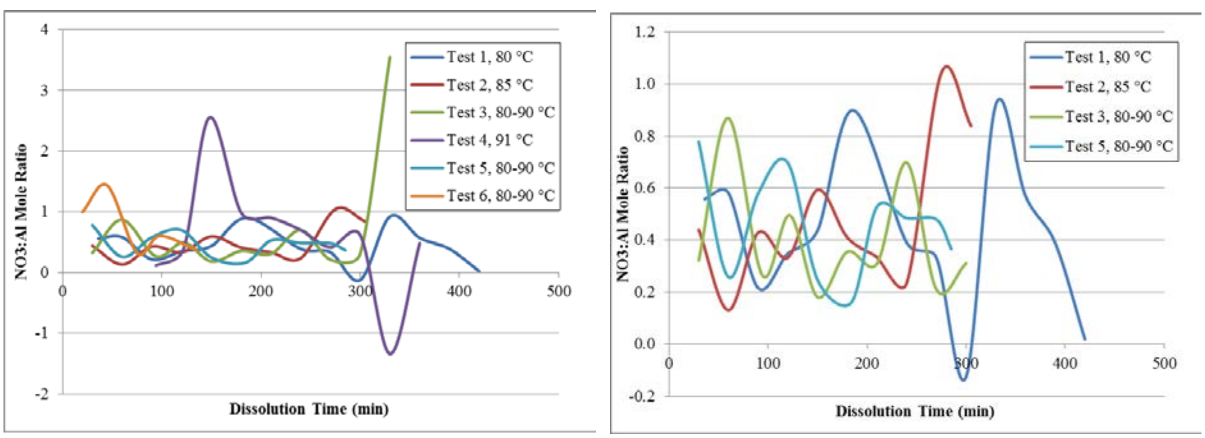


Figure 4-15. Nitrate Consumption to Aluminum Dissolution Molar Ratios

During the dissolution of Al-Si alloys, hydroxide is consumed (Reactions 1 to 3 and 5) As was shown in Section 4.2.2, for these experiments the best method for tracking free hydroxide consumption was the measurement of other base formation. During batch testing, the analyses showed a consistent other base formation of 1.0-1.3 moles of OH^- per mole of Al dissolved, although there were several outliers. The data for these experiments are provided in Table 4-18 and Figure 4-16. Unfortunately, the data show no clear trends and lack the consistency required for meaningful conclusions. Furthermore, the variability in the analytical method produces several negative values which have no technical relationship to the known Al dissolution mechanisms. Consequently, the only data of significant value are the average moles of other base formation per mole of dissolved Al, and even these have an appreciably more scatter than any of the other analytical methods discussed previously.

Table 4-18. Other Base Formation to Aluminum Dissolution Molar Ratios

Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Time (min)	Base-to-Al	Time (min)	Base-to-Al	Time (min)	Base⁻-to-Al	Time (min)	Base-to-Al	Time (min)	Base-to-Al	Time (min)	Base-to-Al
36	1.388	30	1.070	30	1.192	30	---	30	1.545	20	1.515
60	1.260	60	0.332	60	-0.045	60	---	60	0.079	45	0.862
90	-0.302	90	0.494	94	0.659	94	0.712	90	2.907	75	0.262
120	0.072	120	0.809	122	0.440	122	1.752	120	1.543	98	0.373
150	-0.092	150	1.592	150	0.316	148	-2.647	150	0.708	135	0.378
186	0.596	180	0.493	180	0.561	180	-1.039	184	-0.875	165	---
240	0.251	210	-0.056	210	1.074	210	2.541	210	3.794	195	---
270	-0.438	240	2.163	240	-0.148	240	0.256	240	1.430	225	---
300	2.544	275	4.003	270	0.022	270	0.013	270	-8.129	270	---
330	0.730	305	3.181	300	0.810	300	1.388	285	-15.135	315	---
360	-1.049	---	---	330	11.258	330	1.709	---	---	---	---
390	0.044	---	---	---	---	360	3.815	---	---	---	---
420	0.352	---	---	---	---	---	---	---	---	---	---
Avg = 0.507#		**Avg = 0.900#**		**Avg = 0.577#**		**Avg = 0.867#**		**Avg = 1.206#**		**Avg = 1.247#**	
Shaded cells designate end of NH_3 generation, which may coincide with cessation of Al metal dissolution # Average values calculated by dividing total number of moles of other base generated (Table 4-5) by the moles (calculated from the mass) of Al in the initial samples (Table 3-1).											

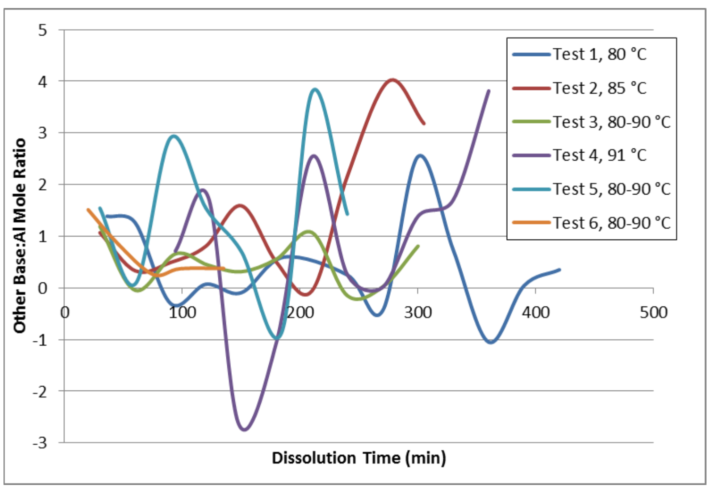


Figure 4-16. Other Base Formation to Aluminum Dissolution Molar Ratios

4.4.3 Precipitation and Residual Solids

In every experiment, there were undissolved solids in the dissolver vessel at the conclusion of testing. During batch testing, an undissolved solid sample was analyzed.[5] It contained Al (as bayerite, β-$Al(OH)_3$), Na, and the minor alloy components (Fe, Mg, Si, Zn). A picture of the residues after dissolution from Test 1 is provided in Figure 4-17. The solids shown in Figure 4-17 were typical for all experiments. As the solids remained in solution for greater than 24 hours, the bayerite (dark solid) began to be converted to gibbsite (γ-$Al(OH)_3$, white solid). For each test, the volume of dissolver solution (before filtration) and the volume of residues before conversion to gibbsite are provided in Table 4-19. To measure the residue volume, the contents of the dissolver vessel were transferred to a 2000-mL graduated cylinder and the residues were allowed to settle overnight. The total and residue volumes were then recorded as a flocculent solid. No efforts were made to measure the dry solids volumes or masses.

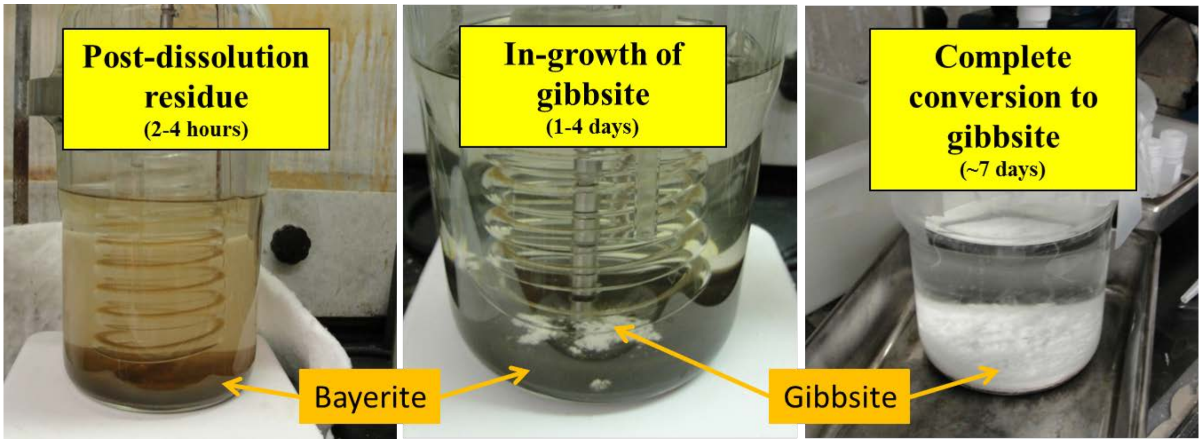


Figure 4-17. Aging of Post-Dissolution Residues

The residue volumes for Tests 2 to 4 are similar with the variations possibly being a function of settling time. Depending on the time of completion for a particular test, overnight might represent 3-6 hours difference in settling times. However, the majority of settling should occur such that this factor does not explain the variations in residue volumes. It is not known why Test 5 contained significantly fewer residues when it involved the dissolution of more sample mass under conditions comparable to Test 3.

Table 4-19. Liquid and Settled Residue Volumes at Test Conclusion

Test #	1	2	3	4	5	6
Alloy	6063	6063	6063	6063	6063	4043
Sample Dissolved (g)	~46.5	~46.5	~46.5	~46.5	56.86	38.38
Liquid Vol (mL)	1150	1125	1150	1270	1404	1120
Residue Vol (mL)	---	130	85	80	48	45
Note: Settled solids volume determined after allowing solids to settle overnight						

The solutions and residues from these tests were provided to the filtration development task.[12] The characterization of the solids and their impact on filtration will be reported as a component of that study. The variability of the data in Table 4-19 underscores the need to recognize that the measured residue volumes should not be used as a metric for equipment design or critical technical decisions. They merely provide an order-of-magnitude measure of residue volumes.

4.5 Engineering Considerations

4.5.1 Flammable Gas Considerations

Based on the results from Test 5, the dissolution cycle can likely be completed in six hours. This means that all flammable gases will be released over a shorter period of time compared to the ORNL cycle times (for a full Mark-18A target).

Hydrogen generation for Test 6 (with Alloy 4043 at 4.5-6.0 wt % Si), which will be conservative for the Mark-18A target (calculated at ~3.5 wt % Si), yielded 0.111 mol H_2 per mole of Al dissolved (Table 4-15). This equates to 0.41 mol H_2 per 100 g of 4043 alloy. Dissolution batch sizes of one-fourth of a target will contain approximately 932 g (or 34.5 mol) of Al alloy. The total H_2 generation for the target material mass (assuming an Alloy 4043 composition) would be 3.83 mol, or 7736 mg. This translates into an hourly rate of 1290 mg/h for dissolving the target in six hours. It is estimated that 3.5 wt % Si-95.5 wt % Al will yield ~20% less H_2 than Alloy 4043.

In the case of NH_3, approximately 90-95% of the released NH_3 absorbs into the dissolver solution. The net quantity released during Test 6 was 537 mL from 38.4 g of Al, or about 0.0169 mol NH_3 per mole of Al metal. This equates to 0.063 mol NH_3 per 100 g of 4043 alloy. Note that this differs from the Test 6 value in Table 4-14 because the data in that table accounts for all NH_3 generated, both absorbed in solution as NH_4^+ and released as NH_3 gas. The total NH_3 released for the duration of dissolving one-fourth of a target (34.5 mol Al) will be 0.58 mol. Because the flammability range for NH_3 is 16-25% and the amount of NH_3 released (0.58 mol) compared to H_2 released (3.83 mol) is small, NH_3 is a much lower flammability issue than H_2. Consideration must be given to whether a composite lower flammability level calculation is warranted.

4.5.2 Vessel Heating and Cooling

During target dissolution at ORNL, a full target was processed at a time at a dissolver temperature of 90-95 °C while limiting the reaction by limiting NaOH addition. The initial dissolver solution contained no NaOH. For a full target, it was common at ORNL for the target dissolution to be limited by temperature and heat generation. However, there are some distinct differences between ORNL and the SRNL flowsheet and operating approaches which include a) temperature, b) cycle time, c) initial NaOH concentration, and d) NaOH addition rate.

It is proposed that SRNL will process one-fourth of a Mark-18A at a time. The dissolution flowsheet operates at 80 °C for about 120 min, increased to 85 °C for 90 min, then 90 °C for the remainder of the process cycle (estimated to be 150 min). The initial solution contains 2.1 M $NaNO_3$ and 0.425 M NaOH, which allows adequate dissolution at a lower process temperature. Sodium hydroxide is then added gradually over 4 to 5 hours to maintain sufficient NaOH concentration to sustain the dissolution rate. This approach suppresses the initial dissolution rate and enables the rate to be more uniform throughout the process cycle. Test 5 entailed the dissolution of 56.9 g of sample. During that test (and all six tests), the coil inside the dissolution vessel was not used for cooling. Rather, it was operated within 10 °C of the initial dissolution temperature (80 °C). The coil was a major source of putting heat into the system to compensate for the heat being lost through the side walls.

The use of a lower initial dissolution temperature than ORNL (90-95 °C) results in reduced heat generated from the reaction when the Al dissolution rates are the highest. As the test progressed and the dissolution rate decreased, additional heat was supplied to the system through the coil as it was operated within 5 °C of the dissolution temperature. The test data (Table 4-12) show fairly uniform Al dissolution (and therefore heat generation) rates across the dissolution cycle. This also produces more-uniform H_2 generation rates (Table 4-15).

The operation in the SRNL Shielded Cells Facility will dissolve approximately 15 to 20 times more aluminum in the same general time frame. The dissolution vessel will have 5 to 8 times more surface area. Also, the materials of construction are likely to be metal instead of glass, which will more readily lose heat to the surroundings. Calculations will be completed when the vessel is designed and fabricated, but current experience indicates that the SRNL dissolution approach should not be limited by heat generation.

4.5.3 Vessel Mixing

Considerations should be given circulation of solution in the dissolution vessel. Testing described in this report benefited from process solutions having ready access to the sample surface. In particular, the pipe sample tested was 2.5 cm tall. The actual Mark-18A target materials (one-fourth of a target) will be approximately 15 times taller. Consequently, the natural mixing that will occur due to gas generation must be augmented by a means of solution circulation to maintain uniform solution concentrations in the dissolution vessel, especially at the inside surface of the target. Failure to do so could potentially reduce the rate of material dissolution while increasing the relative quantity of H_2 gas released.

5.0 Conclusions

Using the lessons learned from batch dissolution testing, a continuous dissolution flowsheet has been successfully demonstrated using prototypic-shaped materials (pipe sample) and chemically-conservative materials (Alloy 4043 rods). The SRNL target dissolution flowsheet departs from the baseline ORNL flowsheet in two significant ways. First, the initial dissolver solution contains 0.425 M NaOH (compared to none for ORNL). This facilitates faster initial reaction rates at a given temperature. This effect of having NaOH present at the outset enables the second difference – starting at 80 °C (compared to 90 to 95 °C for ORNL) and incrementally increasing the temperature to a final temperature of 90 °C. This processing approach suppresses the initial dissolution rate and results in uniform dissolution rates across a process cycle. The SRNL approach enables NaOH to be added at a constant rate (versus being regulated as the temperature-controlling agent for ORNL), which simplifies operations in the shielded cells. In all six continuous dissolution tests, the process was easy to control with minimal operator interface.

Multiple tests indicate that the total time at the dissolution temperatures will be about six hours (versus 18 to 24 hours for ORNL). Although ORNL dissolved a full target and SRNL is planning for one-fourth of a target, the target thickness is the same, which is comparable to the thickness of the pipe samples dissolved in these studies. The shorter dissolution time provides the benefit of a single-shift dissolver operation. Off gas sampling has measured the quantities of flammable H_2 and NH_3 that can be expected in the process off gas. It will be necessary to calculate a composite lower flammability limit to factor the effects of a H_2-NH_3-air mixture.

Specifically, the proposed flowsheet for dissolution of one-fourth of a Mark-18A target is as follows. Insert the target section into 20 L of 2.1 M $NaNO_3$-0.425 M NaOH. Heat the dissolver solution to 80 °C. When the dissolver solution reaches 75 °C, initiate feeding 5 L of 10 M NaOH at 15-20 mL/min. After 80 °C is achieved, hold the dissolver at temperature for 120 min. After 120 min at 80 °C, increase the dissolver temperature to 85 °C for 90 min. Last, increase the dissolver temperature to 90 °C for 150 min before cooling to ambient temperature. A conservative estimate of H_2 gas generation during dissolution (based on dissolution of Alloy 4043) is 3.83 mol (7736 mg). The estimated NH_3 gas release is calculated to be 0.58 mol (9877 mg).

Analyses of process solutions throughout the experiments provide a better understanding of the overall system behavior and the process mass balance. The data show very consistent behavior across several similar but different test conditions. Between the batch-test and continuous-test data, if future changes to the flowsheet are required, sufficient data exist to adequately predict how the system will respond to those changes. Furthermore, the quantity of data from batch and continuous dissolution testing presents an opportunity to develop a kinetic model for predicting reaction progress as a function of composition and temperature.

6.0 Future Work

Future work will focus on design, fabrication, and evaluation of a system for dissolution of one-fourth of a Mark-18A target. The process parameters are adequately understood and the system can be operated safely. Although process cycle times can be estimated from the data in this report, full-scale testing will be required to refine the process operation. The system design will first be tested in a laboratory environment to validate experimental results at the next scale of equipment development. After successful demonstration, the equipment will be transferred to the shielded cells mock-up shop to evaluate the suitability of the design and operation of the unit in a remote handling environment.

Consideration should also be given to the development of a kinetic model to predict reaction behavior for process changes or for tracking dissolution during processing of actual Mark-18A targets.

7.0 References

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[1]

8.0 Appendix – Process Data and Calculations

8.1 Gas Volume, Flow, and Concentration Calculations

1. The gas volumes measured as a function of time are adjusted based on the system pressure as indicated by the manometer readings (see Table 8-1, Columns 3 to 8)
2. The gas flow rate for a given time frame is calculated by dividing the change of volume since the last measurement by the change in time (see Table 8-1, Columns 2 and 9)
3. When Raman samples were collected every 60 seconds, if the gas volume readings were more than one minute apart, a linear interpolation was applied based on the two nearest flow rate measurements. (See Table 8-2) where the pink-shaded times indicate an interpolated value and the white-shaded times the measured value from Table 8-1). The results from the Raman spectrometer in Table 8-3 are reported in volume percent.
4. Corrections are made to the gas data to compensate for times when the gas collection apparatus was vented.

Gas Volume Calculations

$$Uncorrected\ Gas\ Volume\ (mL) = \frac{\pi d^2}{4} h$$

Where, *d* is the diameter (5.877 cm) of the column in cm, and *h* is the height in cm of the water in the column (displaced by the gas in the Tedlar® bag).

The derivation of the pressure corrected gas volume is shown below.

Boyle's law states that pressure and volume of an ideal gas have an inverse relationship, when temperature is held constant. The gas generated is assumed to behave ideally, and since the small change in temperature of the system has a negligible effect on the volume, temperature is assumed to be held constant.

Therefore,

$$Pressure\text{–}\ Corrected\ Gas\ Volume = Uncorrected\ Gas\ Volume * \left(\frac{P_1}{P_2}\right)$$

where, $P_2 = P_{atm}$

$$P_1 = P_{atm} + P_{gauge}$$

$$P_{gauge} = \frac{manometer\ high\ reading - monometer\ low\ reading}{2.54\ cm/in}$$

Where, manometer readings are in cm, and P_{gauge} is in inH_2O.

Assuming the pressure in the lab is at 1 atm, the pressure-corrected gas volume can be derived as

$$Pressure\text{–}\ Corrected\ Gas\ Volume$$
$$= Uncorrected\ Gas\ Volume * \left(\frac{P_{atm} + (P_{gauge} * \frac{1\text{ psi}}{27.7\text{ inH}_2\text{O}} * \frac{1\text{ atm}}{14.696\text{ psi}}}{P_{atm}}\right)$$

Gas Volume Calculation with Post-Vent Adjustment

Gas generated from dissolution filled the water-submerged Tedlar® bag which expanded and forced water to rise in the graduated column. The Tedlar® bag was periodically vented to the hood exhaust to prevent water from overflowing the column. The following approach was implemented to calculate the gas volume after venting the bag.
Venting lowered the water to a certain height on the column. This height was adjusted to a 0 mm baseline for gas volume calculation purposes.

The uncorrected gas volume was calculated as mentioned above using the adjusted water height on the column.

The pressure-corrected gas volume was also calculated as mentioned above.

To account for the volume of gas being generated for the minute while venting the system, the average gas generation rate over the last three readings (normally six minutes) prior to venting was added to the pressure-corrected gas volume calculation.

$$Post\text{–}\ Vent\ Pressure\text{–}\ Corrected\ Gas\ Volume = Pressure\text{–}\ Corrected\ Gas\ Volume + \mu_{gen}$$

where, μ_{gen} is the average gas generation rate over the last three readings prior to venting in units of mL/min.

Gas Volume Calculation with Post-Sample Adjustment

After each liquid sample was taken, N_2 gas was fed into the dissolver vessel via the sample port to flush the remaining liquid in the sample port back down into the dissolver vessel. The water rise in the graduated column due to the quick addition of N_2 gas into the system was measured. The measured rise due to the addition of N_2 was subtracted from the subsequent readings of the water height in the column when calculating the uncorrected gas volume.

Table 8-1. Test 5 Gas Height and Pressure Measurements

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9	**Column 10**
notes	Time (min)	Gas Height (cm)	Corrected gas height (cm)	Manometer High (cm)	Manometer Low (cm)	Uncorrected Gas Volume (mL)	System Pressure (in. H2O)	Corrected Gas Volume (mL)	**Gas Generation (mL/min)**
hotplate 78 C	2	0.8	0.0	43.2	22.3	0.00	8.23	0.00	
chiller 73 C	3	1.4	0.6	43.6	21.8	16.28	8.58	16.62	**16.62**
NaOH pump on	4	2.0	1.2	44.3	21.1	32.55	9.13	33.28	**16.66**
@ 2:30	5	2.8	2.0	44.8	20.6	54.25	9.53	55.52	**22.24**
	6	3.6	2.8	45.3	20.0	75.96	9.96	77.81	**22.29**
	7	4.5	3.7	46.3	19.1	100.37	10.71	103.01	**25.20**
	8	5.7	4.9	46.8	18.6	132.92	11.10	136.55	**33.54**
	9	6.6	5.8	47.5	17.8	157.34	11.69	161.85	**25.31**
	10	7.7	6.9	48.2	17.1	187.18	12.24	192.80	**30.95**
	11	9.0	8.2	49.3	16.3	222.44	12.99	229.54	**36.73**
	12	10.0	9.2	49.9	15.5	249.57	13.54	257.87	**28.33**
	13	11.0	10.2	50.6	14.7	276.69	14.13	286.30	**28.43**
	14	11.8	11.0	51.3	14.1	298.40	14.65	309.13	**22.83**
	15	12.8	12.0	51.7	13.7	325.52	14.96	337.48	**28.35**
chiller 72 C	16	13.6	12.8	52.2	13.2	347.22	15.35	360.32	**22.83**
	17	14.3	13.5	52.6	12.8	366.21	15.67	380.31	**19.99**
Removed blanket	18	14.7	13.9	52.8	12.6	377.06	15.83	391.72	**11.41**
	19	15.1	14.3	53.0	12.4	387.92	15.98	403.14	**11.42**
hotplate 79 C	20	15.5	14.7	53.4	12.0	398.77	16.30	414.73	**11.59**
	21	15.8	15.0	53.7	11.7	406.90	16.54	423.43	**8.70**
chiller 73 C	22	16.2	15.4	53.9	11.5	417.75	16.69	434.88	**11.45**
hotplate 80 C	23	16.5	15.7	54.0	11.4	425.89	16.77	443.44	**8.55**
Added blanket	24	16.8	16.0	54.4	11.0	434.03	17.09	452.24	**8.81**
hotplate 78 C	25	17.2	16.4	54.9	10.5	444.88	17.48	463.98	**11.74**
	26	17.8	17.0	55.3	10.1	461.16	17.80	481.31	**17.33**
	27	18.3	17.5	55.5	9.9	474.72	17.95	495.65	**14.34**
	28	18.7	17.9	55.9	9.5	485.57	18.27	507.36	**11.70**
	29	19.2	18.4	56.2	9.2	499.14	18.50	521.82	**14.46**
	30	19.5	18.7	56.8	8.6	507.27	18.98	530.91	**9.10**
hotplate 79 C	31	19.7	18.9	57.0	8.4	512.70	19.13	536.79	**5.88**
vent	32	0.0	0.0	41.5	23.9	0.00	6.93	546.60	**9.81**
	33	0.4	0.4	42.2	23.2	10.85	7.48	557.65	**11.05**
chiller 73.5 C	34	0.6	0.6	42.7	22.7	16.28	7.87	563.19	**5.54**
	35	0.9	0.9	42.9	22.5	24.41	8.03	571.50	**8.30**
	36	1.2	1.2	43.2	22.2	32.55	8.27	579.82	**8.32**
chiller 74 C	37	1.5	1.5	43.6	21.8	40.69	8.58	588.15	**8.33**
	38	1.8	1.8	43.8	21.6	48.83	8.74	596.48	**8.33**
	39	2.1	2.1	44.0	21.4	56.97	8.90	604.81	**8.33**
	40	2.4	2.4	44.4	21.0	65.10	9.21	613.18	**8.37**
chiller 75 C	41	2.7	2.7	44.6	20.8	73.24	9.37	621.53	**8.35**
	42	3.0	3.0	44.9	20.5	81.38	9.61	629.90	**8.37**
	43	3.4	3.4	45.0	20.4	92.23	9.69	641.03	**11.12**
	44	3.7	3.7	45.3	20.1	100.37	9.92	649.42	**8.39**
	45	4.1	4.1	45.6	19.8	111.22	10.16	660.60	**11.18**
	46	4.4	4.4	45.7	19.7	119.36	10.24	668.96	**8.36**
	47	4.7	4.7	46.2	19.2	127.50	10.63	677.43	**8.47**
	48	5.0	5.0	46.3	19.1	135.63	10.71	685.80	**8.38**
	49	5.3	5.3	46.5	18.9	143.77	10.87	694.21	**8.41**
	50	5.6	5.6	46.8	18.6	151.91	11.10	702.66	**8.44**
	51	5.9	5.9	47.0	18.4	160.05	11.26	711.08	**8.42**
	52	6.2	6.2	47.2	18.2	168.19	11.42	719.51	**8.43**
	53	6.4	6.4	47.4	18.0	173.61	11.57	725.15	**5.64**
	54	6.7	6.7	47.5	17.9	181.75	11.65	733.55	**8.40**
	55	6.9	6.9	47.6	17.8	187.18	11.73	739.17	**5.62**
	56	7.2	7.2	47.7	17.7	195.31	11.81	747.58	**8.41**
+60 mL NaOH	57	7.4	7.4	48.0	17.4	200.74	12.05	753.28	**5.70**
	58	7.7	7.7	48.1	17.3	208.88	12.13	761.70	**8.42**
chiller 75.5 C	59	7.9	7.9	48.3	17.1	214.30	12.28	767.37	**5.67**
	60	8.2	8.2	48.5	16.9	222.44	12.44	775.84	**8.47**

Note: Change in shading indicates where gas bag was vented and appropriate corrections applied.

Table 8-2. Test 5 Gas Flow Rate Interpolations

Time (min)		2	3	4	5	6	7	8	9	10
Gas Generation (mL/min)			**16.62**	**16.66**	**22.24**	**22.29**	**25.20**	**33.54**	**25.31**	**30.95**
Integral Step										
Time (min)	11	12	13	14	15	16	17	18	19	20
Gas Generation (mL/min)	**36.73**	**28.33**	**28.43**	**22.83**	**28.35**	**22.83**	**19.99**	**11.41**	**11.42**	**11.59**
Integral Step										
Time (min)	21	22	23	24	25	26	27	28	29	30
Gas Generation (mL/min)	**8.70**	**11.45**	**8.55**	**8.81**	**11.74**	**17.33**	**14.34**	**11.70**	**14.46**	**9.10**
Integral Step										
Time (min)	31	32	33	34	35	36	37	38	39	40
Gas Generation (mL/min)	**5.88**	**9.81**	**11.05**	**5.54**	**8.30**	**8.32**	**8.33**	**8.33**	**8.33**	**8.37**
Integral Step										
Time (min)	41	42	43	44	45	46	47	48	49	50
Gas Generation (mL/min)	**8.35**	**8.37**	**11.12**	**8.39**	**11.18**	**8.36**	**8.47**	**8.38**	**8.41**	**8.44**
Integral Step										
Time (min)	51	52	53	54	55	56	57	58	59	60
Gas Generation (mL/min)	**8.42**	**8.43**	**5.64**	**8.40**	**5.62**	**8.41**	**5.70**	**8.42**	**5.67**	**8.47**
Integral Step										
Time (min)	61	62	63	64	65	66	67	68	69	70
Gas Generation (mL/min)	**2.88**	**5.77**	7.12	**8.47**	7.77	**7.08**	7.81	**8.54**	8.55	**8.56**
Integral Step			0.5		0.5		0.5		0.5	
Time (min)	71	72	73	74	75	76	77	78	79	80
Gas Generation (mL/min)	7.85	**7.14**	7.83	**8.52**	8.54	**8.56**	8.59	**8.61**	8.58	**8.55**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	81	82	83	84	85	86	87	88	89	90
Gas Generation (mL/min)	8.58	**8.60**	9.35	**10.10**	9.35	**8.59**	8.66	**8.73**	7.26	**5.78**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	91	92	93	94	95	96	97	98	99	100
Gas Generation (mL/min)	6.54	**7.30**	7.26	**7.22**	7.24	**7.27**	8.04	**8.80**	8.78	**8.77**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	101	102	103	104	105	106	107	108	109	110
Gas Generation (mL/min)	8.83	**8.89**	8.87	**8.86**	8.84	**8.82**	10.45	**12.09**	13.61	**15.12**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	111	112	113	114	115	116	117	118	119	120
Gas Generation (mL/min)	16.03	**16.95**	17.68	**18.42**	20.32	**22.23**	22.27	**22.32**	21.66	**21.00**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	121	122	123	124	125	126	127	128	129	130
Gas Generation (mL/min)	19.65	**18.30**	15.51	**12.72**	13.43	**14.14**	13.43	**12.72**	12.03	**11.34**
Integral Step	0.5		0.5		0.5		0.5		0.5	

Time (min)	131	132	133	134	135	136	137	138	139	140
Gas Generation (mL/min)	10.67	**9.99**	9.99	**9.98**	11.40	**12.81**	11.42	**10.02**	10.73	**11.45**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	141	142	143	144	145	146	147	148	149	150
Gas Generation (mL/min)	11.44	**11.43**	10.77	**10.12**	10.11	**10.10**	10.11	**10.12**	9.44	**8.76**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	151	152	153	154	155	156	157	158	159	160
Gas Generation (mL/min)	8.75	**8.74**	9.45	**10.17**	9.55	**8.92**	8.88	**8.84**	9.59	**10.34**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	161	162	163	164	165	166	167	168	169	170
Gas Generation (mL/min)	9.61	**8.88**	8.21	**7.53**	9.77	**12.02**	11.29	**10.57**	9.12	**7.67**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	171	172	173	174	175	176	177	178	179	180
Gas Generation (mL/min)	7.73	**7.80**	8.74	**9.68**	9.70	**9.71**	7.64	**5.56**	7.64	**9.72**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	181	182	183	184	185	186	187	188	189	190
Gas Generation (mL/min)	8.35	**6.97**	7.68	**8.38**	7.69	**7.00**	9.11	**11.22**	8.41	**5.60**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	191	192	193	194	195	196	197	198	199	200
Gas Generation (mL/min)	5.62	**5.63**	6.33	**7.02**	7.03	**7.05**	7.72	**8.40**	10.53	**12.66**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	201	202	203	204	205	206	207	208	209	210
Gas Generation (mL/min)	10.59	**8.51**	11.34	**14.17**	14.20	**14.22**	14.94	**15.67**	19.24	**22.81**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	211	212	213	214	215	216	217	218	219	220
Gas Generation (mL/min)	18.59	**14.36**	13.63	**12.91**	12.22	**11.54**	9.43	**7.33**	9.44	**11.56**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	221	222	223	224	225	226	227	228	229	230
Gas Generation (mL/min)	11.61	**11.66**	14.55	**17.44**	17.54	**17.63**	17.03	**16.42**	16.46	**16.50**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	231	232	233	234	235	236	237	238	239	240
Gas Generation (mL/min)	15.92	**15.33**	15.14	**14.94**	13.70	**12.46**	12.49	**12.51**	11.13	**9.75**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	241	242	243	244	245	246	247	248	249	250
Gas Generation (mL/min)	9.76	**9.77**	9.79	**9.81**	9.12	**8.44**	8.42	**8.41**	8.41	**8.42**
Integral Step	0.5		0.5		0.5		0.5		0.5	
Time (min)	251	252	253	254	255	256	257	258	259	260
Gas Generation (mL/min)	5.63	**2.85**	4.23	**5.62**	3.52	**1.41**	1.41	**1.41**	0.70	**0.00**
Integral Step	0.5		0.5		0.5		0.5		0.5	

Table 8-3. Test 5 Raman Measurements and Component Flow Calculations

Clock Time	8:15:43	8:16:34	8:17:34	8:18:34	8:19:34	8:20:34	8:21:34	8:22:33	8:23:33	8:24:33	8:25:33	8:26:33	8:27:33	8:28:33	8:29:33	8:30:33	8:31:33	8:32:32	8:33:32	8:34:32	8:35:32	8:36:32	8:37:32		
Elapsed Time (min)			0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20		
N2 (vol %)	97.977223	98.05378	97.70149	96.79646	97.90161	97.57107	96.57821	98.341	96.85237	97.7801	95.47065	95.00201	95.76441	93.3894	93.00129	91.73004	89.46722	89.92399	88.92226	89.4014	87.47223	87.50048	86.55128		
O2 (vol %)	0.6202783	0.869445	0.810376	1.857362	0.210465	0.604584	1.153038	-0.0176	0.572526	-0.11179	1.046509	1.163535	-0.60226	0.946539	0.662412	0.947828	1.905775	1.2345	0.969156	0.433929	1.089594	0.175565	0.719068		
N2O (vol %)	0.0366559	-0.05872	0.393225	-0.12926	-0.01022	-0.2709	0.356093	-0.10562	0.072119	-0.69644	0.257139	0.507783	-0.31397	0.530128	0.298545	-0.13287	0.690478	0.112701	0.101912	-0.52345	-0.08572	-0.27327	-0.43627		
H2 (vol %)	-0.094743	-0.18664	0.228038	-0.07248	0.128082	0.139804	0.324726	0.17715	0.628929	1.086114	1.210672	1.340314	2.589718	2.843043	3.7719	4.749049	5.201855	6.210494	7.27482	7.683866	8.417273	9.152253	9.933942		
H2O (vol %)	1.1902334	1.220436	0.89685	1.503067	1.791938	2.002494	1.541845	1.506919	1.809133	1.853603	1.953945	1.732236	2.04624	2.005276	1.907877	2.1921	2.330731	1.896106	1.875873	2.364991	2.205046	2.314808	2.343756		
NH3 (vol %)	0.270352	0.101701	-0.02998	0.044847	-0.02188	-0.04705	0.04609	0.09815	0.06492	0.088415	0.061083	0.254121	0.515854	0.28561	0.357976	0.513854	0.403942	0.622205	0.855979	0.639272	0.901578	1.130167	0.888228		
N2O (vol %) [5 min avg]			0.046337	-0.01518	0.067787	-0.03198	0.008294	-0.12895	-0.02334	0.006996	-0.03467	0.056928	0.255925	0.177923	0.214462	0.299796	0.214153	0.049753	0.059184	-0.13357	-0.24336	-0.16941	-0.02909		
Headspace = 1598 mL - NaOH feed + sampling																									
		1650	1650	1648.8	1647.6	1646.4	1645.2	1644	1642.8	1641.6	1640.4	1639.2	1638	1636.8	1635.6	1634.4	1633.2	1632	1630.8	1629.6	1628.4	1627.2	1626		
Gas Generation Rate (mL/min)	2888.2			**16.60**	**16.60**	**16.62**	**16.66**	**22.24**	**22.29**	**25.20**	**33.54**	**25.31**	**30.95**	**36.73**	**28.33**	**28.43**	**22.83**	**28.35**	**22.83**	**19.99**	**11.41**	**11.42**	**11.59**		
H2 Generated - (vol %)				-29.92	20.03	1.30	18.58	-10.73	33.93	30.87	7.30	9.74	68.71	14.13	57.40	60.92	37.59	64.26	83.29	41.03	113.05	113.85	119.65		
H2 Gen (vol %) [5-min avg]				-4.94	-2.86	2.50	-0.15	12.62	14.79	15.99	14.22	30.11	26.15	31.46	42.18	47.75	46.86	60.69	57.42	67.85	83.10	94.17	95.76		
NH3 Generated (vol %)				7.48	-6.64	-2.54	9.24	3.95	-2.38	1.62	-1.28	12.76	14.37	-9.97	4.54	9.47	-7.46	13.18	17.55	-17.03	38.32	33.69	-33.07		
NH3 Gen (vol %) [5-min avg]				7.48	0.42	-0.57	1.88	2.30	0.32	1.98	2.23	2.93	5.02	3.50	4.08	6.23	2.19	1.95	7.46	3.14	8.91	17.15	7.89		
H2 Gen for Time Period (mL)	Total (mL)	2243.5		-0.82	-0.48	0.42	-0.02	2.81	3.30	4.03	4.77	7.62	8.09	11.56	11.95	13.58	10.70	17.21	13.11	13.56	9.48	10.76	11.09		
Corrected H2 Gen (mL)	Total (mL)	1952.5		0.00	0.00	0.42	0.00	2.81	3.30	4.03	4.77	7.62	8.09	11.56	11.95	13.58	10.70	17.21	13.11	13.56	9.48	10.76	11.09		
NH3 Gen Total (mL)	Total (mL)	688.5		1.24	0.07	-0.09	0.31	0.51	0.07	0.50	0.75	0.74	1.55	1.29	1.16	1.77	0.50	0.55	1.70	0.63	1.02	1.96	0.91		
Corrected NH3 Gen (mL)	Total (mL)	761.6		1.24	0.07	0.00	0.31	0.51	0.07	0.50	0.75	0.74	1.55	1.29	1.16	1.77	0.50	0.55	1.70	0.63	1.02	1.96	0.91		
Clock Time	8:38:32	8:39:31	8:40:31	8:41:31	8:42:31	8:43:30	8:44:30	8:45:30	8:46:30	8:47:29	8:48:29	8:49:29	8:50:29	8:51:28	8:52:28	8:53:28	8:54:28	8:55:28	8:56:27	8:57:27	8:58:27	8:59:27	9:00:27	9:01:27	9:02:27
Elapsed Time (min)	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
N2 (vol %)	84.458348	84.91586	84.41852	82.52073	81.97088	80.89569	80.13617	79.51372	79.74876	78.70945	77.30115	85.6542	80.92709	77.13162	76.49511	74.96277	73.76289	72.19045	72.47486	71.41484	71.60271	72.91574	70.29671	68.73714	69.15081
O2 (vol %)	1.4089211	0.074191	0.355502	1.11627	0.976334	1.738341	1.217791	0.788585	0.411502	0.868852	1.196941	0.714906	-0.24455	2.262257	0.381672	0.997284	1.063825	2.810875	1.610867	1.338282	1.866024	-0.19163	1.425161	1.97007	1.416348
N2O (vol %)	0.4716684	0.178155	-0.0899	0.512382	-0.0026	-0.26356	0.148203	-0.23	0.008476	0.26184	0.160575	0.096319	0.378885	-0.28985	-0.44203	0.500683	0.13953	-0.38435	0.229599	0.960684	-0.55127	-0.17937	0.003011	0.209072	0.10523
H2 (vol %)	10.366986	11.6008	11.97024	12.45399	13.49344	14.58624	15.06102	16.11247	16.10927	16.62892	16.79274	7.678575	13.20753	16.5603	18.64555	19.34768	20.41067	20.37878	21.31986	21.42538	22.5442	23.55001	23.41277	23.90031	24.38738
H2O (vol %)	2.0953006	1.981777	1.822698	1.831835	1.921333	1.944699	1.788288	2.155879	1.741178	2.262389	2.580227	3.673391	3.808881	2.314278	2.555839	2.00534	2.163988	2.228582	2.093939	2.040618	1.518345	1.951435	1.961136	2.113395	1.651408
NH3 (vol %)	1.1987758	1.249218	1.522933	1.564794	1.640621	1.098594	1.648528	1.659352	1.980818	1.268549	1.968369	2.182607	1.922154	2.021389	2.363848	2.186234	2.459102	2.775668	2.270869	2.820194	3.019996	1.953819	2.901203	3.070015	3.288826
N2O (vol %) [5 min avg]	-0.029923	0.127207	0.213941	0.066895	0.060905	0.032884	-0.0679	-0.01501	0.069818	0.059441	0.181219	0.121554	-0.01922	0.048802	0.057444	-0.0952	0.008687	0.289229	0.078838	0.015058	0.09253	0.088425	-0.08267	0.167883	0.22281
									5																
Headspace Volume (mL)	1624.8	1623.6	1622.4	1621.2	1620	1618.8	1617.6	1616.4	1615.2	1619	1617.8	1616.6	1615.4	1614.2	1613	1611.8	1610.6	1609.4	1608.2	1607	1605.8	1604.6	1603.4	1602.2	1601
Gas Generation Rate (mL/min)	**8.70**	**11.45**	**8.55**	**8.81**	**11.74**	**17.33**	**14.34**	**11.70**	**14.46**	**9.10**	**5.88**	**9.81**	**11.05**	**5.54**	**8.30**	**8.32**	**8.33**	**8.33**	**8.33**	**8.37**	**8.35**	**8.37**	**11.12**	**8.39**	**11.18**
H2 Generated - (vol %)	91.24	186.51	82.04	101.48	156.97	116.66	68.62	161.32	15.75	109.12	61.89	-1494.02	821.48	993.32	423.65	155.41	225.82	14.22	202.90	41.69	237.69	216.31	3.63	117.00	94.14
H2 Gen (vol %) [5-min avg]	124.86	118.66	116.18	123.65	128.73	105.15	121.01	103.86	94.29	83.34	-229.19	-97.16	98.36	161.26	179.97	523.94	362.48	204.40	128.01	144.46	142.56	140.45	123.27	133.76	113.01
NH3 Generated (vol %)	59.20	8.40	53.44	9.27	12.11	-49.53	63.68	3.15	37.89	-125.50	194.63	37.48	-36.15	30.93	68.88	-32.23	55.19	63.95	-95.13	108.33	41.44	-202.38	139.45	35.31	34.62
NH3 Gen (vol %) [5-min avg]	16.22	21.31	24.33	19.45	28.48	6.74	17.79	7.74	13.46	-14.06	34.77	29.53	21.67	20.28	59.15	13.78	17.32	37.34	12.13	20.02	34.76	-16.76	-1.66	24.43	9.69
H2 Gen for Time Period (mL)	10.86	13.59	9.94	10.89	15.11	18.22	17.35	12.16	13.64	7.58	-13.47	-9.53	10.87	8.94	14.95	43.58	30.21	17.02	10.67	12.09	11.90	11.76	13.71	11.22	12.63
Corrected H2 Gen (mL)	8.70	11.45	8.55	8.81	11.74	17.33	14.34	11.70	13.64	7.58	0.00	0.00	10.87	5.54	8.30	8.32	8.33	8.33	8.33	8.37	8.35	8.37	11.12	8.39	11.18
NH3 Gen Total (mL)	1.41	2.44	2.08	1.71	3.34	1.17	2.55	0.91	1.95	-1.28	2.04	2.90	2.39	1.12	4.91	1.15	1.44	3.11	1.01	1.68	2.90	-1.40	-0.18	2.05	1.08
Corrected NH3 Gen (mL)	1.41	2.44	2.08	1.71	3.34	1.17	2.55	0.91	1.95	0.00	2.04	2.90	2.39	1.12	4.91	1.15	1.44	3.11	1.01	1.68	2.90	0.00	0.00	2.05	1.08

Clock Time	9:03:26	9:04:26	9:05:26	9:06:26	9:07:26	9:08:26	9:09:26	9:10:25	9:11:25	9:12:25	9:13:25	9:14:25	9:15:25	9:16:25	9:17:25	9:18:25	9:19:25	9:20:25	9:21:25	9:22:24	9:23:24	9:24:24	9:25:24	9:26:24	9:27:24
Elapsed Time (min)	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70
N2 (vol %)	68.390204	68.73554	67.04552	68.08209	67.1943	66.60762	65.82829	65.50992	63.70536	64.20651	63.09284	63.67275	61.00826	63.79502	62.44376	62.03695	59.87421	59.30638	59.39391	59.24498	58.82439	58.66776	58.82252	57.41731	57.84059
O2 (vol %)	1.6263398	-0.21989	2.607046	-0.12225	0.528873	0.585057	1.490928	0.447591	2.025622	1.100776	2.103281	0.286159	2.63601	0.587854	0.579855	1.947325	0.671257	1.101675	2.408092	1.555213	1.322641	0.838572	0.95323	1.307176	1.813719
N2O (vol %)	0.7014747	0.095262	-0.17615	0.306146	0.886206	1.154036	0.269158	-0.07483	0.602501	0.691506	0.104712	0.343331	0.872359	-0.19418	0.138985	-0.33616	0.312991	0.09712	0.133943	0.514589	0.815721	0.668246	0.180108	-0.03664	0.455809
H2 (vol %)	24.957281	25.90179	25.64703	26.55958	25.99955	27.02227	27.67225	28.27113	28.29256	29.087	29.44418	29.95634	29.55182	31.06356	31.15102	30.98837	32.16036	32.63399	31.57694	32.0711	33.13654	33.30838	34.5004	34.90414	34.44194
H2O (vol %)	2.1007087	2.098885	1.563251	1.732757	1.713629	1.975162	2.244958	2.111859	1.794036	1.814746	1.886459	1.778627	1.820836	1.599677	1.678831	1.641522	2.602096	2.652065	2.302034	2.22963	1.696926	2.063948	2.033581	1.949399	2.214874
NH3 (vol %)	2.2239918	3.388411	3.313299	3.441675	3.677447	2.655861	2.494417	3.734339	3.579925	3.099468	3.368528	3.962794	4.110709	3.148067	4.007558	3.721983	4.379083	4.208768	4.185082	4.38448	4.203787	4.453092	3.510164	4.458616	3.233075
N2O (vol %) [5 min avg]	0.1869773	0.206392	0.362588	0.4531	0.487879	0.508143	0.567414	0.528474	0.318609	0.333443	0.522882	0.363546	0.253042	0.164868	0.1588	0.003752	0.069376	0.144497	0.374873	0.445924	0.462521	0.428404	0.416648	0.336187	0.359433
															5										
Headspace Volume (mL)	1599.8	1598.6	1597.4	1596.2	1595	1593.8	1592.6	1591.4	1590.2	1589	1587.8	1586.6	1585.4	1584.2	1588	1586.8	1585.6	1584.4	1583.2	1582	1580.8	1579.6	1578.4	1577.2	1576
Gas Generation Rate (mL/min)	**8.36**	**8.47**	**8.38**	**8.41**	**8.44**	**8.42**	**8.43**	**5.64**	**8.40**	**5.62**	**8.41**	**5.70**	**8.42**	**5.67**	**8.47**	**2.88**	**5.77**	7.12	**8.47**	7.77	**7.08**	7.81	**8.54**	8.55	**8.56**
H2 Generated - (vol %)	133.96	204.25	-22.93	199.81	-79.79	220.57	150.49	197.11	32.35	253.83	96.88	172.54	-46.62	453.46	47.55	-58.54	354.13	138.04	-166.06	132.66	271.15	68.07	254.83	109.41	-50.70
H2 Gen (vol %) [5-min avg]	110.60	105.28	121.84	87.06	104.38	93.63	137.64	104.15	170.87	146.13	150.54	101.79	186.02	144.76	113.68	150.00	186.93	63.02	80.05	145.98	88.77	112.13	167.22	130.55	97.90
NH3 Generated (vol %)	-201.44	223.26	-11.01	27.81	48.22	-190.67	-28.01	353.31	-25.64	-132.82	54.16	169.40	31.96	-265.82	165.16	-153.48	184.90	-33.69	-0.24	44.97	-36.16	54.89	-170.78	179.47	-222.53
NH3 Gen (vol %) [5-min avg]	-38.89	46.24	16.15	14.65	17.37	19.52	-30.73	42.13	31.44	-4.77	44.20	83.68	19.41	-28.62	30.97	-10.56	-7.46	-20.59	32.53	8.49	31.95	5.95	-21.46	14.48	-39.02
H2 Gen for Time Period (mL)	9.25	8.91	10.21	7.32	8.81	7.89	11.60	5.88	14.36	8.21	12.66	5.80	15.66	8.21	9.63	4.32	10.79	4.49	6.78	11.35	6.28	8.75	14.28	11.16	8.38
Corrected H2 Gen (mL)	8.36	8.47	8.38	7.32	8.44	7.89	8.43	5.64	8.40	5.62	8.41	5.70	8.42	5.67	8.47	2.88	5.77	4.49	6.78	7.77	6.28	7.81	8.54	8.55	8.38
NH3 Gen Total (mL)	-3.25	3.91	1.35	1.23	1.47	1.64	-2.59	2.38	2.64	-0.27	3.72	4.77	1.63	-1.62	2.62	-0.30	-0.43	-1.47	2.75	0.66	2.26	0.46	-1.83	1.24	-3.34
Corrected NH3 Gen (mL)	0.00	3.91	1.35	1.23	1.47	1.64	0.00	2.38	2.64	0.00	3.72	4.77	1.63	0.00	2.62	0.00	0.00	0.00	2.75	0.66	2.26	0.46	0.00	1.24	0.00

Clock Time	9:28:24	9:29:24	9:30:24	9:31:24	9:32:24	9:33:24	9:34:24	9:35:24	9:36:24	9:37:24	9:38:24	9:39:24	9:40:24	9:41:24	9:42:24	9:43:24	9:44:24	9:45:24	9:46:25	9:47:25	9:48:25	9:49:25	9:50:25	9:51:25	9:52:25
Elapsed Time (min)	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95
N2 (vol %)	56.669352	57.16372	56.52254	56.18158	56.54622	54.96031	55.13607	54.61272	54.19874	55.12119	52.98363	52.91247	52.96444	51.08335	51.66854	51.27079	49.55494	49.99025	48.91552	49.00207	48.90481	48.74511	47.67607	48.29216	47.14479
O2 (vol %)	1.5519358	1.236246	2.208688	1.51968	1.350436	1.530162	1.593233	1.770034	1.173202	0.714578	1.085501	2.089224	1.234864	3.041496	0.694047	0.59135	2.141802	0.802354	1.42619	1.567075	1.114414	1.245473	1.205744	0.638534	1.316675
N2O (vol %)	0.4134165	0.784473	0.174877	-0.68724	0.818006	0.290949	0.209089	0.984137	0.394185	-0.14052	0.492744	0.075026	0.014887	0.40178	-0.02744	0.131979	0.977573	0.448272	0.689218	-0.16747	1.064058	-0.46119	0.556349	0.663871	0.271596
H2 (vol %)	34.806113	34.85051	35.9652	36.43552	36.30109	37.26944	36.87568	37.4988	37.63535	39.07812	38.47521	38.38089	39.84967	39.42667	40.70749	40.82473	41.22191	41.33089	41.55603	42.1638	41.69571	43.12568	43.19993	44.17097	44.04239
H2O (vol %)	1.9580658	1.304732	1.617152	1.425718	1.297482	1.258743	0.95332	1.398483	1.338029	1.726625	1.619202	1.581633	1.458307	1.576874	1.196997	1.548102	1.504764	1.649334	1.684144	1.631546	1.557297	1.444237	1.467199	1.082776	1.064613
NH3 (vol %)	4.6011167	4.660316	3.511542	5.124737	3.686766	4.6904	5.232605	3.735822	5.260489	3.500008	5.343715	4.96075	4.477827	4.469826	5.760366	5.633051	4.599012	5.778898	5.728904	5.802982	5.663708	5.900692	5.894704	5.151693	6.159934
N2O (vol %) [5 min avg]	0.3583867	0.228268	0.300707	0.276214	0.161137	0.322989	0.539273	0.347569	0.387928	0.361115	0.167265	0.168784	0.191399	0.119246	0.299756	0.386433	0.44392	0.415914	0.60233	0.314577	0.336192	0.331123	0.418936	0.168001	0.388617
																				5					
Headspace Volume (mL)	1574.8	1573.6	1572.4	1571.2	1570	1568.8	1567.6	1566.4	1565.2	1564	1562.8	1561.6	1560.4	1559.2	1558	1556.8	1555.6	1554.4	1553.2	1557	1555.8	1554.6	1553.4	1552.2	1551
Gas Generation Rate (mL/min)	7.85	**7.14**	7.83	**8.52**	8.54	**8.56**	8.59	**8.61**	8.58	**8.55**	8.58	**8.60**	9.35	**10.10**	9.35	**8.59**	8.66	**8.73**	7.26	**5.78**	6.54	**7.30**	7.26	**7.22**	7.24
H2 Generated - (vol %)	107.90	44.64	259.85	123.16	11.59	214.67	-35.01	150.86	62.54	302.86	-71.37	21.26	284.91	-25.85	254.21	62.07	112.58	60.74	89.75	205.75	-69.65	347.82	59.10	253.03	16.51
H2 Gen (vol %) [5-min avg]	93.22	94.22	96.97	109.43	130.78	114.85	93.05	80.93	139.18	81.98	93.23	120.04	102.36	92.63	119.32	137.59	92.75	115.87	106.18	79.83	126.88	126.55	159.21	121.36	177.63
NH3 Generated (vol %)	279.20	17.71	-227.22	302.57	-260.60	188.55	104.21	-268.56	283.32	-318.37	341.25	-64.57	-76.10	3.24	220.89	-17.44	-181.18	215.94	-4.97	25.74	-27.47	56.40	4.61	-154.66	222.02
NH3 Gen (vol %) [5-min avg]	24.05	16.61	5.33	29.95	22.33	4.21	21.51	13.24	9.39	-2.17	28.37	-5.39	33.11	-22.91	84.94	13.20	-10.12	48.29	46.65	7.62	5.61	53.13	10.86	-19.08	20.18
H2 Gen for Time Period (mL)	7.31	6.72	7.59	9.32	11.17	9.84	7.99	6.97	11.95	7.01	8.00	10.32	9.57	9.36	11.15	11.82	8.03	10.11	7.70	4.62	8.30	9.23	11.55	8.76	12.87
Corrected H2 Gen (mL)	7.31	6.72	7.59	8.52	8.54	8.56	7.99	6.97	8.58	7.01	8.00	8.60	9.35	9.36	9.35	8.59	8.03	8.73	7.26	4.62	6.54	7.30	7.26	7.22	7.24
NH3 Gen Total (mL)	1.89	1.19	0.42	2.55	1.91	0.36	1.85	1.14	0.81	-0.19	2.43	-0.46	3.10	-2.31	7.94	1.13	-0.88	4.21	3.38	0.44	0.37	3.88	0.79	-1.38	1.46
Corrected NH3 Gen (mL)	1.89	1.19	0.42	2.55	1.91	0.36	1.85	1.14	0.81	0.00	2.43	0.00	3.10	0.00	7.94	1.13	0.00	4.21	3.38	0.44	0.37	3.88	0.79	0.00	1.46

Clock Time	9:53:25	9:54:25	9:55:25	9:56:26	9:57:26	9:58:26	9:59:26	10:00:26	10:01:26	10:02:26	10:03:27	10:04:27	10:05:27	10:06:27	10:07:27	10:08:27	10:09:28	10:10:28	10:11:28	10:12:28	10:13:28	10:14:29	10:15:29	10:16:29	10:17:29
Elapsed Time (min)	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
N2 (vol %)	48.361534	47.16019	47.0759	46.44935	45.04665	45.55727	44.06241	43.98004	44.13691	42.93426	42.55816	42.93569	41.57848	42.13069	40.67293	39.44575	39.24306	40.00891	38.02544	38.26182	36.59141	35.71362	35.53698	35.23077	35.20406
O2 (vol %)	1.2691212	0.27613	0.501039	0.453136	1.296205	-0.1232	1.329835	0.549085	0.091981	0.842308	1.297142	1.297315	0.3296	-0.03324	1.458321	1.811638	1.248032	1.22763	1.344441	0.21451	1.169649	2.050718	1.170749	1.007786	1.312086
N2O (vol %)	-0.190619	0.641886	-0.09561	-0.32311	0.232482	0.082977	-0.01388	0.259232	-0.11813	0.729122	0.314026	0.367749	0.50625	0.131811	-0.22696	0.594597	0.553124	0.690029	1.055145	0.295954	-0.10107	0.077686	0.745845	0.724312	0.361916
H2 (vol %)	44.825324	45.90521	46.32904	45.30325	45.17801	46.72368	46.79974	47.2127	47.38909	46.95839	47.54372	49.14433	48.87805	49.466	49.62479	49.38433	50.22425	48.75783	49.4993	51.79904	51.30475	51.09556	51.29235	51.30789	53.8458
H2O (vol %)	1.6417745	1.5592	1.682832	1.574593	1.743826	1.220916	1.236399	1.439629	1.64854	1.875317	1.170823	1.45343	1.56746	1.316776	1.068805	1.565241	1.276704	3.507253	2.205647	1.37849	2.004562	1.692981	1.807669	1.785225	1.790621
NH3 (vol %)	4.0928652	4.457386	4.506796	6.542787	6.502824	6.538353	6.585497	6.559319	6.851608	6.660598	7.116128	4.801485	7.140159	6.987971	7.402118	7.198446	7.454825	5.808345	7.870023	8.050187	9.030703	9.369431	9.446413	9.944021	7.485516
N2O (vol %) [5 min avg]	0.2582251	0.060829	0.053006	0.107725	-0.02343	0.047539	0.088536	0.187864	0.234073	0.3104	0.359803	0.409791	0.218576	0.27469	0.311765	0.348521	0.533188	0.63777	0.498635	0.403548	0.414711	0.348544	0.361737	0.530396	0.480069
																									5
Headspace Volume (mL)	1549.8	1548.6	1547.4	1546.2	1545	1543.8	1542.6	1541.4	1540.2	1539	1537.8	1536.6	1535.4	1534.2	1533	1531.8	1530.6	1529.4	1528.2	1527	1525.8	1524.6	1523.4	1522.2	1526
Gas Generation Rate (mL/min)	**7.27**	8.04	**8.80**	8.78	**8.77**	8.83	**8.89**	8.87	**8.86**	8.84	**8.82**	10.45	**12.09**	13.61	**15.12**	16.03	**16.95**	17.68	**18.42**	20.32	**22.23**	22.27	**22.32**	21.66	**21.00**
H2 Generated - (vol %)	211.68	254.02	120.86	-135.28	23.11	317.04	60.00	118.96	78.07	-28.05	149.61	284.40	15.06	115.76	65.72	26.41	126.08	-78.06	111.01	224.58	17.37	36.78	64.72	52.40	238.29
H2 Gen (vol %) [5-min avg]	158.87	171.22	93.56	94.88	115.95	77.15	76.77	119.44	109.21	75.72	120.60	99.82	107.36	126.11	101.47	69.81	51.18	50.23	82.00	80.20	62.34	90.89	79.17	81.91	53.84
NH3 Generated (vol %)	-436.44	74.71	13.20	364.96	-0.54	12.75	14.77	2.01	57.69	-26.60	86.55	-335.40	304.15	-10.17	49.38	-12.26	30.61	-136.58	178.89	21.59	76.34	32.56	14.70	44.92	-171.19
NH3 Gen (vol %) [5-min avg]	-61.61	-57.95	-56.23	47.69	3.18	93.02	81.03	78.79	17.34	12.12	26.88	-43.15	17.28	3.70	18.90	-0.86	72.34	-15.80	22.01	16.45	34.17	34.56	64.82	38.02	-0.53
H2 Gen for Time Period (mL)	11.55	13.76	8.23	8.33	10.17	6.81	6.82	10.60	9.67	6.69	10.64	10.44	12.98	17.16	15.35	11.19	8.67	8.88	15.11	16.30	13.85	20.24	17.67	17.74	11.30
Corrected H2 Gen (mL)	7.27	8.04	8.23	8.33	8.77	6.81	6.82	8.87	8.86	6.69	8.82	10.44	12.09	13.61	15.12	11.19	8.67	8.88	15.11	16.30	13.85	20.24	17.67	17.74	11.30
NH3 Gen Total (mL)	-4.48	-4.66	-4.95	4.19	0.28	8.21	7.20	6.99	1.54	1.07	2.37	-4.51	2.09	0.50	2.86	-0.14	12.26	-2.79	4.05	3.34	7.59	7.70	14.47	8.23	-0.11
Corrected NH3 Gen (mL)	0.00	0.00	0.00	4.19	0.28	8.21	7.20	6.99	1.54	1.07	2.37	0.00	2.09	0.50	2.86	0.00	12.26	0.00	4.05	3.34	7.59	7.70	14.47	8.23	0.00

Clock Time	10:18:29	10:19:30	10:20:30	10:21:30	10:22:30	10:23:31	10:24:31	10:25:31	10:26:31	10:27:32	10:28:32	10:29:32	10:30:32	10:31:33	10:32:33	10:33:33	10:34:34	10:35:34	10:36:34	10:37:35	10:38:35	10:39:35	10:40:36	10:41:36	10:42:36
Elapsed Time (min)	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145
N2 (vol %)	34.279994	35.26318	33.06086	32.70185	31.9651	31.7454	31.08431	30.18449	30.66831	29.7605	29.12729	30.57028	29.3479	28.51832	27.58832	27.5402	27.44802	26.97695	27.11603	27.02366	25.70868	26.25681	25.53629	24.54002	25.15928
O2 (vol %)	0.9750777	0.407897	1.165418	-0.07601	0.996168	0.730508	0.533337	1.288305	-0.41961	0.481443	0.752531	0.389478	0.417332	1.343457	0.853521	0.887575	0.444097	2.022144	0.307259	0.213661	1.234043	0.441242	-0.35812	2.180599	0.908656
N2O (vol %)	0.7422189	-0.17394	0.293451	0.79594	0.390254	0.40587	0.319305	0.546751	0.584182	-0.07967	0.436303	0.451058	0.049899	0.997628	0.472252	0.658357	0.553609	0.976863	0.797982	0.685326	0.81726	0.263689	0.922878	0.835585	0.617607
H2 (vol %)	51.595779	55.12163	52.71974	53.08088	53.43602	53.85388	54.43745	54.61016	55.48739	56.06771	56.39147	58.44594	57.17336	56.52129	58.28962	58.2837	58.87948	57.4001	58.63415	58.80265	59.22685	59.67718	60.29276	59.41361	60.08407
H2O (vol %)	1.7118431	1.321803	1.36704	1.781336	1.435186	1.566663	1.609274	1.377952	1.786241	1.388182	1.225321	1.667153	1.211608	1.270855	1.017246	0.88205	1.092762	1.115339	1.3455	1.336567	1.311624	1.468072	1.60631	1.152775	1.168689
NH3 (vol %)	10.695088	8.059433	11.39349	11.71601	11.77727	11.69768	12.01632	11.99234	11.89349	12.38183	12.06708	8.476089	11.7999	11.34845	11.77904	11.74812	11.58203	11.50861	11.79907	11.93814	11.70155	11.89301	11.99988	11.87741	12.06169
N2O (vol %) [5 min avg]	0.3895906	0.403916	0.409584	0.342314	0.440964	0.491624	0.449272	0.355287	0.361374	0.387725	0.288354	0.371043	0.481428	0.525839	0.546349	0.731742	0.691813	0.734427	0.766208	0.708224	0.697427	0.704948	0.691404	0.555953	0.541225
Headspace Volume (mL)	1524.8	1523.6	1522.4	1521.2	1520	1518.8	1517.6	1516.4	1515.2	1514	1512.8	1511.6	1510.4	1509.2	1508	1506.8	1505.6	1504.4	1503.2	1502	1500.8	1499.6	1498.4	1497.2	1496
Gas Generation Rate (mL/min)	19.65	**18.30**	15.51	**12.72**	13.43	**14.14**	13.43	**12.72**	12.03	**11.34**	10.67	**9.99**	9.99	**9.98**	11.40	**12.81**	11.42	**10.02**	10.73	**11.45**	11.44	**11.43**	10.77	**10.12**	10.11
H2 Generated - (vol %)	-123.00	348.63	-183.00	96.26	93.63	98.74	120.38	75.20	165.95	133.52	102.31	369.30	-135.31	-42.07	292.27	57.59	137.45	-164.69	231.44	80.91	114.88	118.76	145.91	-70.68	159.32
H2 Gen (vol %) [5-min avg]	116.21	66.66	75.44	46.50	90.85	45.20	96.84	110.78	118.76	119.47	169.25	127.15	85.55	117.30	108.35	61.98	56.11	110.81	68.54	80.00	76.26	138.38	77.96	93.64	101.29
NH3 Generated (vol %)	259.75	-211.35	338.59	50.28	18.71	3.15	48.02	9.13	-0.55	77.56	-32.57	-534.86	514.53	-56.91	68.75	8.11	-10.32	0.49	52.47	30.18	-19.34	37.01	26.86	-6.25	39.34
NH3 Gen (vol %) [5-min avg]	36.15	-12.63	52.15	53.22	91.20	39.88	91.75	25.86	15.69	27.46	20.32	-96.26	4.82	-6.45	-8.21	-0.07	104.83	2.02	23.90	16.19	10.70	20.16	25.44	13.69	15.53
H2 Gen for Time Period (mL)	22.83	12.20	11.70	5.92	12.20	6.39	13.01	14.09	14.29	13.55	18.05	12.70	8.54	11.71	12.35	7.94	6.41	11.10	7.36	9.16	8.72	15.82	8.40	9.47	10.24
Corrected H2 Gen (mL)	19.65	12.20	11.70	5.92	12.20	6.39	13.01	12.72	12.03	11.34	10.67	9.99	8.54	9.98	11.40	7.94	6.41	10.02	7.36	9.16	8.72	11.43	8.40	9.47	10.11
NH3 Gen Total (mL)	7.10	-2.31	8.09	6.77	12.25	5.64	12.32	3.29	1.89	3.12	2.17	-9.62	0.48	-0.64	-0.94	-0.01	11.97	0.20	2.57	1.85	1.22	2.30	2.74	1.39	1.57
Corrected NH3 Gen (mL)	7.10	0.00	8.09	6.77	12.25	5.64	12.32	3.29	1.89	3.12	2.17	0.00	0.48	0.00	0.00	0.00	11.42	0.20	2.57	1.85	1.22	2.30	2.74	1.39	1.57

Clock Time	10:43:37	10:44:37	10:45:38	10:46:38	10:47:38	10:48:39	10:49:39	10:50:39	10:51:40	10:52:40	10:53:41	10:54:41	10:55:41	10:56:42	10:57:42	10:58:43	10:59:43	11:00:44	11:01:44	11:02:44	11:03:45	11:04:45	11:05:46	11:06:46	11:07:47
Elapsed Time (min)	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170
N2 (vol %)	24.808831	24.41628	24.58954	23.82231	24.35057	24.60226	23.35049	23.45425	22.75065	24.27312	23.54201	22.96623	21.76282	21.87649	21.12995	21.41534	21.71205	20.96691	21.2696	20.77667	21.08195	20.94151	20.40265	20.31212	22.22771
O2 (vol %)	1.0812069	0.460678	0.817865	1.113951	0.368163	1.59068	1.765672	1.135797	1.108498	0.874882	1.054364	-0.0552	0.826273	0.35825	1.745046	1.272741	0.624927	0.994857	0.872496	0.542752	1.036518	0.031407	0.798477	0.73462	1.151205
N2O (vol %)	0.1400049	0.190048	0.476303	1.027751	1.006038	0.459647	0.653789	0.536275	0.774799	0.528532	1.215833	1.147193	0.78825	1.265568	0.011067	0.554442	0.798668	1.518921	0.160739	0.816818	0.95317	0.421251	1.072009	1.494436	0.460342
H2 (vol %)	60.708371	61.35259	61.21483	60.79908	63.78988	63.49506	60.57383	60.67196	61.31251	63.64014	63.78878	61.8179	62.48108	62.40047	62.86055	62.40033	62.26002	62.15401	62.98387	63.4734	62.54975	64.1984	63.10984	62.74573	65.06653
H2O (vol %)	0.9545124	1.320249	0.599862	1.009682	1.570269	0.880039	1.30856	1.410888	1.198879	1.610737	1.145864	1.362678	1.221062	1.287762	1.161037	1.282983	1.482784	1.44598	1.308029	1.062886	1.146295	1.025087	1.201492	1.407304	1.595861
NH3 (vol %)	12.307073	12.26016	12.3016	12.22722	8.915081	8.972317	12.34765	12.79083	12.85466	9.072587	9.253152	12.7612	12.92052	12.81147	13.09235	13.07417	13.12155	12.91932	13.40526	13.32747	13.23232	13.38235	13.41553	13.30579	9.498351
N2O (vol %) [5 min avg]	0.4519096	0.490343	0.568029	0.631957	0.724706	0.7367	0.68611	0.590608	0.741846	0.840526	0.890921	0.989075	0.885582	0.753304	0.683599	0.829733	0.608768	0.769918	0.849663	0.77418	0.684797	0.951537	0.880242	0.802448	0.823755
					5																				
Headspace Volume (mL)	1494.8	1493.6	1492.4	1491.2	1495	1493.8	1492.6	1491.4	1490.2	1489	1487.8	1486.6	1485.4	1484.2	1483	1481.8	1480.6	1479.4	1478.2	1477	1475.8	1474.6	1473.4	1472.2	1471
Gas Generation Rate (mL/min)	**10.10**	10.11	**10.12**	9.44	**8.76**	8.75	**8.74**	9.45	**10.17**	9.55	**8.92**	8.88	**8.84**	9.59	**10.34**	9.61	**8.88**	8.21	**7.53**	9.77	**12.02**	11.29	**10.57**	9.12	**7.67**
H2 Generated - (vol %)	153.13	156.56	40.89	-4.88	573.95	13.16	-438.58	76.15	155.18	426.71	88.57	-268.05	173.90	49.93	128.85	-8.56	38.87	43.04	225.85	137.44	-50.88	279.51	-88.70	3.94	510.42
H2 Gen (vol %) [5-min avg]	108.85	87.85	101.01	183.93	155.94	36.91	43.96	75.97	46.53	61.61	95.71	115.26	94.21	34.64	15.21	76.60	50.43	85.61	87.33	78.87	126.99	100.64	56.26	130.86	-193.17
NH3 Generated (vol %)	48.63	5.33	18.42	0.48	-556.06	18.74	589.09	82.71	22.21	-580.87	39.36	599.92	39.69	-4.07	53.38	10.27	21.02	-23.53	108.78	1.57	1.55	32.98	18.04	-4.42	-721.13
NH3 Gen (vol %) [5-min avg]	29.12	22.78	21.09	22.44	-96.64	-102.62	14.13	26.99	31.34	26.38	30.50	32.67	24.06	18.81	145.66	139.84	24.06	11.41	33.98	23.62	21.88	24.27	32.58	9.94	-134.60
H2 Gen for Time Period (mL)	10.99	8.88	10.22	17.36	13.67	3.23	3.84	7.18	4.73	5.88	8.54	10.24	8.33	3.32	1.57	7.36	4.48	7.03	6.58	7.71	15.26	11.36	5.94	11.93	-14.81
Corrected H2 Gen (mL)	10.10	8.88	10.12	9.44	8.76	3.23	3.84	7.18	4.73	5.88	8.54	8.88	8.33	3.32	1.57	7.36	4.48	7.03	6.58	7.71	12.02	11.29	5.94	9.12	0.00
NH3 Gen Total (mL)	2.94	2.30	2.13	2.12	-8.47	-8.98	1.23	2.55	3.19	2.52	2.72	2.90	2.13	1.80	15.06	13.44	2.14	0.94	2.56	2.31	2.63	2.74	3.44	0.91	-10.32
Corrected NH3 Gen (mL)	2.94	2.30	2.13	2.12	0.00	0.00	1.23	2.55	3.19	2.52	2.72	2.90	2.13	1.80	10.34	9.61	2.14	0.94	2.56	2.31	2.63	2.74	3.44	0.91	0.00

Clock Time	11:08:47	11:09:48	11:10:48	11:11:49	11:12:49	11:13:50	11:14:50	11:15:50	11:16:51	11:17:52	11:18:52	11:19:53	11:20:53	11:21:54	11:22:54	11:23:55	11:24:55	11:25:56	11:26:56	11:27:57	11:28:58	11:29:58	11:30:59	11:31:59	11:33:00
Elapsed Time (min)	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195
N2 (vol %)	28.669294	22.73095	20.88749	20.44793	19.51831	20.10278	19.79268	19.29861	18.80915	19.29987	18.66283	18.10874	18.51231	18.64679	18.50226	19.2305	18.83434	18.19881	19.03428	18.8277	18.46913	18.73779	19.19323	18.70062	18.6012
O2 (vol %)	0.3426071	0.380085	0.497833	0.691225	0.302594	0.201317	0.489756	1.223266	1.547785	0.879209	0.788413	0.928408	0.575795	-0.01011	0.989845	0.924568	1.179859	0.622156	-0.11718	1.262882	1.519278	1.695457	0.729887	0.720036	1.428557
N2O (vol %)	0.5642043	0.527782	0.724425	0.760124	1.331807	0.917732	0.799	0.895019	0.471552	0.815675	1.204173	0.846457	1.147065	1.266253	1.458673	0.523851	0.925776	0.912963	0.602098	1.176819	1.346652	0.882098	0.694399	0.983091	0.697572
H2 (vol %)	55.979529	61.85819	62.86863	63.01668	62.96186	63.26513	63.4237	62.51081	63.32834	63.33773	63.40961	63.67936	63.75042	63.96462	63.2927	63.22337	63.16668	63.95113	64.23485	63.16596	63.05376	62.99165	63.62925	64.05378	63.24997
H2O (vol %)	1.5941242	1.397558	1.474681	1.253439	1.801749	1.377456	1.235064	1.581815	1.311142	1.353205	1.406411	1.686282	1.505388	1.224544	1.108984	1.33931	1.132472	1.294396	1.084939	0.992938	0.989623	1.090857	1.118762	0.959375	1.26914
NH3 (vol %)	12.850242	13.10544	13.54694	13.83061	14.08368	14.13558	14.2598	14.49048	14.53203	14.31431	14.52857	14.75076	14.50902	14.9079	14.64754	14.7584	14.76087	15.02054	15.16101	14.5737	14.62156	14.60215	14.63447	14.5831	14.75356
N2O (vol %) [5 min avg]	0.7542378	0.607375	0.781668	0.852374	0.906617	0.940736	0.883022	0.779795	0.837084	0.846575	0.896984	1.055925	1.184524	1.04846	1.064324	1.017503	0.884672	0.828302	0.992862	0.984126	0.940413	1.016612	0.920762	0.822767	0.821113
														5											
Headspace Volume (mL)	1469.8	1468.6	1467.4	1466.2	1465	1463.8	1462.6	1461.4	1460.2	1459	1457.8	1456.6	1455.4	1459.2	1458	1456.8	1455.6	1454.4	1453.2	1452	1450.8	1449.6	1448.4	1447.2	1446
Gas Generation Rate (mL/min)	7.73	**7.80**	8.74	**9.68**	9.70	**9.71**	7.64	**5.56**	7.64	**9.72**	8.35	**6.97**	7.68	**8.38**	7.69	**7.00**	9.11	**11.22**	8.41	**5.60**	5.62	**5.63**	6.33	**7.02**	7.03
H2 Generated - (vol %)	-1671.02	1168.45	232.47	85.43	54.68	109.00	93.80	-177.27	219.53	64.75	75.96	120.02	77.22	101.28	-64.11	48.80	54.11	165.66	113.27	-214.08	34.07	47.01	209.61	151.58	-102.02
H2 Gen (vol %) [5-min avg]	-15.38	48.85	65.15	-26.00	330.01	115.08	33.13	59.95	61.96	55.35	60.60	111.50	87.85	62.07	56.64	43.46	61.15	63.55	33.55	30.61	29.19	37.97	45.64	68.05	108.89
NH3 Generated (vol %)	649.88	61.14	87.65	56.78	52.32	21.96	38.05	75.08	22.47	-18.36	51.94	61.15	-31.33	84.39	-34.72	37.82	15.15	48.69	39.44	-137.76	26.99	9.61	22.03	3.99	49.80
NH3 Gen (vol %) [5-min avg]	-4.93	0.70	14.63	26.87	181.56	55.97	51.36	48.84	41.98	27.84	33.84	38.46	17.18	29.56	26.29	23.46	14.26	30.27	21.28	0.67	-1.50	-2.61	-7.94	-15.03	22.48
H2 Gen for Time Period (mL)	-1.19	3.81	5.70	-2.52	31.99	11.17	2.53	3.34	4.74	5.38	5.06	7.78	6.74	5.20	4.36	3.04	5.57	7.13	2.82	1.71	1.64	2.14	2.89	4.78	7.66
Corrected H2 Gen (mL)	0.00	3.81	5.70	0.00	9.70	9.71	2.53	3.34	4.74	5.38	5.06	6.97	6.74	5.20	4.36	3.04	5.57	7.13	2.82	1.71	1.64	2.14	2.89	4.78	7.03
NH3 Gen Total (mL)	-0.38	0.05	1.28	2.60	17.60	5.43	3.92	2.72	3.21	2.71	2.82	2.68	1.32	2.48	2.02	1.64	1.30	3.40	1.79	0.04	-0.08	-0.15	-0.50	-1.05	1.58
Corrected NH3 Gen (mL)	0.00	0.05	1.28	2.60	9.70	5.43	3.92	2.72	3.21	2.71	2.82	2.68	1.32	2.48	2.02	1.64	1.30	3.40	1.79	0.04	0.00	0.00	0.00	0.00	1.58

Clock Time	11:34:01	11:35:01	11:36:02	11:37:02	11:38:03	11:39:04	11:40:04	11:41:05	11:42:06	11:43:06	11:44:07	11:45:08	11:46:08	11:47:09	11:48:10	11:49:10	11:50:11	11:51:12	11:52:12	11:53:13	11:54:14	11:55:14	11:56:15	11:57:16	11:58:17
Elapsed Time (min)	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220
N2 (vol %)	18.604961	18.78298	17.9735	17.95422	17.37058	17.48411	18.0815	18.47849	17.94466	17.34572	17.26964	17.19067	17.19504	17.09229	17.00548	16.38621	16.65336	16.13798	15.7625	15.64642	15.83249	15.60249	15.33151	14.28241	14.24504
O2 (vol %)	0.5310512	1.337067	1.991649	0.926571	0.77256	0.574371	0.39281	1.087777	0.573022	1.066784	0.31294	1.228575	0.647167	0.143538	1.938392	0.652873	0.470145	0.793353	1.427174	1.712601	0.324197	0.072123	1.539475	0.629179	1.353712
N2O (vol %)	0.8566764	0.873824	1.23348	0.816254	0.438972	1.276025	0.715719	1.100656	0.796329	1.46705	1.189708	1.34132	0.818846	0.609248	0.810358	1.240024	1.472102	0.415558	1.219654	1.208382	0.64861	0.709108	0.944061	1.172934	0.459774
H2 (vol %)	64.099348	63.06901	62.99121	64.30441	64.52694	64.25143	64.24397	62.83742	63.82141	62.94283	64.26477	63.11369	63.52337	63.74029	61.62636	63.02354	62.25776	62.05862	61.21185	61.09291	62.15611	61.97522	61.04202	62.37945	61.93677
H2O (vol %)	1.1221087	1.190775	1.111006	0.971347	1.698404	1.195222	1.238015	1.501989	1.187433	1.280988	0.917573	1.142717	1.179045	1.48653	1.488761	1.095188	1.040585	1.443872	1.263521	0.641355	0.899597	1.24186	0.659115	0.726734	1.136503
NH3 (vol %)	14.785854	14.74635	14.69915	15.0272	15.19254	15.21884	15.32799	14.99367	15.67714	15.89662	16.04537	15.98302	16.63653	16.9281	17.13065	17.60216	18.10605	19.15061	19.1153	19.69833	20.139	20.3992	20.48382	20.80929	20.86819
N2O (vol %) [5 min avg]	0.9289288	0.895561	0.843841	0.927711	0.89609	0.869525	0.86554	1.071156	1.053892	1.179012	1.122651	1.085234	0.953896	0.963959	0.990116	0.909458	1.031539	1.111144	0.992861	0.840262	0.945963	0.936619	0.786897	0.757551	0.835477
														5											
Headspace Volume (mL)	1444.8	1443.6	1442.4	1441.2	1440	1438.8	1437.6	1436.4	1435.2	1434	1432.8	1431.6	1430.4	1429.2	1433	1431.8	1430.6	1429.4	1428.2	1427	1425.8	1424.6	1423.4	1422.2	1421
Gas Generation Rate (mL/min)	**7.05**	7.72	**8.40**	10.53	**12.66**	10.59	**8.51**	11.34	**14.17**	14.20	**14.22**	14.94	**15.67**	19.24	**22.81**	18.59	**14.36**	13.63	**12.91**	12.22	**11.54**	9.43	**7.33**	9.44	**11.56**
H2 Generated - (vol %)	238.28	-129.48	49.64	243.97	89.83	26.81	62.98	-115.29	163.48	-25.81	197.45	-47.16	100.93	79.85	-71.16	170.66	-14.04	41.18	-32.50	47.21	193.51	34.66	-120.28	263.77	7.54
H2 Gen (vol %) [5-min avg]	73.59	41.60	60.08	98.45	56.15	94.65	61.66	45.56	22.44	56.56	34.53	77.78	61.05	51.98	46.62	53.25	41.30	18.83	42.50	47.07	56.81	24.52	83.77	75.84	16.67
NH3 Generated (vol %)	21.41	7.36	6.60	59.91	33.99	18.79	33.76	-27.35	84.90	38.07	31.03	10.01	76.31	38.59	29.85	53.93	68.31	128.68	15.21	87.76	74.58	59.69	36.93	69.82	28.11
NH3 Gen (vol %) [5-min avg]	21.37	20.92	17.83	29.02	25.85	25.33	30.61	23.82	28.82	29.63	32.08	27.33	48.06	38.80	37.16	41.74	53.40	63.87	59.19	70.78	74.91	73.18	54.83	65.76	53.82
H2 Gen for Time Period (mL)	5.18	3.21	5.05	10.37	7.11	10.02	5.25	5.17	3.18	8.03	4.91	11.62	9.56	10.00	10.64	9.90	5.93	2.57	5.48	5.75	6.56	2.31	6.14	7.16	1.93
Corrected H2 Gen (mL)	5.18	3.21	5.05	10.37	7.11	10.02	5.25	5.17	3.18	8.03	4.91	11.62	9.56	10.00	10.64	9.90	5.93	2.57	5.48	5.75	6.56	2.31	6.14	7.16	1.93
NH3 Gen Total (mL)	1.51	1.62	1.50	3.06	3.27	2.68	2.61	2.70	4.08	4.21	4.56	4.08	7.53	7.46	8.48	7.76	7.67	8.71	7.64	8.65	8.65	6.90	4.02	6.21	6.22
Corrected NH3 Gen (mL)	1.51	1.62	1.50	3.06	3.27	2.68	2.61	2.70	4.08	4.21	4.56	4.08	7.53	7.46	8.48	7.76	7.67	8.71	7.64	8.65	8.65	6.90	4.02	6.21	6.22

Clock Time	11:59:17	12:00:18	12:01:19	12:02:20	12:03:20	12:04:21	12:05:22	12:06:23	12:07:23	12:08:24	12:09:25	12:10:26	12:11:26	12:12:27	12:13:28	12:14:29	12:15:30	12:16:30	12:17:31	12:18:32	12:19:33	12:20:34	12:21:35	12:22:35	12:23:37
Elapsed Time (min)	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245
N2 (vol %)	15.712	14.86673	15.09262	14.10733	14.3789	13.95978	13.4457	14.7158	13.977	13.22679	12.17552	12.55263	12.68674	12.5051	11.86954	12.23791	11.83681	11.84596	11.48851	11.94354	11.24946	11.3898	10.57431	11.65611	11.27359
O2 (vol %)	1.5789109	0.785528	1.400847	1.979951	0.444766	0.910507	0.284433	0.515773	0.95782	1.77291	1.284346	1.604076	1.101343	1.20719	2.19491	0.796672	1.79203	0.916038	1.080558	0.089232	0.566774	0.615978	1.465229	1.01169	1.440219
N2O (vol %)	0.5018782	1.098739	1.142	1.062668	0.741013	1.001383	1.510334	1.215317	0.292583	1.170309	1.026465	-0.16191	1.410351	1.4153	0.388958	1.2779	0.976147	1.392527	0.54969	0.664962	0.948024	1.670047	0.606102	1.16037	0.670826
H2 (vol %)	60.604314	61.0466	60.3322	59.84295	61.15741	60.37854	60.68289	59.0548	60.50404	59.17314	60.12072	59.85659	58.39133	58.69491	58.25377	58.36494	57.59729	57.93762	58.28664	58.84732	58.76318	58.30605	59.02675	58.24236	58.32386
H2O (vol %)	1.110635	0.804103	1.056551	1.445139	0.968641	1.264606	0.709876	1.231293	0.54325	0.964797	1.018026	1.184148	1.717169	1.14186	1.28324	1.000005	1.344337	1.350372	1.526834	1.590596	1.220695	0.682835	1.075919	1.192355	1.438405
NH3 (vol %)	20.492262	21.39831	20.97579	21.56196	22.30927	22.48518	23.36677	23.26701	23.72531	23.69205	24.37493	24.96446	24.69307	25.03565	26.00958	26.32257	26.45339	26.55748	27.06776	26.86436	27.25186	27.33529	27.25169	26.73711	26.8531
N2O (vol %) [5 min avg]	0.8750649	0.853012	0.90926	1.009161	1.09148	1.106143	0.952126	1.037985	1.043002	0.708554	0.74756	0.972104	0.815834	0.866121	1.093731	1.090167	0.917045	0.972245	0.90627	1.04505	0.887765	1.009901	1.011074	0.979906	0.828767
																				5					
Headspace Volume (mL)	1419.8	1418.6	1417.4	1416.2	1415	1413.8	1412.6	1411.4	1410.2	1409	1407.8	1406.6	1405.4	1404.2	1403	1401.8	1400.6	1399.4	1398.2	1402	1400.8	1399.6	1398.4	1397.2	1396
Gas Generation Rate (mL/min)	11.61	**11.66**	14.55	**17.44**	17.54	**17.63**	17.03	**16.42**	16.46	**16.50**	15.92	**15.33**	15.14	**14.94**	13.70	**12.46**	12.49	**12.51**	11.13	**9.75**	9.76	**9.77**	9.79	**9.81**	9.12
H2 Generated - (vol %)	-102.32	114.86	-9.26	20.12	167.22	-2.08	85.93	-80.89	184.67	-54.49	143.94	35.63	-77.64	87.22	13.09	70.87	-28.51	96.00	102.13	139.45	46.69	-7.21	161.99	-53.48	70.79
H2 Gen (vol %) [5-min avg]	32.71	54.92	6.19	38.12	58.17	52.39	38.06	70.97	26.63	55.83	45.77	46.42	26.93	40.45	25.83	13.01	47.73	50.72	75.99	71.15	75.41	88.61	57.49	43.76	59.43
NH3 Generated (vol %)	-25.48	131.64	-20.18	69.16	82.61	36.59	96.51	14.69	62.99	20.85	84.78	79.05	-0.50	57.23	125.73	61.53	41.13	38.20	91.16	-2.38	82.87	39.29	15.31	-46.56	44.60
NH3 Gen (vol %) [5-min avg]	33.81	48.20	36.78	36.65	47.55	59.96	52.94	59.91	58.68	46.33	55.97	52.47	49.43	48.28	69.26	64.61	57.02	64.76	71.55	45.93	50.20	49.83	45.25	17.71	27.10
H2 Gen for Time Period (mL)	3.80	6.40	0.90	6.65	10.20	9.24	6.48	11.65	4.38	9.21	7.28	7.12	4.08	6.04	3.54	1.62	5.96	6.35	8.46	6.94	7.36	8.65	5.63	4.29	5.42
Corrected H2 Gen (mL)	3.80	6.40	0.90	6.65	10.20	9.24	6.48	11.65	4.38	9.21	7.28	7.12	4.08	6.04	3.54	1.62	5.96	6.35	8.46	6.94	7.36	8.65	5.63	4.29	5.42
NH3 Gen Total (mL)	3.93	5.62	5.35	6.39	8.34	10.57	9.01	9.84	9.66	7.64	8.91	8.05	7.48	7.21	9.49	8.05	7.12	8.10	7.96	4.48	4.90	4.87	4.43	1.74	2.47
Corrected NH3 Gen (mL)	3.93	5.62	5.35	6.39	8.34	10.57	9.01	9.84	9.66	7.64	8.91	8.05	7.48	7.21	9.49	8.05	7.12	8.10	7.96	4.48	4.90	4.87	4.43	1.74	2.47

Clock Time	12:24:38	12:25:39	12:26:32	12:27:32	12:28:32	12:29:31	12:30:31	12:31:31	12:32:31	12:33:31	12:34:31	12:35:31	12:36:31	12:37:31	12:38:31
Elapsed Time (min)	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260
N2 (vol %)	10.550836	9.823249	10.85604	11.0283	10.89341	11.25212	11.00161	10.8035	10.62636	10.72459	11.17214	10.59131	10.97897	10.16722	10.20372
O2 (vol %)	1.3822159	1.323825	0.477939	1.081183	0.759981	-0.22199	1.462949	-0.14803	-0.07394	0.958835	1.67443	-0.23029	0.643052	0.970485	0.693229
N2O (vol %)	0.7921835	0.914353	0.774792	0.32281	0.530178	1.331753	0.570431	0.45092	1.371088	0.85545	0.618762	0.935551	0.348148	1.553576	1.328952
H2 (vol %)	58.725164	59.12915	59.35893	59.47407	59.53648	59.58788	59.24622	60.39049	59.72667	59.22598	58.66942	60.46462	60.4576	59.65996	59.88847
H2O (vol %)	1.5351997	1.632642	1.469834	1.081149	1.040661	1.162707	0.954762	1.304032	1.385751	1.185858	1.449082	1.06861	0.733131	0.821923	1.119026
NH3 (vol %)	27.014401	27.17678	27.06247	27.01249	27.23929	26.88752	26.76402	27.19909	26.96406	27.04929	26.41617	27.17019	26.8391	26.82684	26.7666
N2O (vol %) [5 min avg]	0.8625049	0.694993	0.666863	0.774777	0.705993	0.641219	0.850874	0.915928	0.77333	0.846354	0.8258	0.862297	0.956998	1.036997	1.080802
Headspace Volume (mL)	1394.8	1393.6	1392.4	1391.2	1390	1390	1390	1390	1390	1390	1390	1390	1390	1390	1390
Gas Generation Rate (mL/min)	**8.44**	8.42	**8.41**	8.41	**8.42**	5.63	**2.85**	4.23	**5.62**	3.52	**1.41**	1.41	**1.41**	0.70	**0.01**
H2 Generated - (vol %)	125.06	125.97	97.41	78.51	69.84	72.27	-107.50	436.14	-104.52	-138.71	-488.38	1830.39	53.51	-1517.99	31823
H2 Gen (vol %) [5-min avg]	86.07	73.15	99.55	99.36	88.80	42.11	109.85	73.25	31.54	-80.59	306.98	230.46	-52.24	6340.06	8047.17
NH3 Generated (vol %)	53.68	54.04	8.13	18.75	64.68	-59.91	-33.51	170.07	-31.19	60.74	-595.88	770.58	-300.60	2.58	-8346
NH3 Gen (vol %) [5-min avg]	21.26	24.21	22.78	35.84	39.86	17.14	-0.37	32.02	22.03	21.24	-85.95	74.86	-19.27	-12.52	-1694
H2 Gen for Time Period (mL)	7.26	6.16	8.37	8.36	7.48	2.37	3.13	3.10	1.77	-2.83	4.34	3.25	-0.73	44.56	0.80
Corrected H2 Gen (mL)	7.26	6.16	8.37	8.36	7.48	2.37	2.85	3.10	1.77	0.00	1.41	1.41	0.00	0.70	0.01
NH3 Gen Total (mL)	1.79	2.04	1.92	3.02	3.36	0.97	-0.01	1.36	1.24	0.75	-1.22	1.06	-0.27	-0.09	-0.17
Corrected NH3 Gen (mL)	1.79	2.04	1.92	3.02	3.36	0.97	0.00	1.36	1.24	0.75	0.00	1.06	0.00	0.00	0.00

8.2 Surface Area and Dissolution Rate Calculations

Section 4.3.1 contains a table of calculated sample surface areas (Table 4-13) and a table of calculated Al dissolution rates (Table 4-12). This appendix describes the methodology for those calculations for the disk samples (Tests 1 to 4) and the pipe sample (Test 5).

8.2.1 Disk Sample Calculations

A spreadsheet was used to perform minute-by-minute Al dissolution calculations for an input dissolution rate. The principle behind these calculations is that the weight loss, volume loss, and surface area change can be calculated for a sample with a known starting configuration (and surface area). For an input dissolution rate (in mg/min/cm^2), the weight loss (in mg) for a sample of known surface area (in cm^2) can be calculated. The volume of sample dissolved (in cm^3) can be calculated using the weight loss and the density of aluminum (2700 mg/cm^3).

Two key assumptions factor into how the sample dimensions change as dissolution progresses. The first assumption is that for the stack of seven disks, all of the disks dissolve in the same manner – the disk at the top of the stack nearest the vessel head space dissolves at the same rate and in the same manner as the disk at the bottom nearest the magnetic stirrer. The second assumption is that thickness (from top and bottom) change at the same rate while the outer radius changes at twice that rate due to solution mixing; these ratios are an approximation of what was empirically observed.

Each disk (see Figure 3-1 and Table 3-1) is 3.22 mm thick and 31.87 mm in diameter. The disk contains a 6.25 mm hole at its center. The starting surface area of the sample edge is calculated as follows where d is the outer diameter of the disk (in cm) and h is the height (in cm).

$$SA(edge) = \pi \mathrm{dh}$$

The calculated SA(edge) is 3.2 cm^2 for each disk. The surface area on the two faces is calculated as follows where r_1 is the overall sample radius (in cm) and r_2 is the radius of the hole (in cm).

$$SA(faces) = (2)[\pi(r_1 - r_2)\ ^2]$$

The calculated SA(faces) is 15.3 cm^2 for each disk. For the seven disks used in Tests 1 to 4, the total initial surface area was

$$(7\ disks)\ (15.3\ cm^2 + 3.2\ cm^2) = 129.5\ cm^2$$

The values from dissolution calculations for Test 1 from 0 to 36 min dissolution time are provided in Table 8-4. At time = 0 min [Column 1], the sample mass for seven disks was 46.49 g [Column 2] and the initial surface area of the seven disks was 129.5 cm^2 [Column 4].

For a given dissolution rate [Column 5], the mass of Al dissolution for that one-minute interval can be calculated by multiplying the dissolution rate and the surface area. For Test 1, 0 to 1 min, the mass dissolved was 0.203 g [Column 6]. Subtracting that mass from the starting mass for that time step yields the final mass for that time step (46.29 g) [Column 7]. This value is copied to Time = 1 min, Column 2, as the initial mass for dissolution from 1 to 2 min.

In a separate set of calculations (Table 8-5) and using the assumptions described above for change of radii and height, a relationship between sample mass and surface area can be established. For the disk samples, the reduced surface area (129.29 cm^2) can be calculated as follows where M is the reduced sample mass (46.29 g).

$$SA = -0.0506M^2 + 1.6754M + 9.6045$$

The calculations are then continued, minute by minute, to calculate the dissolution of the sample. Identifying the appropriate dissolution rate for Column 5 is based on the mass of Al dissolved for a given time frame, as determined analytically. Consulting Table 4-11 for the mass of Al dissolved during Test 1 for 0 to 36 min, the quantity is 7.093 g. The objective of the calculation for Test 1, 0 to 36 min, is to revise the dissolution rate [Column 5] which results in a total mass of Al dissolved [Column 3] from 0 to 36 min of 7.09 g. The corresponding dissolution rate is 1.57 mg/min/cm^2.

The process is continued for each integral time period and Al dissolution mass in Table 4-11. The surface area value recorded in Table 4-13 comes from Table 8-4, time = 36 min, Column 4.

Table 8-4. Test 1 Sample Dissolution Calculations for 0 to 36 Minutes

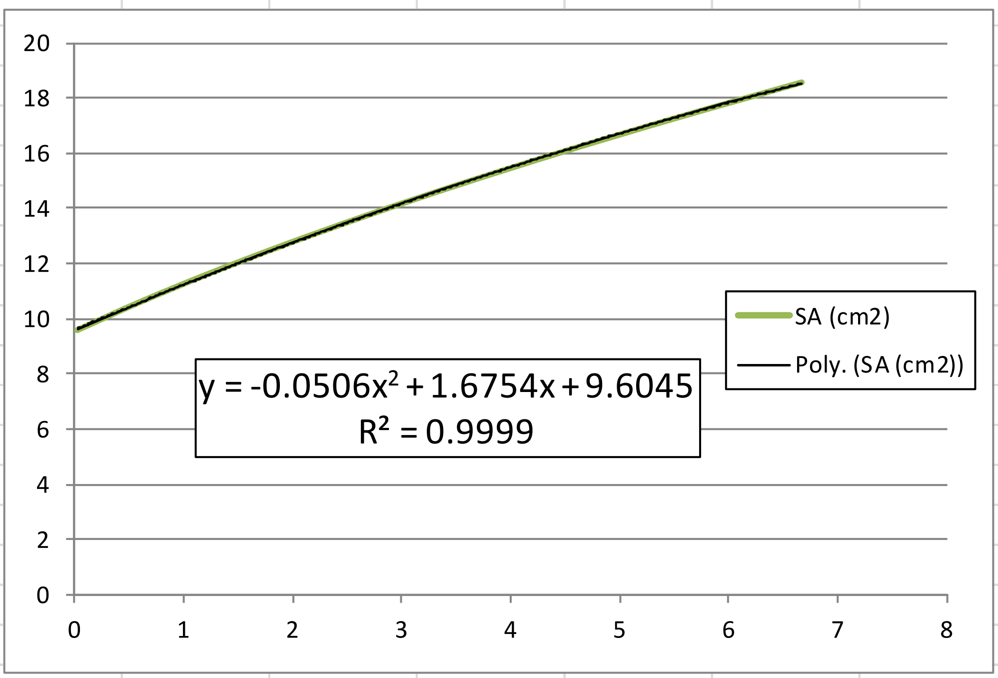
# if Disks =	7.00					
1	2	3	4	5	6	7
Dissolution Time (min)	Initial Al Mass (g)	Total Al Dissolved (g)	Al Surface Area (cm2)	Rxn Rate (mg/min /cm2)	Al Rxn (grams)	Final Al Mass (grams)
0	46.49	0.00	129.50	1.57	0.203	46.29
1	46.29	0.20	129.29	1.57	0.202	46.08
2	46.08	0.41	129.09	1.57	0.202	45.88
3	45.88	0.61	128.89	1.57	0.202	45.68
4	45.68	0.81	128.68	1.57	0.201	45.48
5	45.48	1.01	128.48	1.57	0.201	45.28
6	45.28	1.21	128.27	1.57	0.201	45.08
7	45.08	1.41	128.07	1.57	0.200	44.88
8	44.88	1.61	127.86	1.57	0.200	44.68
9	44.68	1.81	127.66	1.57	0.200	44.48
10	44.48	2.01	127.45	1.57	0.199	44.28
11	44.28	2.21	127.24	1.57	0.199	44.08
12	44.08	2.41	127.04	1.57	0.199	43.88
13	43.88	2.61	126.83	1.57	0.198	43.68
14	43.68	2.81	126.62	1.57	0.198	43.48
15	43.48	3.01	126.42	1.57	0.198	43.29
16	43.29	3.20	126.21	1.57	0.198	43.09
17	43.09	3.40	126.00	1.57	0.197	42.89
18	42.89	3.60	125.79	1.57	0.197	42.69
19	42.69	3.80	125.59	1.57	0.197	42.50
20	42.50	3.99	125.38	1.57	0.196	42.30
21	42.30	4.19	125.17	1.57	0.196	42.11
22	42.11	4.38	124.96	1.57	0.196	41.91
23	41.91	4.58	124.75	1.57	0.195	41.71
24	41.71	4.78	124.54	1.57	0.195	41.52
25	41.52	4.97	124.33	1.57	0.195	41.33
26	41.33	5.16	124.12	1.57	0.194	41.13
27	41.13	5.36	123.91	1.57	0.194	40.94
28	40.94	5.55	123.70	1.57	0.194	40.74
29	40.74	5.75	123.49	1.57	0.193	40.55
30	40.55	5.94	123.28	1.57	0.193	40.36
31	40.36	6.13	123.07	1.57	0.193	40.16
32	40.16	6.33	122.86	1.57	0.192	39.97
33	39.97	6.52	122.65	1.57	0.192	39.78
34	39.78	6.71	122.44	1.57	0.192	39.59
35	39.59	6.90	122.23	1.57	0.191	39.40
36	39.40	7.09	122.02	1.57	0.191	39.21

Table 8-5. Relationship of Disk Dimensional Changes to Sample Mass and Surface Area

Assuming that the outer radius and height change linearly, a relationship can be established between the sample mass and surface area
- Assumption is that the outer radius changes at twice the rate as the height/thickness (from top and bottom).

R1 (cm)	R2 (cm)	H (cm)	Δ (cm)	SA (cm2)	V (cm3)	mass (g)
1.5935	0.3125	0.322	0	18.565	2.470	6.669
1.5535	0.3125	0.282	0.02	17.303	2.052	5.539
1.5135	0.3125	0.242	0.04	16.081	1.667	4.502
1.4735	0.3125	0.202	0.06	14.899	1.316	3.553
1.4335	0.3125	0.162	0.08	13.757	0.996	2.690
1.3935	0.3125	0.122	0.1	12.656	0.707	1.908
1.3535	0.3125	0.082	0.12	11.594	0.447	1.206
1.3135	0.3125	0.042	0.14	10.573	0.215	0.580
1.2735	0.3125	0.002	0.16	9.593	0.010	0.026

R1 = outer radius; R2 = hole radius; H = thickness
Assume Al density of 2.70 g/mL
SA = (2)*[π(R1^2-R2^2)]+2*πR1H
V = π * H * (R1^2 - R2^2)



8.2.2 Pipe Sample Calculations

Similar to the calculation of Appendix 8.2.1, a spreadsheet was used to perform minute-by-minute Al dissolution calculations for an input dissolution rate of the pipe sample for Test 5. The principle behind these calculations is that the weight loss, volume loss, and surface area change can be calculated for a sample with a known starting configuration (and surface area). For an input dissolution rate (in mg/min/cm^2), the weight loss (in mg) for a sample of known surface area (in cm^2) can be calculated. The volume of sample dissolved (in cm^3) can be calculated using the weight loss and the density of aluminum (2700 mg/cm^3).

Two key assumptions factor into how the sample dimensions change as dissolution progresses. The first assumption is that for the pipe piece dissolves uniformly – the top edge of the sample nearer the center of the dissolution vessel dissolves at the same rate and in the same manner as the bottom edge of the sample nearest the magnetic stirrer and hot plate. The second assumption is that thickness and height of the pipe sample dissolve at uniform rates (i.e., the height decrease rate is proportional (three times) the diameter decrease rate; this ratio is an approximation of what was empirically observed.

The pipe segment (see Figure 3-1 and Table 3-1) has an outside diameter of 113 mm, is 2.32 mm thick and 25.4 mm tall. The pipe sample was placed on a glass ring at the bottom of the digestion vessel such that only the top edge of the sample was directly exposed to the solution. The starting surface area of the sample edge is calculated as follows where r_1 is the outer radius (in cm) and r_2 is the inner radius (in cm).

$$SA(edge) = \pi(r_1^2 - r_2^2)]$$

The calculated SA(edge) for each edge 8.1 cm^2. The surface area on the two faces is calculated as follows where d_1 is the outer sample diameter (in cm) and d_2 is the inner sample diameter (in cm).

$$SA(faces) = \pi d_1 \mathrm{h} + \pi d_2 h$$

The calculated SA(faces) were 90.2 cm$_2$ and 86.4 cm^2 (total = 176.6 cm^2), respectively, for the outer and inner surfaces of the pipe. For the pipe segment used in Test 5, the total initial surface area exposed to solution (two faces and two edges) was

$$SA(total) = 16.2\ cm^2 + 90.2\ cm^2 + 86.4\ cm^2 = 192.8$$

The values from dissolution calculations for Test 5 from 0 to 30 min dissolution time are provided in Table 8-6. The small discrepancy between the calculated initial surface area above and Table 8-6 can be attributed to a minor variation associated with a calculated mass-to-surface area relationship discussed below in reference to Table 8-7. At time = 0 min [Column 1], the sample mass for seven disks was 56.86 g [Column 2] and the initial surface area of the pipe segment available for reaction was 194.43 cm^2 [Column 4].

For a given dissolution rate [Column 5], the mass of Al dissolution for that one-minute interval can be calculated by multiplying the dissolution rate and the surface area. For Test 5, 0 to 1 min, the mass dissolved is 0.366 g [Column 6]. Subtracting that mass from the starting mass for that time step yields the final mass for that time step (56.49 g) [Column 7]. This value is copied to Time = 1 min, Column 2, as the initial mass for dissolution from 1 to 2 min.

In a separate set of calculations (Table 8-7) and using the assumptions described above for change of radii and height, a relationship between sample mass and surface area can be calculated.

$$SA = 0.6997M + 154.65$$

For the pipe samples, the reduced surface area can be calculated as follows where M is the reduced sample mass (56.49 g).

The calculations are then continued, minute by minute, to calculate the dissolution of the sample. Identifying the appropriate dissolution rate for Column 5 is based on the mass of Al dissolved for a given time frame, as determined analytically. Consulting Table 4-11 for the mass of Al dissolved during Test 5 for 0 to 30 min, the quantity is 10.774 g. The objective of the calculation for Test 5, 0 to 30 min, is to revise the dissolution rate [Column 5] which results in a total mass of Al dissolved [Column 3] from 0 to 36 min of 10.774 g. The corresponding dissolution rate is 1.88 mg/min/cm^2.

The process is continued for each integral time period and Al dissolution mass in Table 4-11. The surface area value recorded in Table 4-13 comes from Table 8-6, time = 30 min, Column 4.

Table 8-6. Test 5 Sample Dissolution Calculations for 0 to 30 Minutes

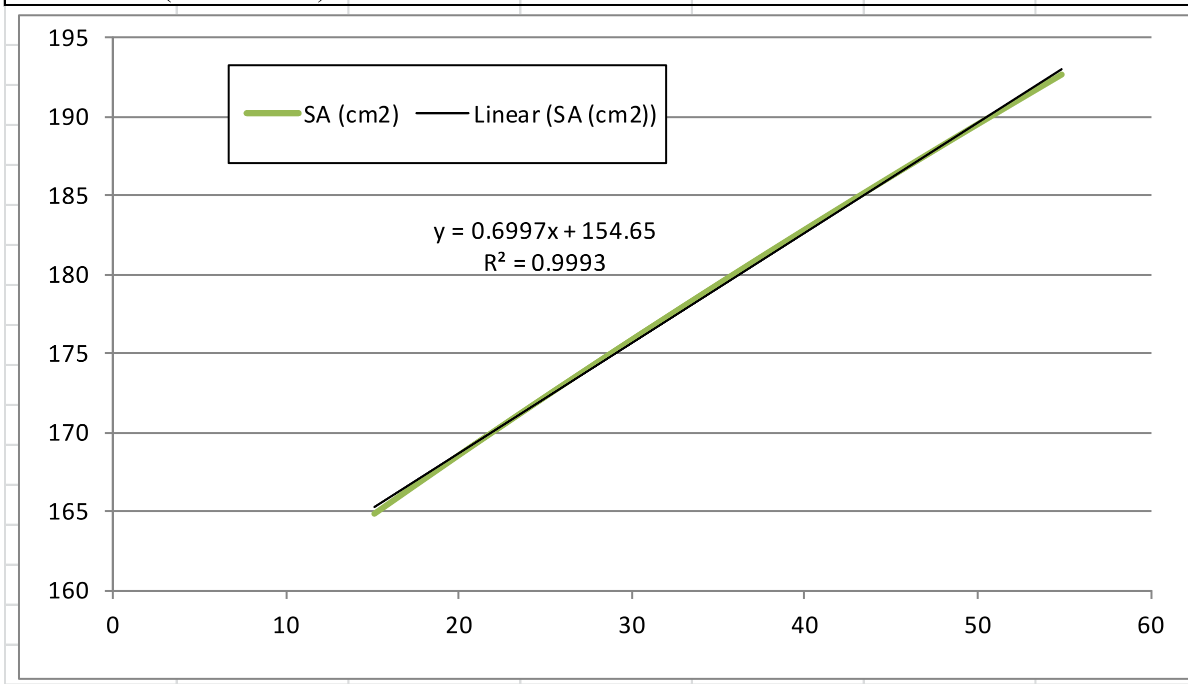
1	2	3	4	5	6	7
Dissolution Time (min)	Initial Al Mass (g)	Total Al Dissolved (g)	Al Surface Area (cm2)	Rxn Rate (mg/min /cm2)	Al Rxn (grams)	Final Al Mass (grams)
0	56.86	0.00	194.43	1.88	0.366	56.49
1	56.49	0.37	194.18	1.88	0.365	56.13
2	56.13	0.73	193.92	1.88	0.365	55.76
3	55.76	1.10	193.67	1.88	0.364	55.40
4	55.40	1.46	193.41	1.88	0.364	55.04
5	55.04	1.82	193.16	1.88	0.364	54.67
6	54.67	2.19	192.90	1.88	0.363	54.31
7	54.31	2.55	192.65	1.88	0.363	53.95
8	53.95	2.91	192.40	1.88	0.362	53.58
9	53.58	3.28	192.14	1.88	0.362	53.22
10	53.22	3.64	191.89	1.88	0.361	52.86
11	52.86	4.00	191.64	1.88	0.361	52.50
12	52.50	4.36	191.38	1.88	0.360	52.14
13	52.14	4.72	191.13	1.88	0.360	51.78
14	51.78	5.08	190.88	1.88	0.359	51.42
15	51.42	5.44	190.63	1.88	0.359	51.06
16	51.06	5.80	190.38	1.88	0.358	50.70
17	50.70	6.16	190.13	1.88	0.358	50.35
18	50.35	6.51	189.88	1.88	0.357	49.99
19	49.99	6.87	189.63	1.88	0.357	49.63
20	49.63	7.23	189.38	1.88	0.356	49.28
21	49.28	7.58	189.13	1.88	0.356	48.92
22	48.92	7.94	188.88	1.88	0.355	48.56
23	48.56	8.30	188.63	1.88	0.355	48.21
24	48.21	8.65	188.38	1.88	0.355	47.85
25	47.85	9.01	188.13	1.88	0.354	47.50
26	47.50	9.36	187.89	1.88	0.354	47.15
27	47.15	9.71	187.64	1.88	0.353	46.79
28	46.79	10.07	187.39	1.88	0.353	46.44
29	46.44	10.42	187.15	1.88	0.352	46.09
30	46.09	10.77	186.90	1.88	0.352	45.74

Table 8-7. Relationship of Pipe Dimensional Changes to Sample Mass and Surface Area

Assuming that the radii and height change linearly, a relationship can be established between the sample mass and surface area
- Assumption is that the outer and inner diameter change at same rate
and the height changes at 3X that rate (1X from top and 2X from bottom)

R1 (cm)	R2 (cm)	H (cm)	Δ (cm)	SA (cm2)	V (cm3)	mass (g)
5.650	5.42	2.54	0	192.667	20.317	54.856
5.640	5.43	2.51	0.01	189.190	18.331	49.494
5.630	5.44	2.48	0.02	185.712	16.387	44.245
5.620	5.45	2.45	0.03	182.234	14.485	39.109
5.610	5.46	2.42	0.04	178.756	12.624	34.085
5.600	5.47	2.39	0.05	175.279	10.805	29.175
5.590	5.48	2.36	0.06	171.801	9.028	24.376
5.580	5.49	2.33	0.07	168.323	7.293	19.691
5.570	5.5	2.30	0.08	164.845	5.599	15.118
5.560	5.51	2.27	0.09	161.368	3.947	10.658
5.550	5.52	2.24	0.10	157.890	2.337	6.310
5.540	5.53	2.21	0.11	154.412	0.769	2.075

R1 = outer radius; R2 = hole radius; H = height
Assume Al density of 2.70 g/mL
SA = (2) * [π(R1^2-R2^2)] + 2 * πR1H + 2 * πR2H
V = π * H * (R1^2 - R2^2)



8.2.3 Rod Sample Calculations

Similar to the calculation of Appendix 8.2.1, a spreadsheet was used to perform minute-by-minute Al dissolution calculations for an input dissolution rate of rod samples for Test 6. The principle behind these calculations is that the weight loss, volume loss, and surface area change can be calculated for a sample with a known starting configuration (and surface area). For an input dissolution rate (in mg/min/cm^2), the weight loss (in mg) for a sample of known surface area (in cm^2) can be calculated. The volume of sample dissolved (in cm^3) can be calculated using the weight loss and the density of aluminum (2593 mg/cm^3).

One key assumption factors into how the sample dimensions change as dissolution progresses. The assumption is that for the rods dissolve uniformly – the top, middle, and bottom of each sample dissolve at the same rate and in the same manner. The rod segments (see Figure 3-1 and Table 3-1) have a diameter of 3.21 mm and are 910 mm long (cut to 101 mm lengths); two rods were dissolved in Test 6.

The starting surface area of the sample is calculated as follows where d is the rod diameter (in cm) and h is the length of each rod.

$$SA = 2 * \pi dh = (2\, rods)\pi(0.321\, cm)(91.0\, cm) = 183.3\, cm^2$$

The volume is calculated by dividing the sample mass (in g) by the density (in g/cm^3).

The values from dissolution calculations for Test 6 from 0 to 30 min dissolution time are provided in Table 8-8. At time = 0 min [Column 1], the sample mass for 18 rods was 38.38 g [Column 2], the sample volume was 14.80 cm3 [Column 4], and the initial surface area of the rods available for reaction was 183.34 cm^2 [Column 5].

For a given dissolution rate [Column 6], the mass of Al dissolution for that one-minute interval can be calculated by multiplying the dissolution rate and the surface area. For Test 6, 0 to 1 min, the mass dissolved is 0.458 g [Column 7]. Subtracting that mass from the starting mass for that time step yields the final mass for that time step (37.92 g) [Column 8]. From the revised mass of Column 8, a revised volume [Column 9], diameter [Column 10], and surface area [Column 11] can be calculated. These values are copied to Time = 1 min, Columns 2 to 5, as the initial conditions for dissolution from 1 to 2 min.

The calculations are then continued, minute by minute, to calculate the dissolution of the sample. Identifying the appropriate dissolution rate for Column 6 is based on the mass of Al dissolved for a given time frame, as determined analytically. Consulting Table 4-11 for the mass of Al dissolved during Test 6 for 0 to 20 min, the quantity is 6.158 g. The objective of the calculation for Test 6, 0 to 20 min, is to revise the dissolution rate [Column 6] which results in a total mass of Al dissolved from 0 to 20 min of 6.16 g. The corresponding dissolution rate is 1.75 mg/min/cm^2. The process is continued for each integral time period and Al dissolution mass in Table 4-11.

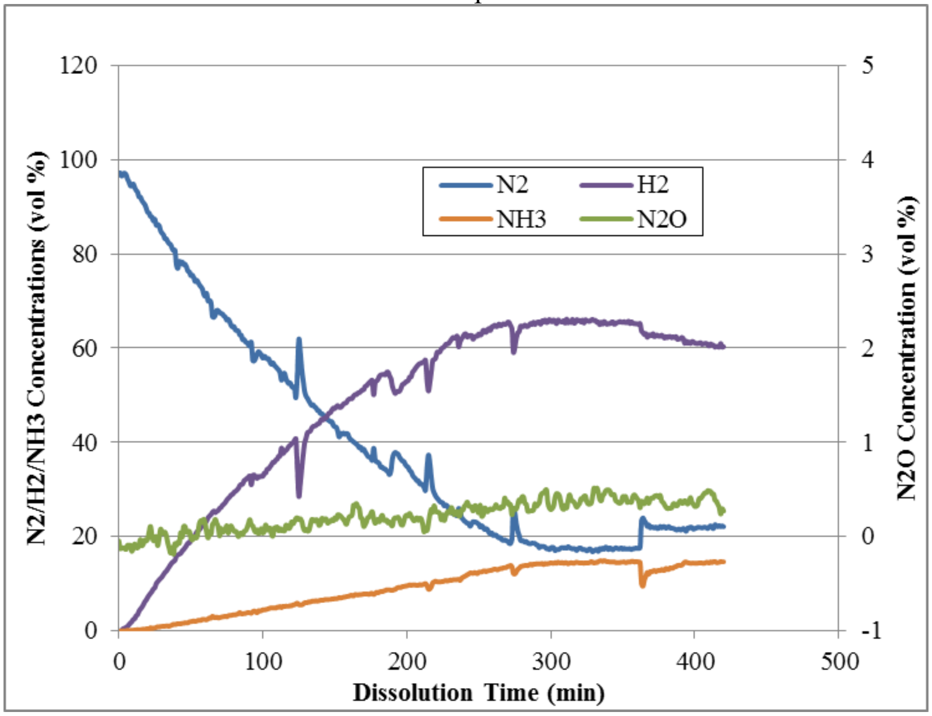
Table 8-8. Test 6 Sample Dissolution Calculations for 0 to 30 Minutes

# of rods =	18.00									
1	2	3	4	5	6	7	8	9	10	11
Dissolve Time (min)	Initial Al Mass (g)	Start Diameter (cm)	Start Volume (cm3)	Start Al Surface Area (cm2)	Rxn Rate (mg/min /cm2)	Al Rxn (grams)	Final Al Mass (grams)	Final Volume (cm3)	Final Diameter (cm)	Final Surface (cm2)
0	38.38	0.321	14.80	183.34	1.75	0.321	38.06	14.68	0.320	183.67
1	38.06	0.320	14.68	182.57	1.75	0.319	37.74	14.55	0.318	182.90
2	37.74	0.318	14.55	181.80	1.75	0.318	37.42	14.43	0.317	182.13
3	37.42	0.317	14.43	181.03	1.75	0.317	37.11	14.31	0.316	181.36
4	37.11	0.316	14.31	180.27	1.75	0.315	36.79	14.19	0.314	180.58
5	36.79	0.314	14.19	179.50	1.75	0.314	36.48	14.07	0.313	179.81
6	36.48	0.313	14.07	178.73	1.75	0.313	36.16	13.95	0.312	179.04
7	36.16	0.312	13.95	177.96	1.75	0.311	35.85	13.83	0.310	178.27
8	35.85	0.310	13.83	177.19	1.75	0.310	35.54	13.71	0.309	177.49
9	35.54	0.309	13.71	176.43	1.75	0.309	35.23	13.59	0.308	176.72
10	35.23	0.308	13.59	175.66	1.75	0.307	34.93	13.47	0.306	175.95
11	34.93	0.306	13.47	174.89	1.75	0.306	34.62	13.35	0.305	175.18
12	34.62	0.305	13.35	174.12	1.75	0.305	34.31	13.23	0.304	174.40
13	34.31	0.304	13.23	173.35	1.75	0.303	34.01	13.12	0.302	173.63
14	34.01	0.302	13.12	172.59	1.75	0.302	33.71	13.00	0.301	172.86
15	33.71	0.301	13.00	171.82	1.75	0.301	33.41	12.88	0.299	172.08
16	33.41	0.299	12.88	171.05	1.75	0.299	33.11	12.77	0.298	171.31
17	33.11	0.298	12.77	170.28	1.75	0.298	32.81	12.65	0.297	170.54
18	32.81	0.297	12.65	169.51	1.75	0.297	32.51	12.54	0.295	169.77
19	32.51	0.295	12.54	168.75	1.75	0.295	32.22	12.43	0.294	168.99
20	32.22	0.294	12.43	167.98	1.75	0.294	31.93	12.31	0.293	168.22
21	31.93	0.293	12.31	167.21	1.67	0.279	31.65	12.20	0.291	167.48
22	31.65	0.291	12.20	166.48	1.67	0.278	31.37	12.10	0.290	166.75
23	31.37	0.290	12.10	165.74	1.67	0.277	31.09	11.99	0.289	166.01
24	31.09	0.289	11.99	165.01	1.67	0.276	30.82	11.88	0.288	165.27
25	30.82	0.288	11.88	164.28	1.67	0.274	30.54	11.78	0.286	164.53
26	30.54	0.286	11.78	163.55	1.67	0.273	30.27	11.67	0.285	163.80
27	30.27	0.285	11.67	162.81	1.67	0.272	30.00	11.57	0.284	163.06
28	30.00	0.284	11.57	162.08	1.67	0.271	29.73	11.46	0.282	162.32
29	29.73	0.282	11.46	161.35	1.67	0.269	29.46	11.36	0.281	161.59
30	29.46	0.281	11.36	160.61	1.67	0.268	29.19	11.26	0.280	160.85

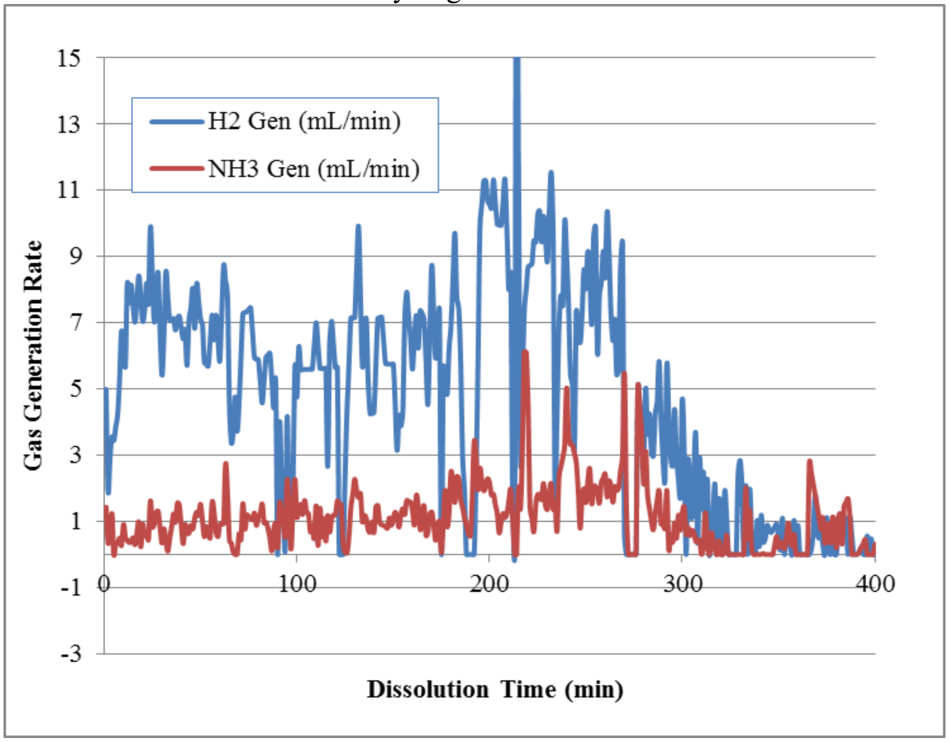
8.3 Gas Concentrations and Generation Rates

8.3.1 Test 1 – Alloy 6063 (Disks) at 80 °C

Raman Gas Composition Profile

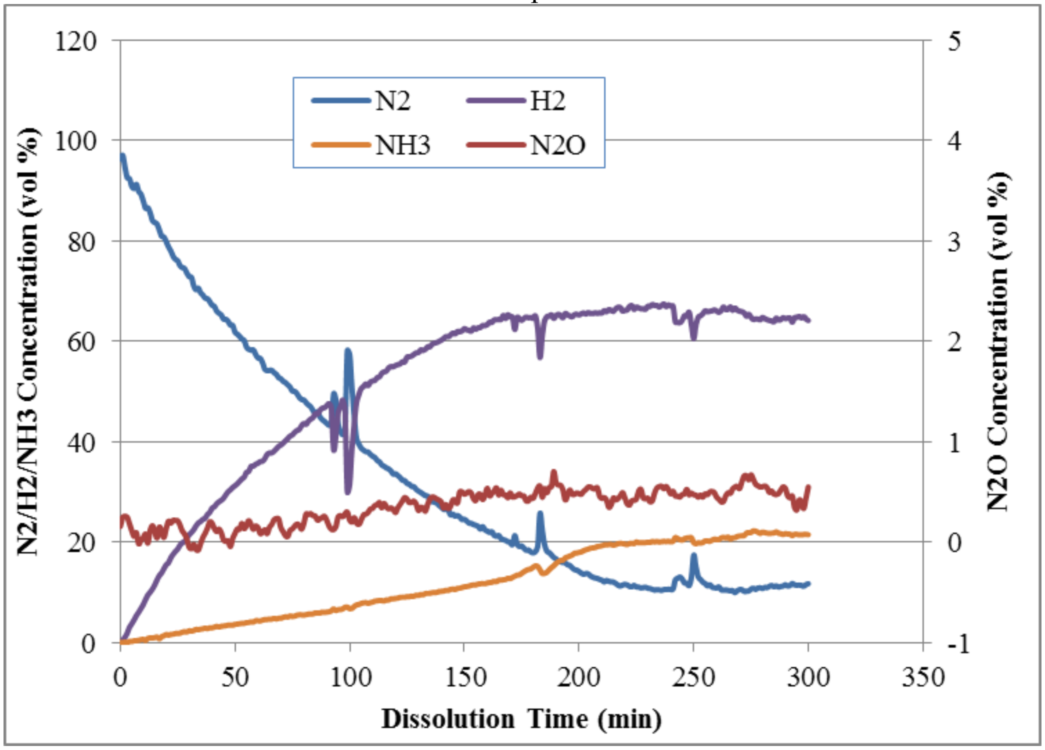


Ammonia and Hydrogen Gas Generation Rates

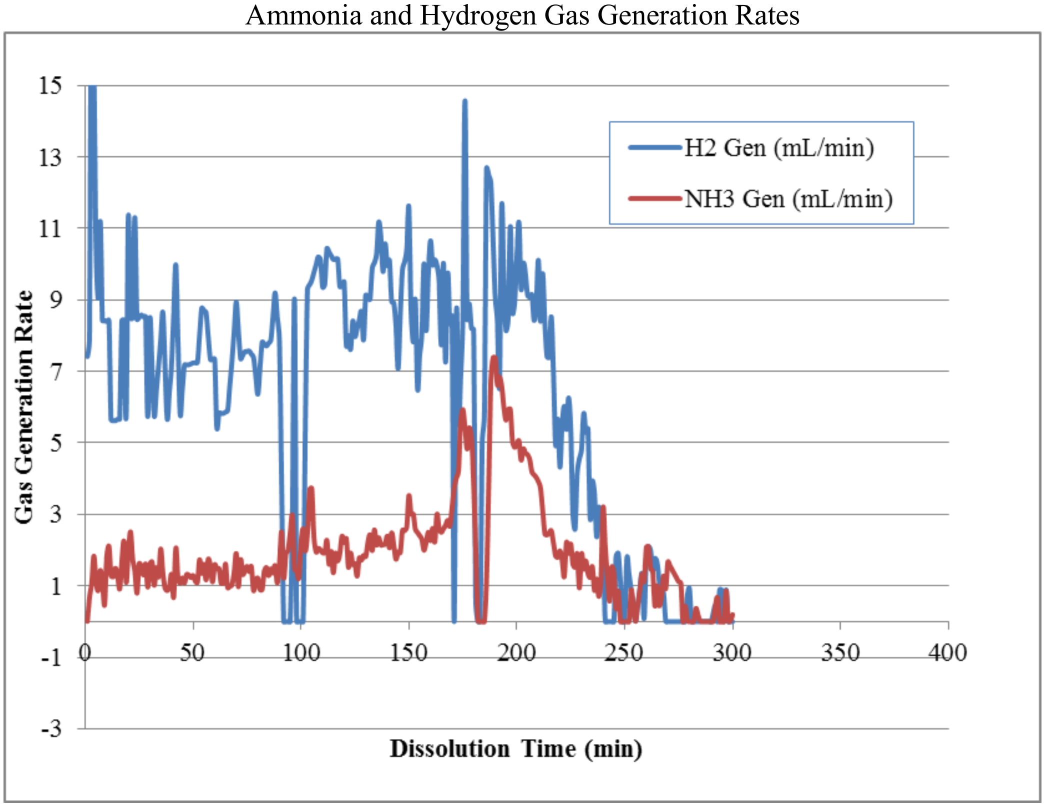


8.3.2 Test 2 – Alloy 6063 (Disks) at 85 °C

Raman Gas Composition Profile

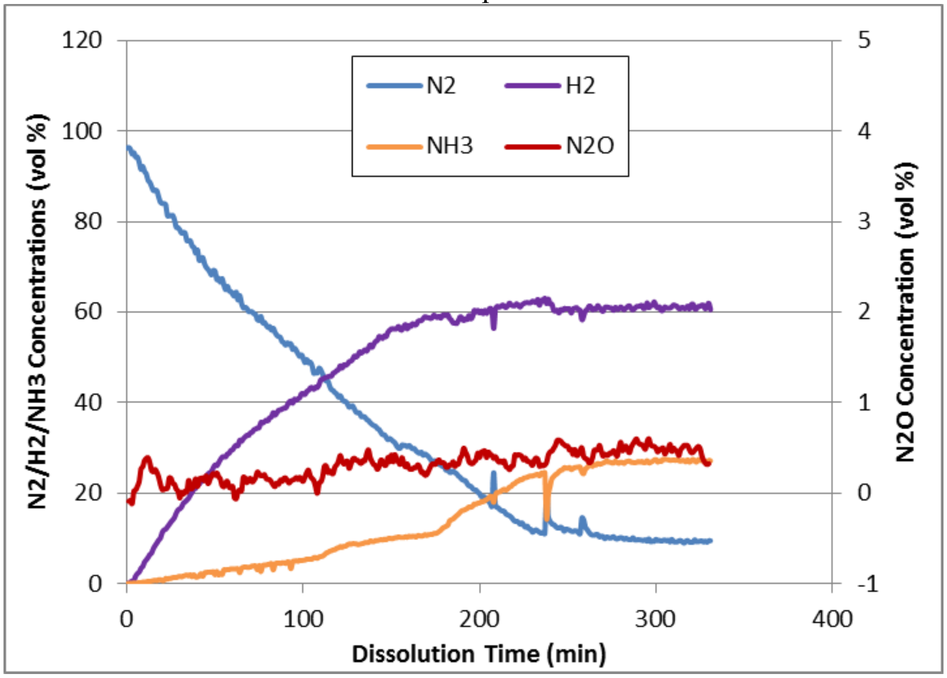


Ammonia and Hydrogen Gas Generation Rates

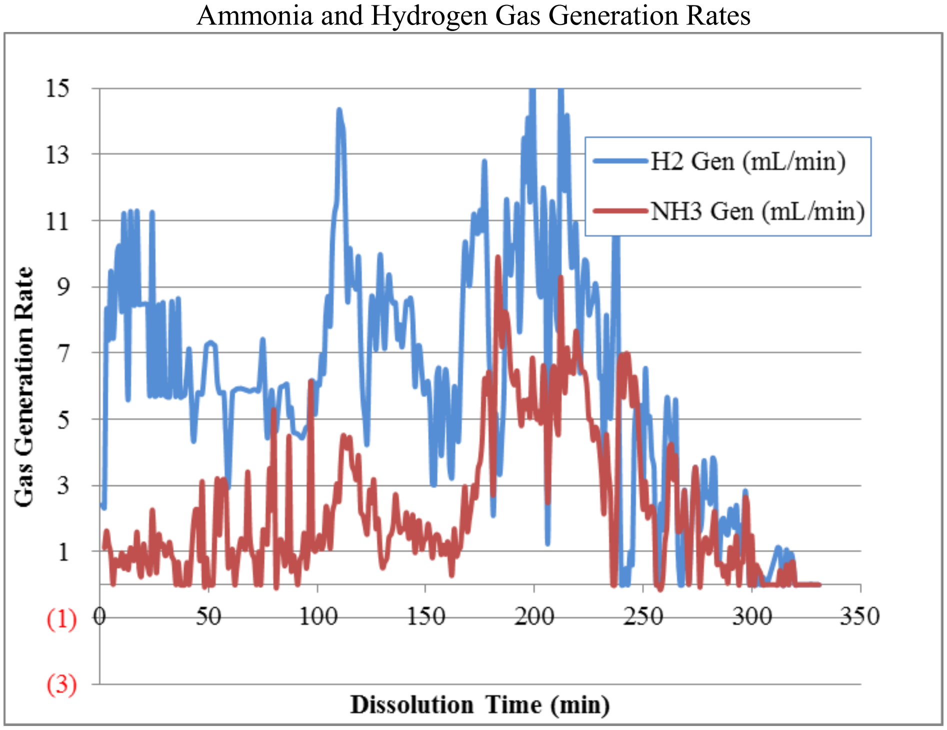


8.3.3 Test 3 – Alloy 6063 (Disks) at 80, 85, 90 °C

Raman Gas Composition Profile

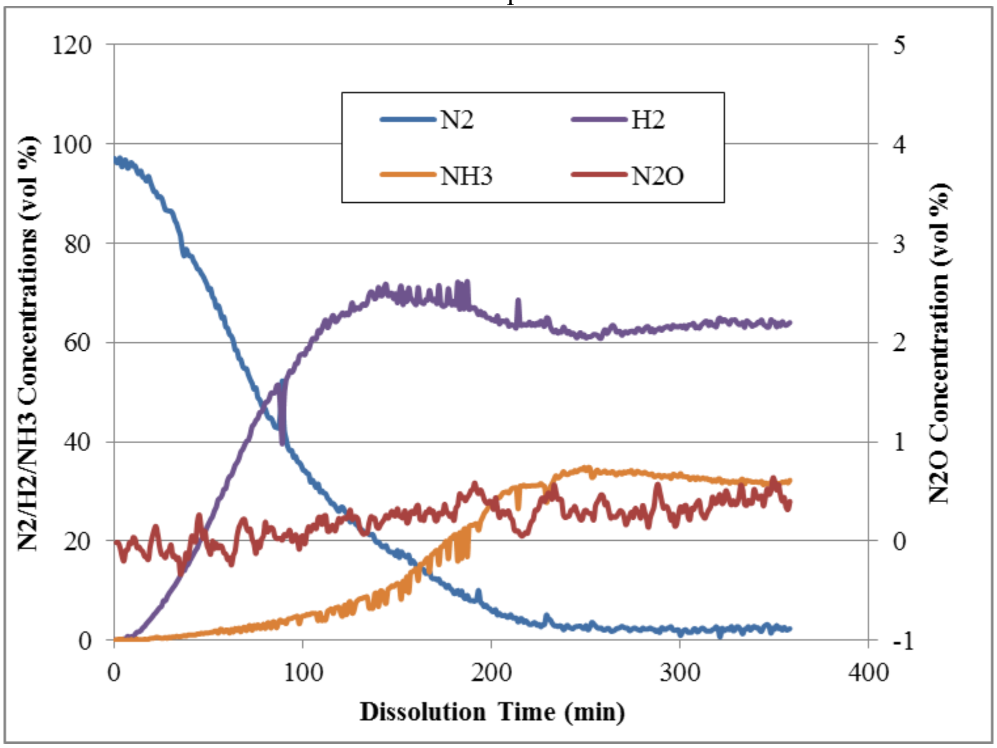


Ammonia and Hydrogen Gas Generation Rates

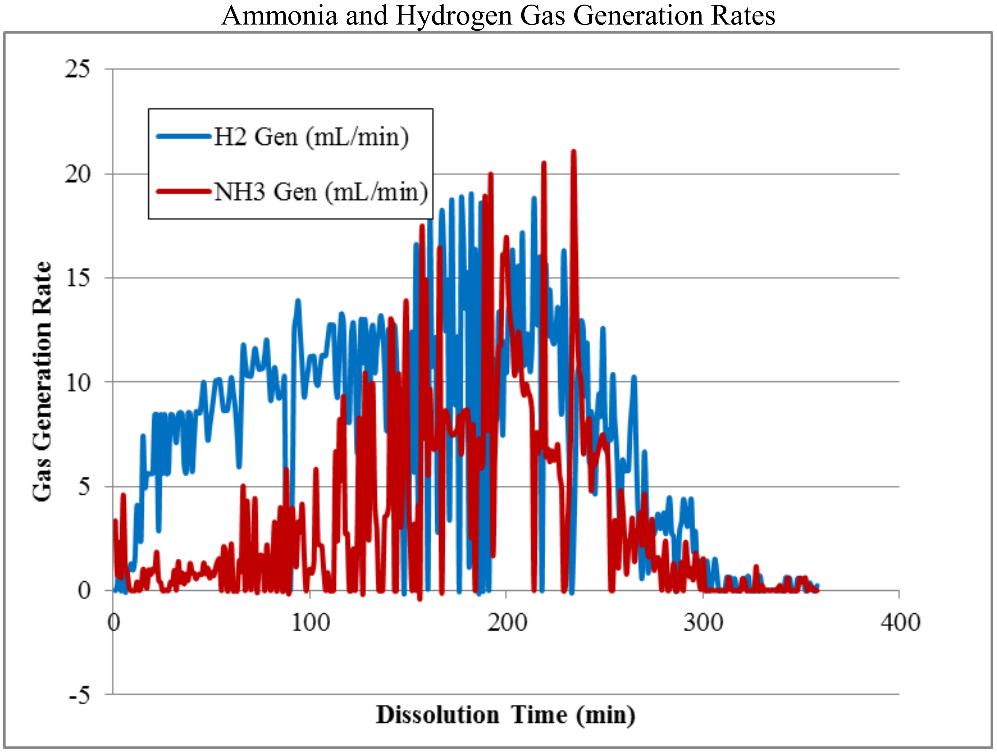


8.3.4 Test 4 – Alloy 6063 (Disks) at 90-92 °C

Raman Gas Composition Profile

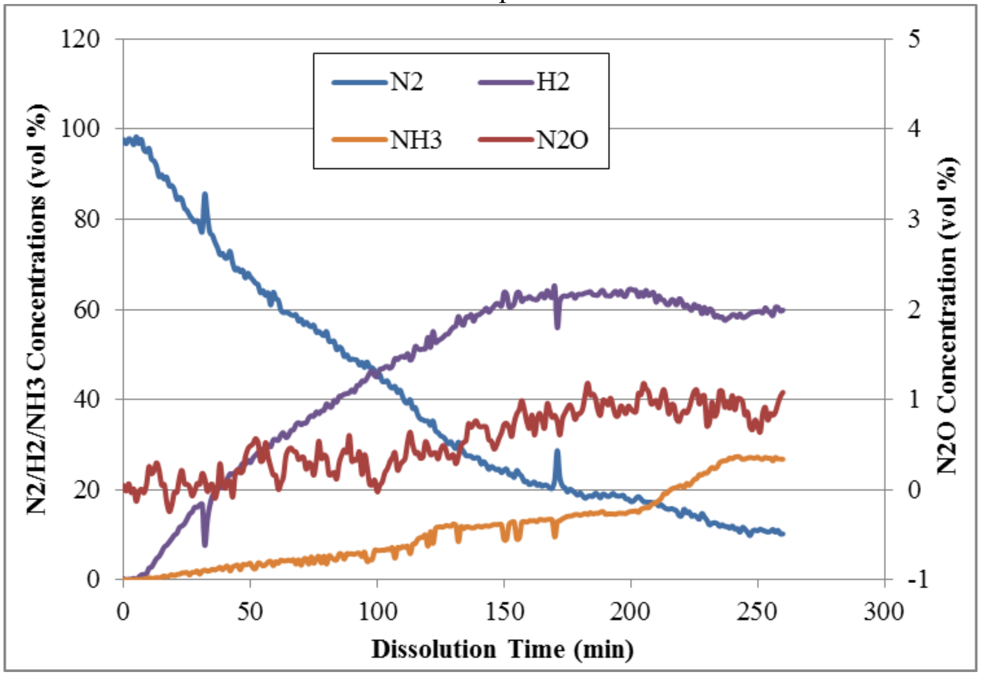


Ammonia and Hydrogen Gas Generation Rates

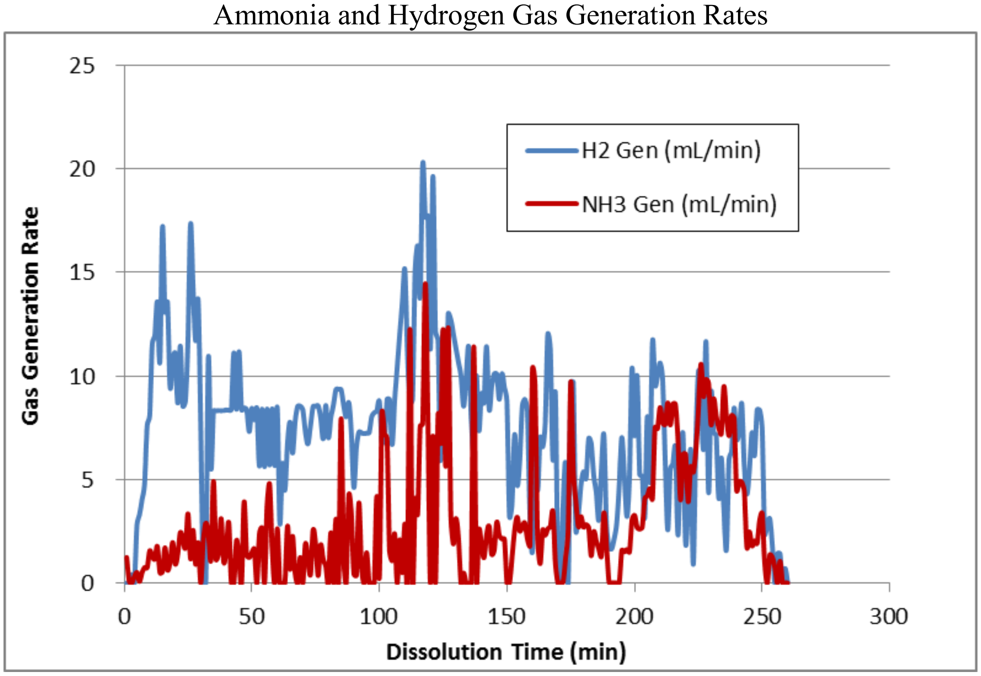


8.3.5 Test 5 – Alloy 6063 (Pipe) at 80, 85, 90 °C

Raman Gas Composition Profile

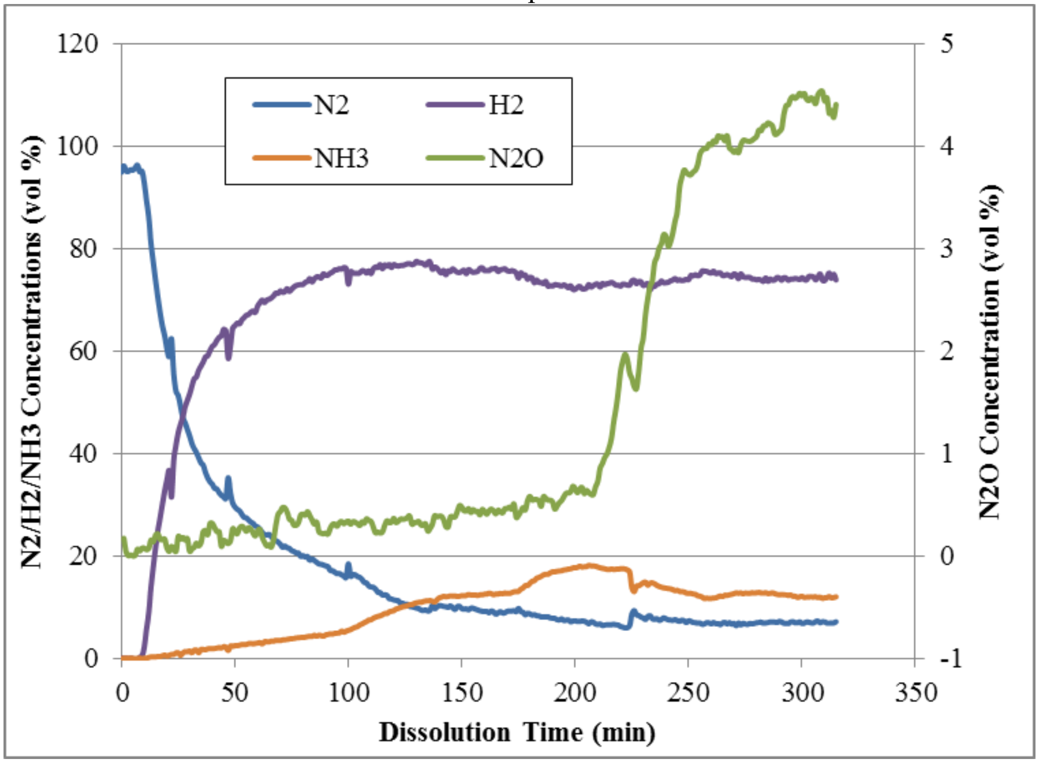


Ammonia and Hydrogen Gas Generation Rates

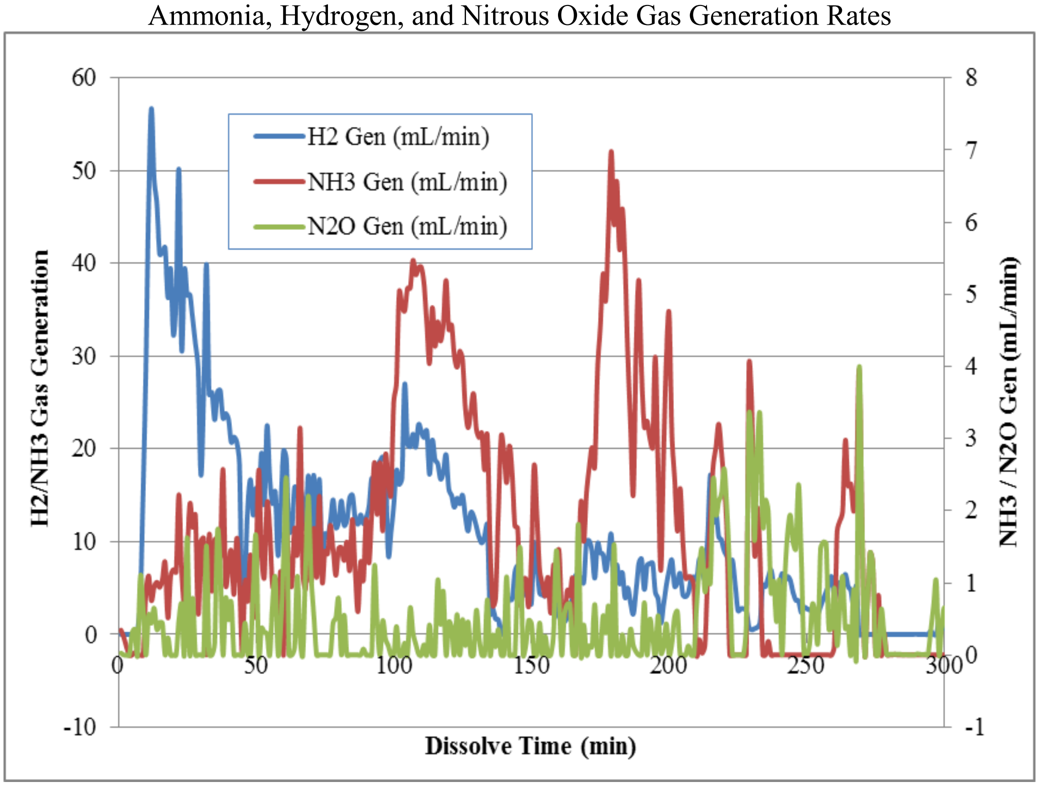


8.3.6 Test 6 – Alloy 4043(Rods) at 80, 85, 90 °C

Raman Gas Composition Profile



Ammonia, Hydrogen, and Nitrous Oxide Gas Generation Rates



8.4 Sample Analyses and Process Data

8.4.1 Ammonium Concentrations in Solution

Sample #	**Test 1**		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
	Time (min)	NH_4^+ (mg/L)	Time (min)	NH_4^+ (mg/L)	Time (min)	NH_4^+ (mg/L)	Time (min)	NH_4^+ (mg/L)	Time (min)	NH_4^+ (mg/L)	Time (min)	NH_4^+ (mg/L)
1	36	1380	30	1690	30	1120	30	464	30	2030	20	889
2	60	2190	60	2600	60	2800	60	1120	60	3370	45	2220
3	90	2980	90	3600	94	3800	94	2090	90	4340	75	3290
4	120	3620	120	4790	122	4890	122	3500	120	5290	98	3970
5	150	4160	150	5570	150	5680	148	4350	150	6240	135	4560
6	186	5120	180	6340	180	6080	180	5210	184	6670	165	4400
7	240	6010	210	7030	210	6560	210	6130	210	6870	195	4330
8	270	6520	240	6720	240	6770	240	6090	240	6910	225	4110
9	300	6700	275	6830	270	6970	270	**4820***	270	7070	270	4160
10	330	6940	305	6860	300	6810	300	6030	285	6910	315	4160
11	360	6810	---	---	330	6870	330	5850	---	---	---	---
12	390	6450	---	---	---	---	360	5850	---	---	---	---
13	420	6880	---	---	---	---	---	---	---	---	---	---

The uncertainty of IC Cation measurements was 10%
* Value has been replaced with 6060 mg/L, which is consistent with the trend within Test 4 as well as the trends of the other five experiments.

8.4.2 Ammonia Gas Volumes in Off Gas

	Test 1		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
Sample #	Time (min)	NH_3 (mL)	Time (min)	NH_3 (mL)	Time (min)	NH_3 (mL)	Time (min)	NH_3 (mL)	Time (min)	NH_3 (mL)	Time (min)	NH_3 (mL)
1	36	23.7	30	40.9	30	27.2	30	23.7	30	35	20	12.5
2	60	22.7	60	39.6	60	34.7	60	27.7	60	55	45	33.3
3	90	26.8	90	39.2	94	40.6	94	54.8	90	42	75	48.3
4	120	34.6	120	63.4	122	71.6	122	66.4	120	101	98	37.4
5	150	33.2	150	63.6	150	51.5	148	123.2	150	98	135	156.6
6	186	46.9	180	101.6	180	64.9	180	233.3	184	98	165	44.0
7	240	104.4	210	131.5	210	188.4	210	306	210	71	195	115.0
8	270	67.7	240	55.9	240	145.8	240	231.5	240	226	225	50.4
9	300	43.2	275	33.3	270	109.3	270	125.5	270	36	270	32.7
10	330	22.1	305	4.3	300	30.4	300	34	285	0	315	6.5
11	360	10.6	---	---	330	10.5	330	2.9	---	---	---	---
12	390	29.7	---	---	---	---	360	5.5	---	---	---	---
13	420	1.6	---	---	---	---	---	---	---	---	---	---
Total	**---**	**467**	**---**	**573**	**---**	**775**	**---**	**1235**	**---**	**762**	**---**	**537**
The uncertainty of Raman gas measurements was 20%												

8.4.3 Hydrogen Gas Volumes in Off Gas

Sample #	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Time (min)	H_2 (mL)	Time (min)	H_2 (mL)	Time (min)	H_2 (mL)	Time (min)	H_2 (mL)	Time (min)	H_2 (mL)	Time (min)	H_2 (mL)
1	36	239	30	262	30	239	30	126	30	268	20	511
2	60	163	60	223	60	193	60	254	60	227	45	702
3	90	172	90	217	94	186	94	317	90	227	75	428
4	120	152	120	193	122	235	122	309	120	315	98	314
5	150	166	150	276	150	216	148	259	150	304	135	637
6	186	223	180	262	180	202	180	356	184	196	165	142
7	240	426	210	255	210	293	210	341	210	152	195	184
8	270	227	240	157	240	261	240	349	240	180	225	234
9	300	95	275	23	270	105	270	211	270	83	270	181
10	330	52	305	5.0	300	55	300	83	285	0	315	12
11	360	21	---	---	330	11.1	330	13	---	---	---	---
12	390	14	---	---	---	---	360	3.8	---	---	---	---
13	420	1.7	---	---	---	---	---	---	---	---	---	---
Total	**---**	**1952**	**---**	**1873**	**---**	**1996**	**---**	**2622**	**---**	**1952**	**---**	**3345**
The uncertainty of Raman gas measurements was 20%												

8.4.4 Nitrate Concentrations in Solution

Sample #	Test 1 Time (min)	Test 1 NO_3^- (mg/L)	Test 2 Time (min)	Test 2 NO_3^- (mg/L)	Test 3 Time (min)	Test 3 NO_3^- (mg/L)	Test 4 Time (min)	Test 4 NO_3^- (mg/L)	Test 5 Time (min)	Test 5 NO_3^- (mg/L)	Test 6 Time (min)	Test 6 NO_3^- (mg/L)
1	36	118000	30	116000	30	121000	30	126000	30	111000	20	114000
2	60	111000	60	112000	60	108000	60	115000	60	105000	45	90700
3	90	107000	90	105000	94	104000	94	109000	90	95700	75	83100
4	120	102000	120	98100	122	94600	122	103000	120	82700	98	74000
5	150	96200	150	90800	150	92300	148	91600	150	77100	135	64600
6	186	87700	180	84200	180	86500	180	85300	184	73300	165	61900
7	240	77300	210	78600	210	81900	210	79700	210	69500	195	59200
8	270	73200	240	75400	240	75200	240	72400	240	63300	225	59000
9	300	72800	275	70800	270	72800	270	67900	270	60500	270	58700
10	330	71000	305	73400	300	70700	300	62500	285	61800	315	59300
11	360	69400	---	---	330	69700	330	66300	---	---	---	---
12	390	71900	---	---	---	---	360	60300	---	---	---	---
13	420	72100	---	---	---	---	---	---	---	---	---	---
The uncertainty of IC anion measurements was 10%												

8.4.5 Nitrite Concentrations in Solution

Sample #	Test 1 Time (min)	Test 1 NO_2^- (mg/L)	Test 2 Time (min)	Test 2 NO_2^- (mg/L)	Test 3 Time (min)	Test 3 NO_2^- (mg/L)	Test 4 Time (min)	Test 4 NO_2^- (mg/L)	Test 5 Time (min)	Test 5 NO_2^- (mg/L)	Test 6 Time (min)	Test 6 NO_2^- (mg/L)
1	36	661	30	726	30	539	30	281	30	802	20	7716
2	60	889	60	1020	60	1000	60	507	60	1210	45	12900
3	90	1090	90	1230	94	1280	94	780	90	1450	75	19400
4	120	1200	120	1320	122	1370	122	971	120	1740	98	22300
5	150	1250	150	1400	150	1490	148	1080	150	2170	135	23300
6	186	1280	180	1480	180	1450	180	1220	184	2430	165	22900
7	240	1320	210	1510	210	1570	210	1370	210	2460	195	22600
8	270	1330	240	1520	240	1590	240	1410	240	2570	225	21900
9	300	1310	275	1440	270	1570	270	1400	270	2580	270	22000
10	330	1290	305	1490	300	1550	300	1162	285	2660	315	22000
11	360	1270	---	---	330	1540	330	1230	---	---	---	---
12	390	1310	---	---	---	---	360	1210	---	---	---	---
13	420	1330	---	---	---	---	---	---	---	---	---	---
The uncertainty of IC anion measurements was 10%												

8.4.6 Total Base Concentrations in Solution

Sample #	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Time (min)	Base (N)	Time (min)	Base (N)	Time (min)	Base (N)	Time (min)	Base (N)	Time (min)	Base (N)	Time (min)	Base (N)
1	36	0.799	30	0.824	30	0.666	30	0.294	30	1.0	20	0.607
2	60	1.06	60	1.15	60	1.08	60	0.656	60	1.3	45	0.928
3	90	1.48	90	1.40	94	1.47	94	1.08	90	1.6	75	1.33
4	120	1.65	120	1.96	122	1.78	122	1.41	120	2.0	98	1.59
5	150	1.91	150	2.32	150	2.02	148	1.71	150	2.5	135	1.87
6	186	2.50	180	2.60	180	2.24	180	2.05	184	2.4	165	2.17
7	240	2.38	210	2.63	210	2.50	210	2.34	210	2.7	195	2.38
8	270	2.56	240	2.96	240	2.78	240	2.66	240	3.0	225	2.54
9	300	3.09	275	3.12	270	2.89	270	2.85	270	3.3	270	2.53
10	330	3.04	305	3.12	300	3.12	300	3.12	285	3.04	315	2.53
11	360	3.01	---	---	330	3.07	330	3.26	---	---	---	---
12	390	3.02	---	---	---	---	360	3.34	---	---	---	---
13	420	2.98	---	---	---	---	---	---	---	---	---	---

The units of normality (N) refer to mole equivalents of base per liter. Because the discussion of test results only refers to those anionic equivalents without associating them with multivalent cations, the sample normality is equivalent to its molarity. The uncertainty of total base measurements was 10%.

8.4.7 Free OH^- Concentrations in Solution

Sample #	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Time (min)	Free OH^- (N)	Time (min)	Free OH^- (N)	Time (min)	Free OH^- (N)	Time (min)	Free OH^- (N)	Time (min)	Free OH^- (N)	Time (min)	Free OH^- (N)
1	36	0.414	30	0.374	30	0.370	30	0.164	30	0.363	20	0.224
2	60	0.464	60	0.516	60	0.642	60	0.357	60	0.532	45	0.455
3	90	0.869	90	0.913	94	0.874	94	0.493	90	0.568	75	0.687
4	120	1.15	120	1.11	122	1.20	122	0.61	120	0.601	98	0.84
5	150	1.31	150	1.29	150	1.34	148	0.909	150	0.757	135	1.10
6	186	1.60	180	1.61	180	1.56	180	1.24	184	1.240	165	0.996
7	240	1.83	210	1.65	210	1.69	210	1.60	210	1.060	195	0.894
8	270	2.07	240	1.75	240	1.83	240	1.74	240	1.200	225	0.973
9	300	2.25	275	1.72	270	2.01	270	1.95	270	1.220	270	1.02
10	330	2.33	305	1.71	300	2.11	300	1.98	285	1.240	315	0.969
11	360	2.15	---	---	330	2.14	330	2.18	---	---	---	---
12	390	2.21	---	---	---	---	360	1.67	---	---	---	---
13	420	2.26	---	---	---	---	---	---	---	---	---	---

The units of normality (N) refer to mole equivalents of base per liter. Because the discussion of test results only refers to those anionic equivalents without associating them with multivalent cations, the sample normality is equivalent to its molarity. The uncertainty of free base measurements was 10%.

8.4.8 Other Base Concentrations in Solution

	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
Sample #	Time (min)	Other Base (N)	Time (min)	Other Base (N)	Time (min)	Other Base (N)	Time (min)	Other Base (N)	Time (min)	Other Base (N)	Time (min)	Other Base (N)
1	36	0.355	30	0.425	30	0.379	30	0.114	30	0.499	20	0.339
2	60	0.535	60	0.461	60	0.363	60	0.289	60	0.503	45	0.537
3	90	0.480	90	0.539	94	0.474	94	0.577	90	1.040	75	0.596
4	120	0.482	120	0.716	122	0.556	122	0.834	120	1.40	98	0.663
5	150	0.460	150	0.934	150	0.600	148	0.660	150	1.54	135	0.764
6	186	0.519	180	1.01	180	0.671	180	0.574	184	1.34	165	1.01
7	240	0.580	210	0.980	210	0.836	210	0.734	210	1.60	195	1.44
8	270	0.510	240	1.22	240	0.804	240	0.752	240	1.79	225	1.43
9	300	0.750	275	1.46	270	0.793	270	0.752	270	1.10	270	1.46
10	330	0.780	305	1.35	300	0.820	300	0.884	285	1.83	315	1.45
11	360	0.727	---	---	330	0.860	330	0.970	---	---	---	---
12	390	0.726	---	---	---	---	360	1.57	---	---	---	---
13	420	0.760	---	---	---	---	---	---	---	---	---	---

The units of normality (N) refer to mole equivalents of base per liter. Because the discussion of test results only refers to those anionic equivalents without associating them with multivalent cations, the sample normality is equivalent to its molarity. The uncertainty of other base measurements was 10%.

8.4.9 Aluminum Concentrations in Solution

Sample #	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Time (min)	Al (mg/L)	Time (min)	Al (mg/L)	Time (min)	Al (mg/L)	Time (min)	Al (mg/L)	Time (min)	Al (mg/L)	Time (min)	Al (mg/L)
1	36	6040	30	7160	30	5690	30	2070	30	7600	20	6040
2	60	9350	60	7170	60	11200	60	2060	60	5430	45	11000
3	90	13300	90	7070	94	9930	94	10900	90	5490	75	14400
4	120	8940	120	8230	122	10500	122	4770	120	7680	98	16900
5	150	9580	150	8540	150	11900	148	5410	150	10200	135	22400
6	186	12000	180	9620	180	12300	180	6710	184	11200	165	28100
7	240	12700	210	11000	210	14500	210	7840	210	12700	195	27500
8	270	13000	240	11700	240	14700	240	8640	240	14200	225	26700
9	300	14500	275	15100	270	15500	270	10000	270	15200	270	27200
10	330	15800	305	14100	300	16700	300	10500	285	15000	315	27100
11	360	15100	---	---	330	17200	330	11300	---	---	---	---
12	390	14900	---	---	---	---	360	12400	---	---	---	---
13	420	16100	---	---	---	---	---	---	---	---	---	---
The uncertainty of ICPES measurements was 10%.												

8.4.10 Silicon Concentrations in Solution

Sample #	**Test 1**		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
	Time (min)	Si (mg/L)	Time (min)	Si (mg/L)	Time (min)	Si (mg/L)	Time (min)	Si (mg/L)	Time (min)	Si (mg/L)	Time (min)	Si (mg/L)
1	36	30.0	30	46.6	30	37.3	30	<34.4	30	37.9	20	81.8
2	60	46.8	60	61.9	60	60.1	60	<34.4	60	61.0	45	167
3	90	63.6	90	81.4	94	79.9	94	48.7	90	81.7	75	263
4	120	79.4	120	107	122	103	122	65.7	120	109	98	334
5	150	95.5	150	122	150	120	148	71.5	150	135	135	605
6	186	107	180	142	180	135	180	77.8	184	153	165	687
7	240	140	210	162	210	152	210	84.1	210	159	195	646
8	270	154	240	173	240	164	240	97.6	240	174	225	544
9	300	163	275	179	270	172	270	96.5	270	183	270	312
10	330	168	305	176	300	175	300	107	285	178	315	<215
11	360	175	---	---	330	175	330	112	---	---	---	---
12	390	165	---	---	---	---	360	129	---	---	---	---
13	420	176	---	---	---	---	---	---	---	---	---	---
The uncertainty of ICPES measurements was 10%.												

8.4.11 Aluminum-to-Silicon Mole Ratios from ICPES Data

	Test 1		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
Sample #	Time (min)	Al:Si Mole Ratio	Time (min)	Al:Si Mole Ratio	Time (min)	Al:Si Mole Ratio	Time (min)	Al:Si Mole Ratio	Time (min)	Al:Si Mole Ratio	Time (min)	Al:Si Mole Ratio
1	36	210	30	160	30	159	30	> 63	30	209	20	76.9
2	60	208	60	121	60	194	60	> 63	60	93	45	68.6
3	90	218	90	90	94	129	94	233	90	70	75	57.0
4	120	117	120	80	122	106	122	76	120	73	98	52.7
5	150	104	150	73	150	103	148	79	150	79	135	38.5
6	186	117	180	71	180	95	180	90	184	76	165	42.6
7	240	94	210	71	210	99	210	97	210	83	195	44.3
8	270	88	240	70	240	93	240	92	240	85	225	51.1
9	300	93	275	88	270	94	270	108	270	86	270	90.7
10	330	98	305	83	300	99	300	102	285	88	315	> 131
11	360	90	---	---	330	102	330	105	---	---	---	---
12	390	94	---	---	---	---	360	100	---	---	---	---
13	420	95	---	---	---	---	---	---	---	---	---	---
The uncertainty of ICPES measurements was 10%.												

8.4.12 Calculated Solution Volumes at Each Sample Time

Sample #	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Time (min)	Vol (mL)	Time (min)	Vol (mL)	Time (min)	Vol (mL)	Time (min)	Vol (mL)	Time (min)	Vol (mL)	Time (min)	Vol (mL)
1	36	1028	30	1028	30	1024	30	1030	30	1236	20	1020
2	60	1043	60	1054	60	1043	60	1055	60	1267	45	1040
3	90	1062	90	1076	94	1054	94	1084	90	1298	75	1065
4	120	1081	120	1098	122	1083	122	1107	120	1329	98	1083
5	150	1100	150	1120	150	1090	148	1128	150	1360	135	1115
6	186	1124	180	1142	180	1119	180	1155	184	1396	165	1140
7	240	1162	210	1164	210	1138	210	1180	210	1422	195	1165
8	270	1181	240	1186	240	1157	240	1205	240	1453	225	1165
9	300	1200	275	1195	270	1176	270	1230	270	1460	270	1160
10	330	1195	305	1185	300	1195	300	1255	285	1455	315	1155
11	360	1190	---	---	330	1198	330	1280	---	---	---	---
12	390	1185	---	---	---	---	360	1303	---	---	---	---
13	420	1180	---	---	---	---	---	---	---	---	---	---

Note: Volumes calculated based on 10 M NaOH addition rates and sample volume removal.

8.4.13 Iron, Magnesium, and Sodium Concentration Measurements

Iron (Fe), mg/L													
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Test 1	< 0.478	0.71	0.66	< 0.478	< 0.478	< 0.478	< 0.478	< 0.478	0.73	0.8	0.9	< 0.478	2.2
Test 2	0.51	< 0.413	< 0.413	< 0.413	< 0.413	< 0.413	< 0.413	0.75	1.2	1.26	---	---	---
Test 3	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	---	---
Test 4	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	---
Test 5	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	< 4.08	---	---	---
Test 6	9.17	0.5	142	1.59	0.83	5.6	6.7	9.1	< 4.13	< 4.13	---	---	---
Magnesium (Mg), mg/L													
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Test 1	< 0.253	< 0.253	< 0.253	< 0.253	< 0.253	0.5	0.72	0.52	1.27	0.5	1.03	1.63	16.5
Test 2	< 0.0823	< 0.0823	< 0.0823	0.17	0.43	0.3	0.68	2.24	3.99	0.65	---	---	---
Test 3	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	1.08	< 0.476	< 0.476	< 0.476	0.54	---	---
Test 4	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	---
Test 5	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	< 0.476	---	---	---
Test 6	< 0.0823	0.12	< 0.0823	0.12	0.15	< 0.823	< 0.823	< 0.823	< 0.823	< 0.823	---	---	---
Sodium (Na), mg/L													
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Test 1	55200	58000	60900	64800	67600	70900	77300	80600	81700	84200	86200	85900	84300
Test 2	55000	59200	62800	67500	71200	75000	81800	83400	86600	85400	---	---	---
Test 3	61900	66900	71000	75600	78500	82800	86500	88500	92900	95000	95700	---	---
Test 4	53500	53400	63700	68000	71800	77900	83500	86300	91000	94200	97900	101000	---
Test 5	62500	68700	69800	71500	83700	88800	91600	95300	97900	95200	---	---	---
Test 6	53800	56600	72400	67600	68300	71800	75700	77300	79600	79400	---	---	---

Note: The uncertainty of ICPES measurements was 10%.

8.4.14 Calculated Sodium Concentrations

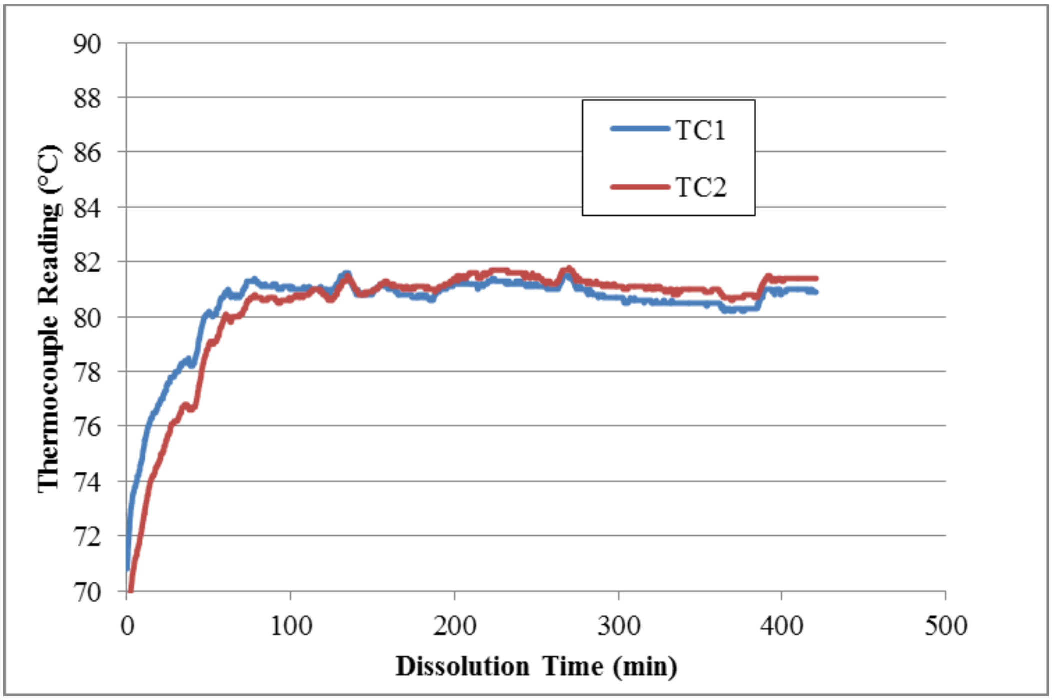
Sodium (Na), mg/L													
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Test 1	62882	66208	70217	74084	77819	82045	87905	91161	94314	94314	94314	94314	94314
Test 2	62480	66825	71225	75449	79507	83408	87162	90777	94766	94766	---	---	---
Test 3	62050	66208	71447	74287	78533	81426	84913	88285	91549	94708	94708	---	---
Test 4	53546	58811	64446	68919	72933	77595	81793	85817	89678	93385	96947	101937	---
Test 5	63028	68015	72764	77292	81613	86224	89690	93470	94911	94911	---	---	---
Test 6	61393	65736	70666	74372	79863	84159	88271	89257	89257	89257	---	---	---

8.4.15 Percent Agreement between Measured and Calculated Sodium Values

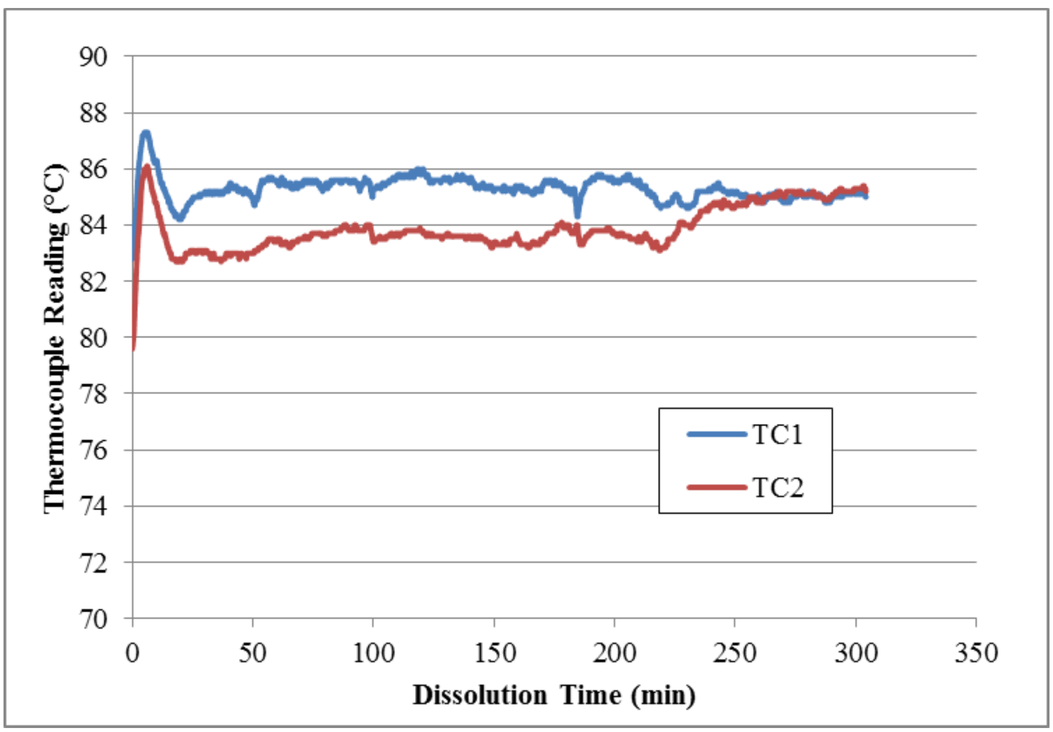
Test 1		**Test 2**		**Test 3**		**Test 4**		**Test 5**		**Test 6**	
Time (min)	% Agree	Time (min)	% Agree	Time (min)	% Agree	Time (min)	% Agree	Time (min)	% Agree	Time (min)	% Agree
36	88	30	88	30	100	30	100	30	99	20	88
60	88	60	89	60	101	60	89	60	101	45	86
90	87	90	88	94	99	94	99	90	96	75	102
120	87	120	89	122	102	122	99	120	93	98	91
150	87	150	90	150	100	148	98	150	103	135	86
186	86	180	90	180	102	180	100	184	103	165	85
240	88	210	94	210	102	210	102	210	102	195	86
270	88	240	92	240	100	240	101	240	102	225	87
300	87	275	91	270	101	270	101	270	103	270	89
330	89	305	90	300	100	300	101	285	100	315	89
360	91	---	---	330	101	330	101	---	---	---	---
390	91	---	---	---	---	360	99	---	---	---	---
420	89	---	---	---	---	---	---	---	---	---	---
Nonrad ICPES		Nonrad ICPES		Radioactive ICPES		Radioactive ICPES		Radioactive ICPES		Nonrad ICPES	

8.5 Experimental Temperature Measurements

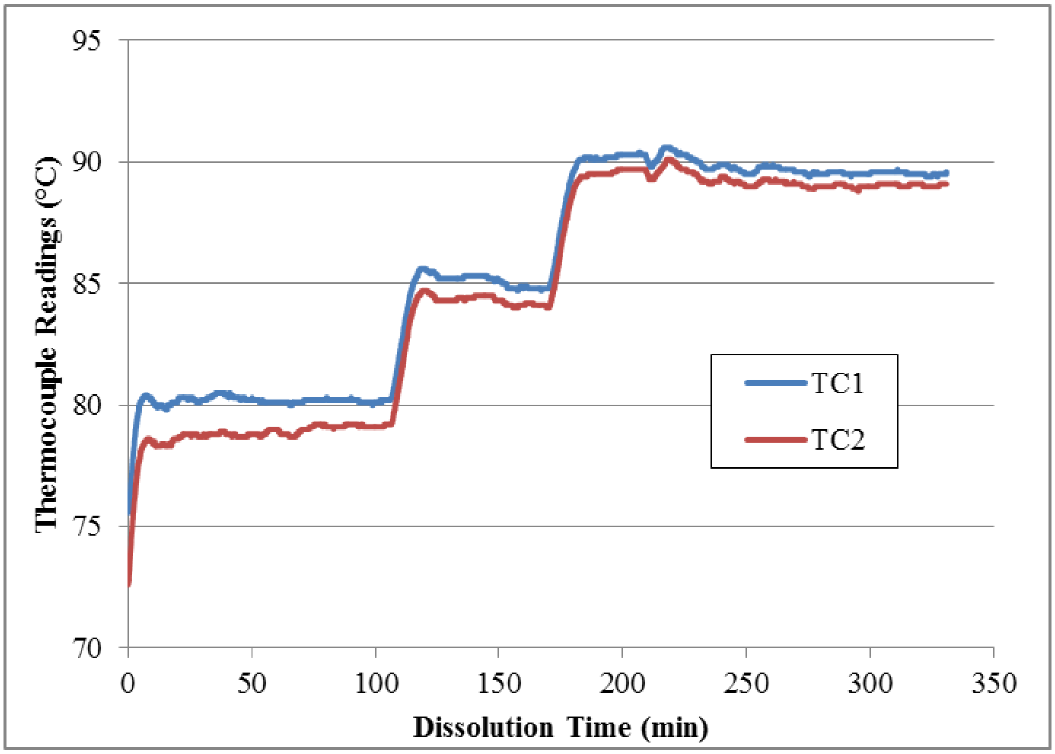
8.5.1 Test 1 Temperature Profile



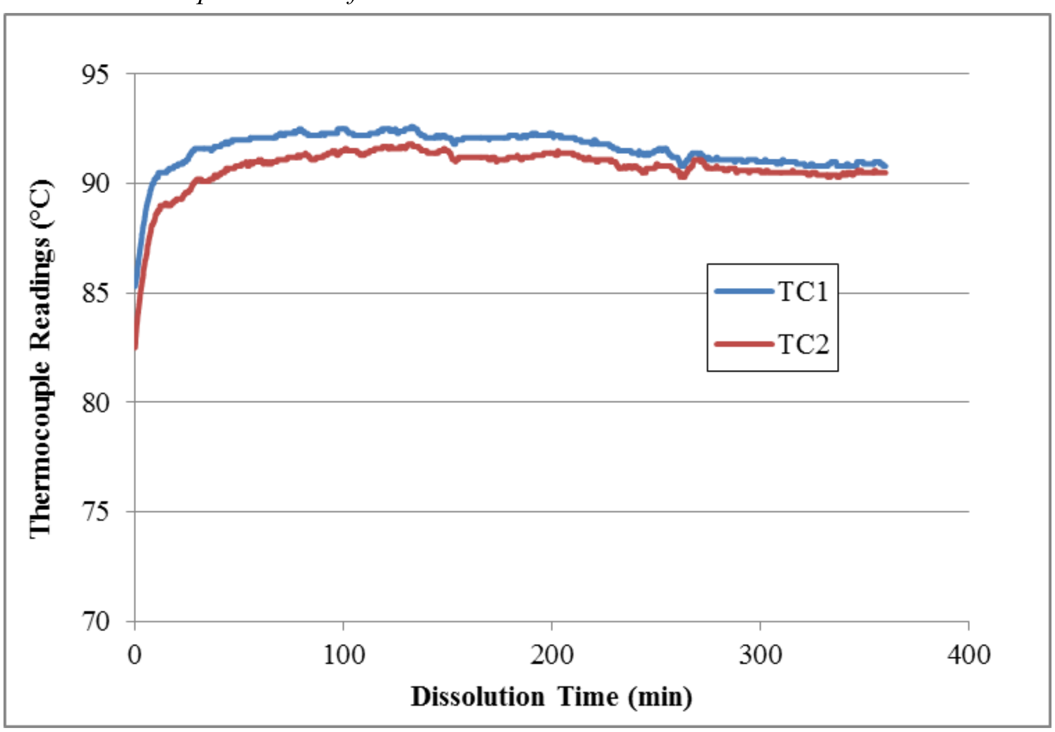
8.5.2 Test 2 Temperature Profile



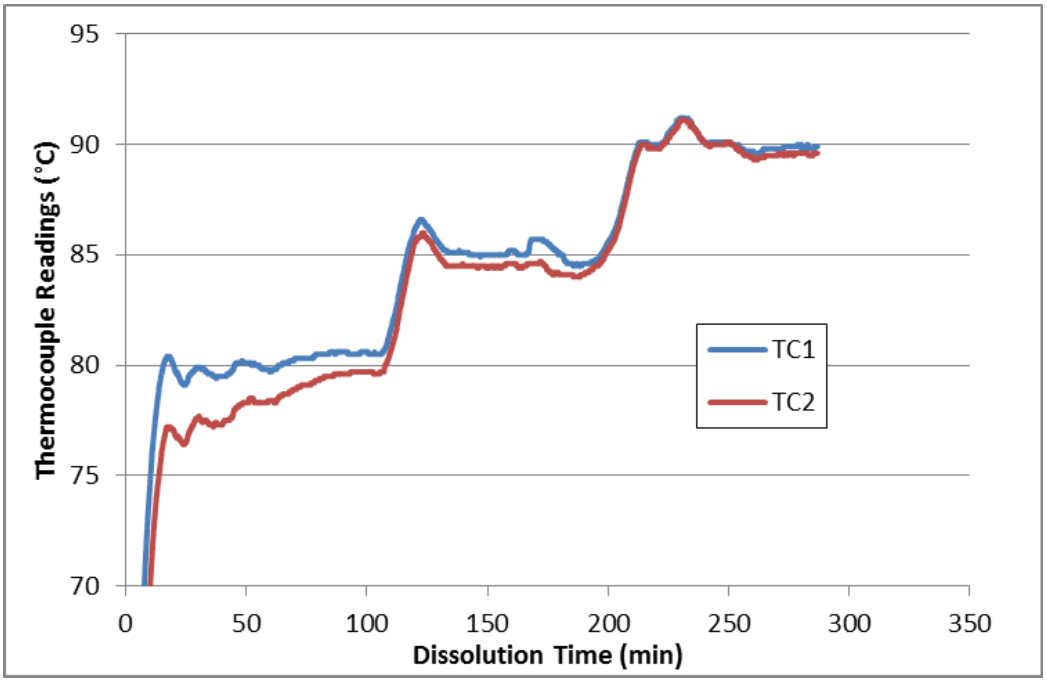
8.5.3 Test 3 Temperature Profile



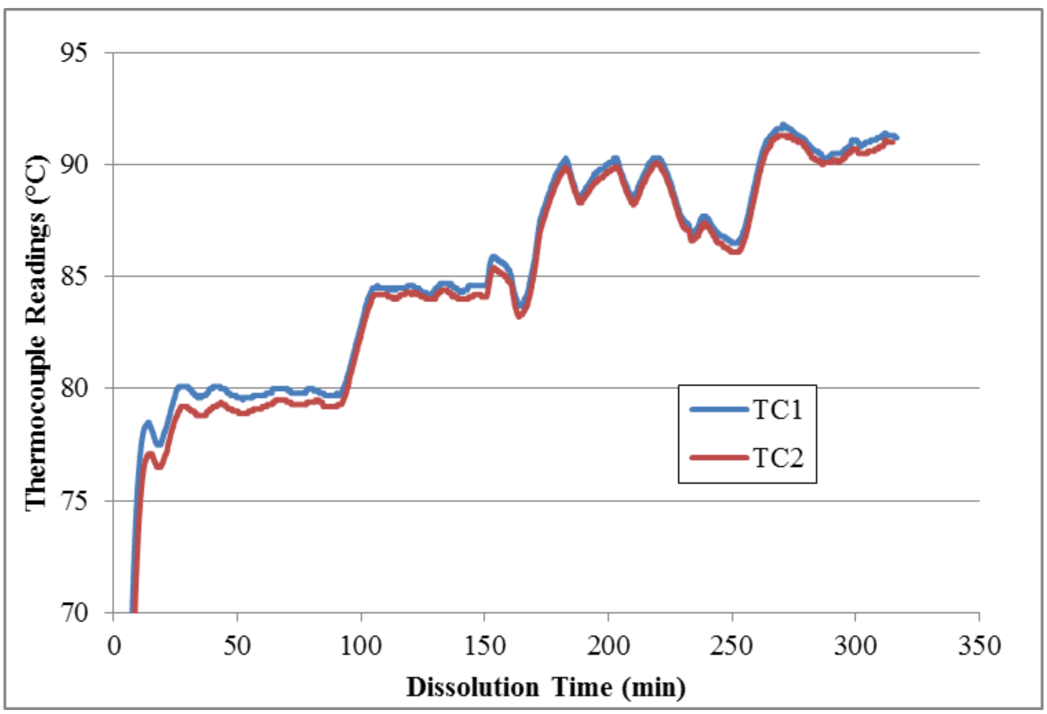
8.5.4 Test 4 Temperature Profile



8.5.5 Test 5 Temperature Profile



8.5.6 Test 6 Temperature Profile



Distribution:

T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 773-A
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
C. C. Herman, 773-A
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
K. M. Kostelnik, 773-42A
D. A. McGuire, 773-42A
F. M. Pennebaker, 773-42A
G. N. Smoland, 773-42A
B. J. Wiedenman, 773-42A
W. R. Wilmarth, 773-A
F. D. Sinclair, 717-K
W. F. Swift, 703-H
N. J. Bridges, 773-A
C. A. Nash, 773-42A
N. S. Karay, 773-A
T. E. Smith, 773-A
M. R. Williams, 786-5A
Records Administration (EDWS)