

Contract No.:

This manuscript has been authored by Savannah River Nuclear Solutions (SRNS), LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

Dissolution Flowsheet for High Flux Isotope Reactor Fuel at SRS

William E. Daniel, Jr., Tracy S. Rudisill, Patrick E. O'Rourke, and Nicholas S. Karay

Savannah River National Laboratory, Aiken, SC 29808

For all correspondence, contact W. E. (Gene) Daniel

Gene Daniel

Savannah River National Laboratory

Building 999-W

Aiken, SC 29808

e-mail: gene.daniel@srnl.doe.gov

telephone: 803-819-8463

fax number: 803-819-8432

Key Words

High Flux Isotope Reactor Fuel

Dissolution

H-Canyon

Running Title

HFIR Dissolution Flowsheet

DISCLAIMER: This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States.

ABSTRACT

H-Canyon at Savannah River Site has started dissolving High Flux Isotope Reactor (HFIR) fuel as part of the Spent Nuclear Fuel (SNF) processing campaign. Each HFIR fuel core contains inner and outer fuel elements fabricated from uranium oxide (U_3O_8) dispersed in a continuous Al phase. Fuels fabricated in this manner, like other SNF's processed in H-Canyon, dissolve by the same general mechanisms with similar gas generation rates including the production of H_2 . The objective of this work was to identify flowsheet conditions through literature review and laboratory experimentation to safely and efficiently dissolve the HFIR fuel in H-Canyon. The work showed that a full HFIR core could be dissolved using nominally 0.002 M Hg to catalyze the dissolution and the margin between the predicted H_2 concentration and the calculated Lower Flammability Limit (LFL) was greater when the dissolving solution was allowed to boil for 45 min prior to initiating the Hg addition.

INTRODUCTION

As part of the Spent Nuclear Fuel (SNF) processing campaign, Savannah River Site (SRS) H-Canyon is planning to begin dissolving High Flux Isotope Reactor (HFIR) fuel in the last quarter of 2017. During the HFIR campaign, 200 fuel cores will be processed. Each HFIR fuel core contains an inner and an outer fuel element as shown in Fig. 1.[1] The fuel cores are fabricated as concentric cylinders with the fuel plates located in the annulus between the inner and outer cylinders. The fuel plates project radially outward from the inner cylinder to the outer cylinder. The plates are curved in the shape of an involute to maintain constant spacing between adjacent plate surfaces.

The HFIR fuel plates are fabricated from U_3O_8 and Al powders using a powder metallurgy process. Boron-10 (as boron carbide – B_4C) is also added to the U_3O_8 and Al powders as a burnable poison.[2] The dissolution behavior of fuel fabricated by powder metallurgy was previously assessed and found to exhibit similar dissolution behavior to fuels fabricated from traditional metallurgy techniques.[3] Since fuels fabricated from traditional and powder metallurgical processes are both comprised of U-Al alloys

(or other U compounds) dispersed in a continuous Al phase, each should dissolve by the same general mechanisms with similar gas generation rates including the production of H_2 .

The HFIR fuel cores will be dissolved in H-Canyon and the recovered U will be down-blended into low-enriched U. HFIR fuel was previously processed in H-Canyon using a unique insert in both the 6.1D and 6.4D dissolvers as shown in Fig. 2.[4] Multiple cores will be charged to the same dissolver solution. After the fuel is dissolved, the solution will be processed through Head End and centrifuged to remove particulate matter. After Head End treatment, the U will be recovered and purified by solvent extraction (1st and 2nd Uranium Cycles), and the waste processed for transfer to the H-Area Tank Farm. The relatively high Al content in the dissolved fuel limits the downstream processing due to issues associated with Al solubility.[5] The number of cores dissolved in a dissolver batch will be dependent on the final Al concentration in the solution. Typically, H-Canyon does not exceed approximately 1.7 M $Al(NO_3)_3$ in the dissolver (at 2 M HNO_3), but higher $Al(NO_3)_3$ concentrations (≤ 2 M) were evaluated as part of this study.

Bundles of SNF containing U-Al assemblies are currently dissolved using a Hg-catalyzed, HNO_3 flowsheet.[6] The Hg catalyst is added gradually after the dissolver has reached the solution boiling point to achieve a maximum catalyst concentration of 0.012 – 0.015 M; a Hg concentration of 0.002 M Hg was previously used to dissolve foreign and domestic research reactor fuels prior to implementation of the current flowsheets.[6]

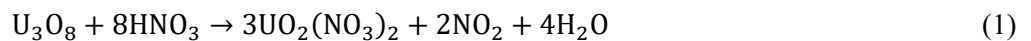
The initial HNO_3 concentration is dependent on the amount of Al and U to be dissolved, targeting a final HNO_3 concentration of 0.5–1.0 M after completion of the dissolution of the last charge. Boric acid or $Gd(NO_3)_3$ may be used as a nuclear safety poison. Solids do not precipitate in surrogate dissolver solutions containing concentrations of B or Gd less than 2 g/L.[5]

The objective of this study was to identify flowsheet conditions through literature review and laboratory experimentation to safely and efficiently dissolve the HFIR fuel in H-Canyon. During this task, the generation of H₂ was evaluated from the dissolution of the fuel to determine if a full HFIR core (inner and outer elements) could be charged to the dissolver without exceeding 60% of the lower flammability limit (LFL) of H₂ in air (4%) during the initial and subsequent charges. In addition, the downstream processing of the dissolver solution (including Head End and 1st Cycle operations) were evaluated to ensure any processing issues were identified and resolved.

EXPERIMENTAL

The HFIR fuel cores contain both high purity Al (like Al 1100) and Al 6061 alloy.[1,2] High purity Al metal powder is mixed with U₃O₈ and B₄C to form the fissionable component of the fuel.[2] The Al 6061 alloy is used for the cladding and other components of the fuel.[1] The HFIR fuel does not contain any components within the core that serve primarily as structural components; mechanically, the elements are self-supporting. To provide dimensional stability, Al 6061 T6511 (tempered for stress relief) was selected for use in the outer side plates of the elements. Other Al 6061 components in the fuel are fabricated using Al 6061 alloy with a T6 temper.[1]

To select the surrogate materials to model the HFIR fuel during the flowsheet development, a series of scoping experiments were initially performed using both Al 1100 and Al 6061 T6 to characterize the offgas and measure the generation rate of H₂. The scoping experiments were also used to evaluate the effect of high Al concentrations on the dissolution rate of the two alloys. Based on these experiments, it was concluded that the offgas and H₂ generation rates were bounded by the dissolution of the Al 1100 alloy. The results from the scoping experiments are discussed in the results section. The dissolution of the U₃O₈ in the fuel meat will generate a small amount of NO₂ gas (equation 1), but no H₂ is expected. Gray dissolved a mixture of UO₃ and U₃O₈ powders in dilute (2 M) HNO₃ and did not measure any H₂ in the offgas.[6]



Three scoping experiments designed to select the surrogate materials for the HFIR flowsheet development and five experiments designed to define the process conditions were completed using Al 1100 and Al 6061 T6 alloys. A summary of the objective and dissolution conditions for each experiment are provided in Table 1. All experiments were performed at the boiling point of the solution.

The Al 1100 and Al-6061 T6 alloys used in the dissolution experiments were prepared by cutting corrosion coupons to the desired length. The coupons were lightly sanded, washed with soap and water, and then weighed and measured. The sanding was to remove any initial oxide layer thus maximizing initial reactivity as well as generating consistent initial conditions across the coupons. For the majority of the experiments the coupons had a mass of approximately 6 g each with a surface area of approximately 5 cm². The masses, dimensions, and surface areas of the coupons used in the experiments are provided in Table 2. The surface areas are based on a 10 mm (1 cm) immersion depth along the length of each coupon in the HNO₃ solution. The surface area calculation is illustrated by equation 2:

$$SA(\text{cm}^2) = 2 \cdot (1 \text{ cm}) \cdot t(\text{cm}) + 2(1 \text{ cm}) \cdot w(\text{cm}) + t(\text{cm}) \cdot w(\text{cm}) \quad (2)$$

where SA is the surface area of the immersed coupon, t is the thickness of the coupon, and w is the width of the coupon.

The vessel and offgas condenser used to perform the Al alloy dissolution experiments were fabricated from borosilicate glass by the SRNL Glass Shop. A photograph of the equipment is shown in Fig. 3. The dissolving vessel was made from a 300-mL round-bottom flask. Penetrations were added for a condenser, thermocouple, vessel purge, and Hg addition syringe pump. The bottom of the flask was flattened slightly to facilitate heating and agitation using a hot plate/stirrer with a magnetic stir bar. The solution temperature was controlled using an immersed thermocouple monitored by the hot plate. Online analysis of the offgas by mass spectrometry and Raman spectroscopy was performed to characterize the offgas and measure the offgas generation rate. The mass spectrometer (MS) sample line was connected above the condenser to an offgas sample port. A manometer, also connected to the offgas sample port, acts as a

pressure relief device and provides a measurement of the pressure in the system. The offgas leaving the condenser subsequently passes through a cell containing a Raman probe and terminates in a bubbler (i.e., beaker containing 700 mL or 8.9 cm of deionized water). The bubbler prevents air in-leakage from the vent side of the system. This configuration allows the offgas analyzers to measure the non-condensable gases such as H₂, N₂, O₂, Ar, NO, N₂O and NO₂ in real time during the experiment.

The MS used during the dissolution experiments was a Monitor Instruments LAB 3000 Cycloidal MS. The Monitor MS samples a portion of the non-condensable offgas stream using vacuum and provides the volume percent of the gases in the sample based on calibration gas standards. The MS was calibrated using H₂, N₂, O₂, Ar, NO, N₂O and NO₂ standards.

To calculate offgas generation rates, an Ar tracer gas was metered into the system through a flow controller at a set rate (10 cm³/min @ 21.1 °C, 1 atm). The total offgas rate was then calculated by dividing the set input rate by the measured Ar concentration in the offgas.

The Raman spectrometer non-intrusively analyzes the offgas through a quartz window using the excitation of a laser passing through a fixed portion of the offgas stream. The scattering technique of the Raman identifies and measures the concentration of gases in the offgas stream to a sensitivity of about 0.2 vol%. The spectrometer was also calibrated using standard gases and The Raman spectrometer measures the concentrations of the offgas species were measured approximately every 12-13 seconds. Since the Raman spectrometer directly measures the concentrations in the offgas stream, there is zero dead time between the offgas concentration measurement and the reading other than the analysis time of 12-13 seconds. The spectrometer was controlled by and data was logged using a computer.

To calculate offgas generation rates in experiments in which only the Raman spectrometer was used to characterize the offgas, a CO₂ tracer gas was metered into the system through a flow controller at a set

rate (20, 30, or 50 cm³/min @ 70 °F, 1 atm). The total offgas rate was then calculated by dividing the set input rate by the measured CO₂ concentration in the offgas.

The MS was calibrated using NIST-traceable standards before each experiment and the calibration gases checked prior to starting the experiment. The 2 σ value or twice the standard deviation for the MS H₂ analysis was 0.38 vol %. The Raman spectrometer was also calibrated using the NIST-traceable standards and calibration gases checked before each experiment. The 2 σ value or twice the standard deviation for the Raman spectrometer H₂ analysis was 1.39 vol %.

Prior to performing a dissolution experiment, the dissolving system was checked for leaks by connecting a Tedlar[®] bag inside a glass kettle filled with water (Fig. 3) to the dissolver and adding sufficient Ar, N₂, or CO₂ to the bag to generate a column of water 18-28 cm tall. The Tedlar[®] bag system was then closed and monitored for any observable decrease in the water column height over approximately 3 min. After the system integrity was confirmed, the experiment was started.

To perform a dissolution, the Al alloy coupon was initially placed in a perforated glass basket. The basket was lowered until the coupon was immersed 10 mm lengthwise into a 7 M HNO₃ dissolving solution at room temperature. The solution was then heated to boiling. Chilled water (at 3 °C) was circulated through the condenser during the dissolution to remove water vapor from the offgas stream prior to analysis by the MS and before the gas flowed through the Raman cell. Once the solution reached boiling, either the Hg solution was added right away or there was a hold time of 45 minutes before starting the Hg addition to reduce the initial offgas surge.

RESULTS AND DISCUSSION

Review of Past HFIR Dissolution Data

Based on prior dissolution data of HFIR fuel processed at the SRS, the dissolution (i.e., reflux) times for a single HFIR core (per batch) ranged from 14 to 28 hours when 0.004 M Hg was used as the catalyst concentration.[7,8,9] However, a majority of the dissolutions were completed in 20 hours or less. If 0.002 M Hg is used to catalyze the dissolution, the dissolution time should double assuming the fuel dissolution rate is directly proportional to the Hg concentration. Therefore, an estimate of the dissolution time for the initial HFIR core is 28 to 56 hours. The dissolution times of subsequent cores using the same dissolving solution would be expected to increase as the Al concentration in the dissolver also increases.

Selection of Surrogate Materials

To establish which Al alloy provides a bounding estimate for the generation of H_2 during the flowsheet development for HFIR fuel, dissolution experiments were performed using both Al 1100 and Al 6061 T6 alloys. The dissolution of the U_3O_8 in the HFIR fuel meat does not need to be evaluated since the dissolution of U_3O_8 will generate a small amount of NO_2 gas, but no H_2 is expected. In the experimental work, both Al alloys were dissolved using the equipment described earlier using a solution containing 7 M HNO_3 . The Hg concentration was adjusted to 0.002 M. The offgas generation rates and gas concentrations were measured using the MS during dissolution of both alloys. The H_2 generation rate per unit surface area is plotted as a function of the dissolved Al concentration in Fig. 4 for both alloys. The concentration of Al in the dissolving solution as a function of time was estimated by relating the overall stoichiometric reaction of Al dissolution to the amount of offgas being generated. This method is described in more detail in another report.[10] The plot shows that the dissolution of the Al 1100 alloy is bounding in terms of the H_2 generation rate when compared to the dissolution of the Al 6061 T6 alloy. From the scoping experiments, it was concluded that the dissolution of the Al 6061 T6 alloy proceeds at a slower rate than the Al 1100 alloy and should be used to verify that the target Al concentration in solution can be achieved for a given concentration of Hg.

Based on these results, data from the dissolution of Al 1100 were used to evaluate the H₂ generation rate from the dissolution of HFIR fuel.

During the dissolution of the Al alloys, it was observed that holding the coupon in the boiling HNO₃ solution for 45 minutes prior to starting the Hg addition significantly reduced the initial surge of offgas and the H₂ generation rate. Therefore, this practice was used for subsequent dissolution experiments. The reduced reactivity of the Al coupons was likely due to the passivation of the surface by the HNO₃ solution during the hold time.

In Experiment 94, Al 1100 was dissolved in 7 M HNO₃ where the addition of 0.002 M Hg was initiated immediately after reaching boiling. In Experiment 95, Al 1100 was dissolved in 7 M HNO₃ and the addition of 0.002 M Hg was initiated 45 minutes after the solution reached the boiling point. The H₂ generation rates for the two experiments are shown in Fig. 5 and demonstrate that holding the Al at the solution boiling point for 45 minutes then starting the Hg addition reduces the H₂ generation rate especially during the peak H₂ generation at the beginning of the dissolution.

Flowsheet Development

Three experiments were performed using the Al 1100 and Al 6061 T6 alloys with high (e.g., 1.8-2.0 M) targeted Al end points to evaluate the rate of dissolution and to determine if there were any solubility issues following dissolution. Experiments 96 and 97, performed with the Al 1100 alloy, targeted final Al concentrations of 1.8 and 2.0 M, respectively. Experiment 99 was performed with Al 6061 T6 alloy and targeted a final Al concentration of 2.0 M. The H₂ generation curves (which illustrate the extent of dissolution) for the three experiments are plotted as a function of time in Fig. 6. Time zero for each curve represents the start of the Hg addition. The figure shows that the Al 1100 alloy dissolves at about twice the rate of the Al 6061 T6 alloy. Complete dissolution of the Al coupon was achieved in each experiment. However, following the dissolution experiments, solids were observed in the solution. Al 1100 Si and Fe

combined content can be up to 0.95 wt% and Al 6061 Si content can be 0.4-0.8 wt%. Analysis of the solids by XRD showed only amorphous material. No crystalline materials, such as $\text{Al}(\text{NO}_3)_3$ were observed.[10] Amorphous and silicon-containing solids from the dissolution of HFIR fuel in an H-Canyon dissolver should be easily removed by the Head End centrifuge using the standard gelatin strike process.

The rate of flammable gas generation from the HFIR fuel is proportional to the surface area exposed to the dissolving solution. The surface area calculations were completed by taking into account that closely spaced internal surfaces will be blanketed by product gases generated during a dissolution, therefore, these surfaces are not exposed to the dissolving acid. In previous work, it was demonstrated that the dissolution rate for two concentric fuel tubes containing a 16 wt % U-Al alloy was essentially the same as for a single tube of the same alloy.[11] This result indicated that the outside surface area of the outer tube controlled the dissolution rate.

To estimate the concentration of H_2 in the offgas during the dissolution of HFIR fuel, experiments were performed using both Al 1100 and Al 6061 T6 alloys. Preliminary experiments demonstrated that the dissolution of the Al 1100 alloy was bounding in terms of the H_2 generation rate when compared to the dissolution of the Al 6061 T6 alloy. Experiments 96, 97, and 98 were performed to measure the H_2 generation rate for Al 1100 at nominally 0.002 M Hg and for an increased concentration of 0.004 M. In these experiments, the Hg addition was not started until the solution boiled for 45 minutes. This methodology was used to reduce the initial surge of offgas when Hg is added to the dissolving solution. In each case, 7 M HNO_3 was used as the dissolving solution.

The H_2 generation rates for Experiments 94, 96, 97, and 98 are plotted as a function of the dissolved Al concentration in Fig. 7. The H_2 generation rates were calculated from the measured offgas generation rates, measured H_2 concentrations, and the measured surface area of the Al 1100 coupons. The

concentration of Al in the dissolving solution as a function of time was estimated using the method described by Almond et al.[10] The figure shows that the H₂ generation rates surge after the start of the Hg addition and the rate for Experiment 98 (0.004 M Hg) is approximately twice the values for Experiments 96 and 97 (0.002 M Hg) based on the Raman data.

The maximum concentration of H₂ calculated during the dissolution of HFIR fuel must be compared to the appropriate percentage of the LFL for H₂ at the maximum temperature of the offgas. Since the offgas from the H-Canyon dissolvers flow through an iodine reactor, which operates at 200 °C, the LFL for H₂ is corrected for the increase in temperature.[10] When automatic instrumentation with safety interlocks is provided, the combustible concentration is permitted to be maintained at or below 60% of the LFL.[12] The H₂ LFL at 200 °C is required due to the I₂ reactor in the offgas stream of the H-Canyon dissolvers which operates at this temperature. Lower flammability limit data reported by Scott et al. for air, H₂, NO, and N₂O mixtures [13] were used to calculate the LFL for comparison to the H₂ concentrations calculated for an H-Canyon dissolver. Scott's calculation of the H₂ LFL depends on the NO:N₂O volume ratios which are shown for the dissolution experiments 94, 96, 97, and 98 in Fig. 8.

The H₂ generation rates calculated for Experiments 94, 96, 97, and 98 (Fig. 7) were used to predict the H₂ concentration in the offgas stream from an H-Canyon dissolver. The experiments were performed using 0.002 to 0.004 M Hg and targeted a final Al concentration of 1.8 to 2 M. The offgas generation rate for a HFIR core was based on the outer surface area of the inner and outer elements and the carriers since the fuel and carriers will be completely immersed in the dissolver. For complete immersion of the fuel, the exposed surface area for one HFIR core (and carriers) is 23.408 ft².

To estimate the H₂ concentration in the dissolver offgas stream, the total offgas generation rate was initially predicted for a single HFIR core (including the inner and outer element carriers) (equation 3).

$$\text{Predicted Offgas rate (SCFM)} = \text{Measured Offgas Rate} \left(\frac{\text{SCFM}}{\text{ft}^2} \right) \cdot 23.408 \text{ft}^2 \quad (3)$$

The predicted H₂ generation rate for a HFIR core was calculated in a similar manner (equation 4) by scaling-up the H₂ generation rate calculated from the experimental data (Fig. 7).

$$\text{Predicted H}_2 \text{ Offgas rate (SCFM)} = \text{Measured H}_2 \text{ Offgas Rate} \left(\frac{\text{SCFM}}{\text{ft}^2} \right) \cdot 23.408 \text{ft}^2 \quad (4)$$

The predicted H₂ concentration in the dissolver offgas stream was subsequently calculated from the predicted H₂ offgas rate, the predicted (total) offgas rate, and the volumetric flow rate of air used to sparge (i.e., mix) the solution and purge the dissolver (equation 5). A dissolver sparge/purge rate of 40 SCFM was used for all calculations.

$$\text{Predicted H}_2 \text{ Conc (vol\%)} = \frac{\text{Predicted H}_2 \text{ Offgas rate (SCFM)}}{\text{Predicted Offgas rate (SCFM)} + 40 \text{ SCFM}} \left(\frac{100 \text{ vol\%}}{1} \right) \quad (5)$$

The predicted H₂ concentration (with air dilution) in the dissolver offgas stream is compared with 60% of the calculated H₂ LFL at 200 °C in Fig. 9, Fig. 10, Fig. 11, and Fig. 12 for Experiments 94, 96, 97, and 98, respectively, to determine if a full HFIR core can be charged to the dissolver without exceeding the calculated LFL. The comparisons of the predicted H₂ concentration to 60% of the LFL show that a full HFIR core can be dissolved using nominally 0.002 M Hg to catalyze the dissolution (Fig. 9, Fig. 10, and Fig. 11). It should be noted that the margin between the predicted H₂ concentration and the calculated LFL is greater when the dissolving solution was allowed to boil for 45 min prior to initiating the Hg addition (Fig. 10 and Fig. 11). The comparison of the predicted H₂ concentration to 60% of the LFL for Experiment 98 (Fig. 12), which was performed using 0.004 M Hg to catalyze the dissolution, shows that the predicted H₂ concentration exceeds the calculated LFL early in the dissolution (between approximately 0.15 and 0.5 M Al). However, the predicted H₂ concentration would not exceed the LFL if only an outer HFIR element was dissolved; although, this processing option is not very appealing since only outer (or inner) elements could be dissolved until the Al concentration exceeded approximately 0.5 M.

To understand how small uncertainties in the offgas measurements performed by Raman spectroscopy affected the calculations performed to determine if a complete HFIR core could be charged to a dissolver, the measured H₂ concentrations in Experiments 96 and 97 were assumed to be inflated by 1.8 vol% ($>2\sigma$ uncertainty) and the predicted H₂ concentrations were still less than 60% of the calculated LFL for all Al concentrations (Fig. 10 and Fig. 11). In Experiment 94, the H₂ concentrations measured by the MS were inflated by 0.6 vol % ($>2\sigma$ uncertainty) and the predicted H₂ concentrations were also still less than the LFL (Fig. 9). In addition, several aspects of the calculations have built-in conservatism which further address the uncertainty in the calculations. The calculated H₂ concentration in the offgas stream is compared to 60% of the LFL which provides a layer of conservatism. The saturated water vapor in the offgas stream is ignored and would further dilute the H₂ concentration. Given the conservative nature of the experimental design and the calculations performed, the conclusion that a complete HFIR core can be charged to an H-Canyon dissolver using nominally 0.002 M Hg to catalyze the dissolution adequately incorporates the many uncertainties associated with the experimental and modeling work.

Al 1100 alloy dissolution experiments were performed to investigate the effects of higher Hg concentrations on the H₂ generation rate. In Experiment 97, the Al-1100 alloy was dissolved in 7 M HNO₃ by metering in 0.002 M Hg 45 minutes after the solution began to boil. The H₂ generation rate for Experiment 97 is shown in Fig. 16. The Al 1100 alloy dissolution performed in Experiment 98 was a repeat of Experiment 97 except 0.004 M Hg was metered into the solution at the same rate. Doubling the Hg concentration used to catalyze the dissolution results in an approximate doubling of the H₂ generation rate (Fig. 16). Experiment 101 was performed to evaluate the addition of more Hg during an Al 1100 alloy dissolution (Fig. 16). The ability to add more Hg during a HFIR fuel dissolution could be beneficial if slow dissolution rates are observed at high Al concentrations.

Experiment 101 was performed over 2 days. During the first day, an Al 1100 coupon was dissolved to reach approximately 0.6 M Al in the solution. On the next day, a second Al 1100 coupon was dissolved to reach approximately 2 M Al. During the second day, another Hg addition was made when the Al concentration reached approximately 1.3 M to increase the Hg concentration to 0.008 M. The rise in the H₂ generation rate during the second day at approximately 0.85 M Al (Fig. 13) was due to a change in the CO₂ tracer gas flow rate from 30 to 50 cm³/min to prevent the offgas from diluting the tracer gas concentration below detection. The H₂ generation rate returned to a consistent level after the CO₂ flow rate change worked its way through the dissolving system. The second rise in the offgas generation around 1.3 M Al was due to the second addition of Hg to bring the concentration from 0.002 M to 0.008 M.

The predicted H₂ concentrations for Experiments 101 are compared to 60% of the calculated H₂ LFL at 200 °C in Fig. 14 to illustrate that the Hg concentration can be increased from 0.002 to 0.008 M at Al concentrations greater than 1.3 M during a HFIR fuel dissolution. In addition, Fig. 12 shows that the Hg concentration during a HFIR fuel dissolution can be conservatively increased from 0.002 to 0.004 M at Al concentrations greater than 0.5 M.

Conclusions

To achieve complete dissolution of a HFIR core and the associated carriers, a Hg-catalyzed HNO₃ dissolution flowsheet was demonstrated. In laboratory experiments, Al 1100 and Al 6061 T6 alloys were dissolved starting with a 7 M HNO₃ solution. A Hg catalyst concentration of 0.002 M was sufficient to dissolve Al alloy coupons up to a final Al concentration of 2 M. Complete dissolution of the Al coupons was achieved; however, following the dissolutions, solids were observed in the solution. The solids were amorphous by XRD, but likely originated from the Si present in the alloys. No crystalline materials, such as Al(NO₃)₃ were observed. During the course of the experiments, it was determined that delaying the addition of Hg once the HNO₃ solution reaches boiling can reduce the total offgas and H₂ generation

rates. The delay in starting the Hg addition is not necessary for HFIR fuel dissolution, but could be useful in other research reactor dissolution campaigns.

The potential to generate flammable concentrations of H₂ in the offgas during a HFIR fuel dissolution was evaluated using the experimental data. The predicted H₂ concentration (with air dilution) in the dissolver offgas stream was compared with 60% of the calculated H₂ LFL at 200 °C using several prototypical experiments. The calculations showed that a full HFIR core can be dissolved using nominally 0.002 M Hg to catalyze the dissolution. The margin between the predicted H₂ concentration and the calculated LFL was greater when the dissolving solution was allowed to boil for 45 min prior to initiating the Hg addition. When the Hg concentration was increased to 0.004 M, the predicted H₂ concentration exceeded 60% of the calculated LFL early in the dissolution.

The Al alloy dissolution experiments also demonstrated that additional Hg (beyond the initial 0.002 M) could be added as the Al concentration increases. The ability to add more Hg during a HFIR fuel dissolution could be beneficial if slow dissolution rates are observed at high Al concentrations.

Experimental data were used to demonstrate that the predicted H₂ concentration in a dissolver was below 60% of the calculated LFL at 200 °C when 0.004 M Hg is used to catalyze the dissolution if the Al concentration is conservatively greater than 0.5 M. Data also show that the Hg concentration during a HFIR fuel dissolution can be increased from 0.002 to 0.008 M at an Al concentration of 1.3 M.

Following dissolution of the HFIR fuel, the solution will be processed through Head End and the 1st and 2nd Cycles of solvent extraction to recover the enriched U for subsequent down-blending for use as commercial reactor fuel. No issues associated with the processing of the enriched U solutions through Head End and solvent extraction are anticipated. The dissolution of the HFIR fuel will generate undissolved solids such as transition metal fission products (e.g., Zr, Mo, Ru, Tc, Pd, and Ag) and Si (as SiO₂) present in the Al alloys and produced from the transmutation of Al during fuel irradiation. These

solids should be easily removed by the Head End centrifuge using the standard gelatin strike process.[14]

Once the solution is clarified, purification by solvent extraction should proceed in the same manner as other enriched U feedstocks. High and low activity waste generated from the processing will be neutralized and prepared for disposal using existing SRS facilities. No issues are anticipated.

Acknowledgements

The work was supported by the US Department of Energy's Office of Environmental Management. The Savannah River National Laboratory is operated by Savannah River Nuclear Solutions under contract number DE-AC09-08SR22470.

References

1. G. M. Adamson, Jr., Fabrication Procedures for the Initial High Flux Isotope Reactor Fuel Elements, ORNL-4342, Oak Ridge National Laboratory, Oak Ridge, TN (February 1969), United States DOI: 10.2172/4823150.
2. G. A Bowden and R.W. Knight, Specifications for High Flux Isotope Reactor Fuel Elements HFIR-FE-3, ORNL/Tm-9220, Oak Ridge National Laboratory, Oak Ridge, TN (August 1984), United States DOI: 10.2172/6797682.
3. W. C. Perkins, Dissolving Uranium Oxide-Aluminum Fuel, DP-1337, E. I. du Pont de Nemours & Co., Aiken, SC (November 1973).
4. M. L. Hyder, W. C. Perkins, M. C. Thompson, G. A. Burney, E. R. Russell, H. P. Holcomb, and L. F. Landon, Processing of Irradiated Enrich Uranium Fuels at the Savannah River Plant, DP-1500, E. I. du Pont de Nemours & Co., Aiken, SC (April 1979), United States DOI: 10.2172/5819865.

5. E. A. Kyser, Dissolution of Irradiated MURR Fuel Assemblies, SRNL-STI-2010-00005, Savannah River National Laboratory, Aiken, SC (June 2010), United States DOI: 10.2172/990337.
6. J. H. Gray, The Dissolution of Uranium Oxides in HB-Line Phase I Dissolvers, WSRC-TR-2003-00235, Westinghouse Savannah River Company, Aiken, SC (2003), United States DOI: 10.2172/814722.
7. G. H. Sykes and R. W. Zeyfang, High Flux Reactor (HFIR) Fuel Processing, Test Authorization No. 2-685, E. I. du Pont de Nemours & Co., Aiken, SC (May 9, 1969).
8. W. L. Frank, High Flux Isotope Reactor (HFIR) Fuel Processing, Test Conclusion No. 2-685, E. I. du Pont de Nemours & Co., Aiken, SC (July 9, 1974).
9. C. E. Pickett, Fuel Dissolved in H-Canyon – 11/14/1975 to 6/28/2001, File Code 221H-LIB-F-20-144, Westinghouse Savannah River Company, Aiken, SC (January 25, 2004).
10. P. M. Almond, W. E. Daniel, and T. S. Rudisill, Flowsheet Modifications for Sodium Reactor Experiment and Denmark Reactor-3 Used Nuclear Fuel Processing, SRNL-STI-2014-00228, Savannah River National Laboratory, Aiken, SC (June 2014), United States DOI: 10.2172/1136112.
11. V. P. Caracciolo, Dissolver for Uranium-Aluminum Alloy Tubes, DP-398, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC, September (1959).
12. NFPA® 69, Standard on Explosion Prevention Systems, 2008 Edition, NFPA, Quincy, MA.
13. F. E. Scott, M. G. Zabetakis, Flammability of Hydrogen-Air-Nitrogen Oxide Mixtures, AECU-3178 or BM-3507, United States Department of the Interior; Bureau of Mines, Pittsburgh, PA (1956).
14. Rudisill, T, and F. Fernando Fondeur, Removal Of Solids From Highly Enriched Uranium Solutions Using The H-Canyon Centrifuge, SRNL-STI-2009-00002, Savannah River National Laboratory, Aiken, SC (January 2009), United States: DOI:10.2172/948560.

TABLE 1
Al Alloy Dissolution Experiments

Exp. No.	Type	Objective	Al Alloy	Hg Conc. (M)	Target Al Conc. (M)
93	scoping	offgas generation and rate of dissolution	Al 6061 T6	0.002→0.004	1.6
94	scoping	offgas generation and rate of dissolution	Al 1100	0.002	1.7
95	scoping	effect of hold time on peak offgas rate	Al 1100	0.002	1.6
96	flowsheet	offgas generation rate at 0.002 M Hg	Al 1100	0.002	1.8
97	flowsheet	rate of dissolution at high Al conc.	Al 1100	0.002	2.0
98	flowsheet	offgas generation rate at 0.004 M Hg	Al 1100	0.004	2.0
99	flowsheet	rate of dissolution at high Al conc.	Al 6061 T6	0.002	2.0
101	flowsheet	increasing Hg from 0.002 to 0.008 M	Al 1100	0.002→0.008	0.6→2.0

TABLE 2
Al Alloy Coupon Characteristics

Exp. No.	Mass (g)	Length (cm)	Width (cm)	Thickness (cm)	Surface Area (cm ²)
93	6.1670	2.428	1.497	0.633	5.208
94	6.0136	3.965	1.917	0.299	5.005
95	5.8068	3.985	1.913	0.284	4.937
96	6.2365	4.161	1.915	0.295	4.985
97	6.2365	4.090	1.905	0.290	4.942
98	6.2206	4.210	1.910	0.291	4.958
99 _{Day 1}	7.1708	2.827	1.499	0.631	5.206
99 _{Day 2}	0.8629	2.003	0.967	0.623	5.011
101 _{Day 1}	1.7747	1.276	1.918	0.276	4.917
101 _{Day 2}	4.6717	3.282	1.916	0.283	4.953



Fig. 1. Inner and Outer HFIR Fuel Elements

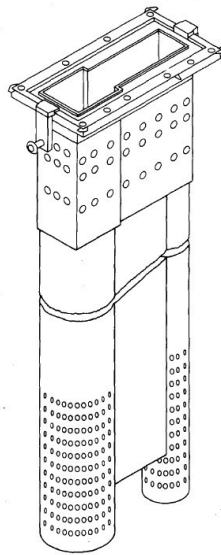


Fig. 2. HFIR Insert



Fig. 3. Dissolver Setup with Online MS and Raman Offgas Analyzers

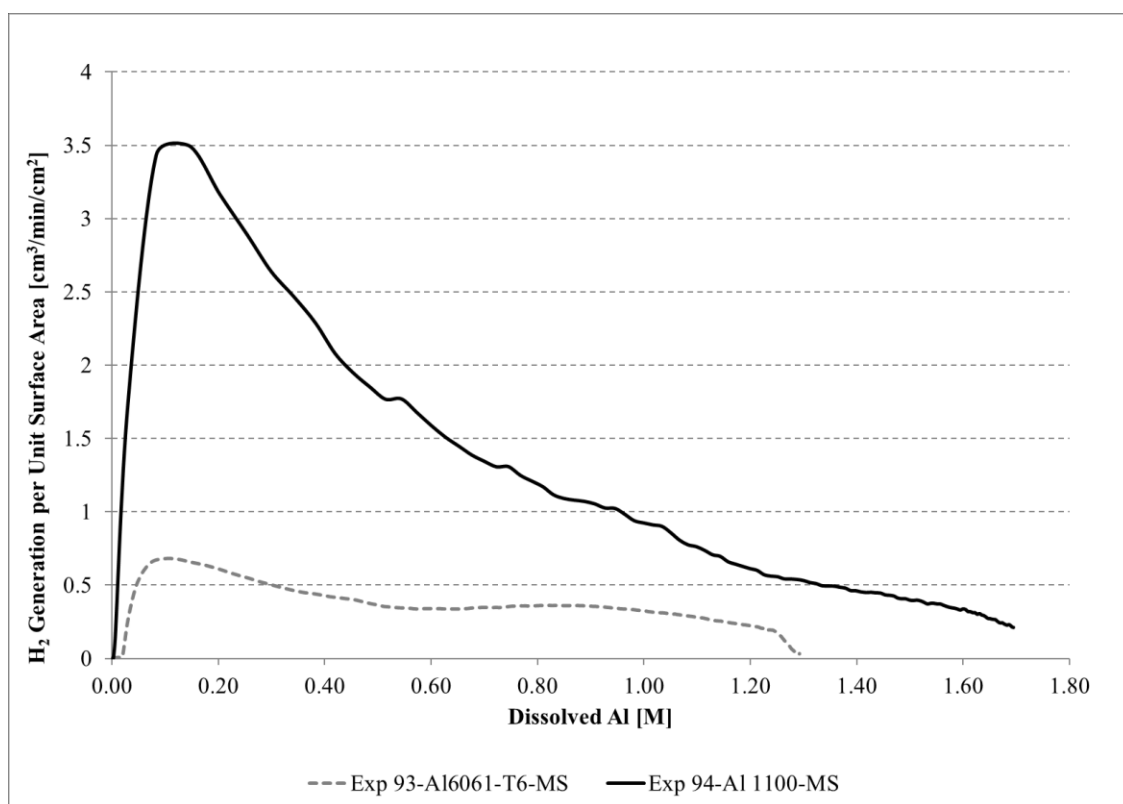


Fig. 4. H₂ generation Rate during the Dissolution of Al 1100 and Al 6061 T6 Alloys

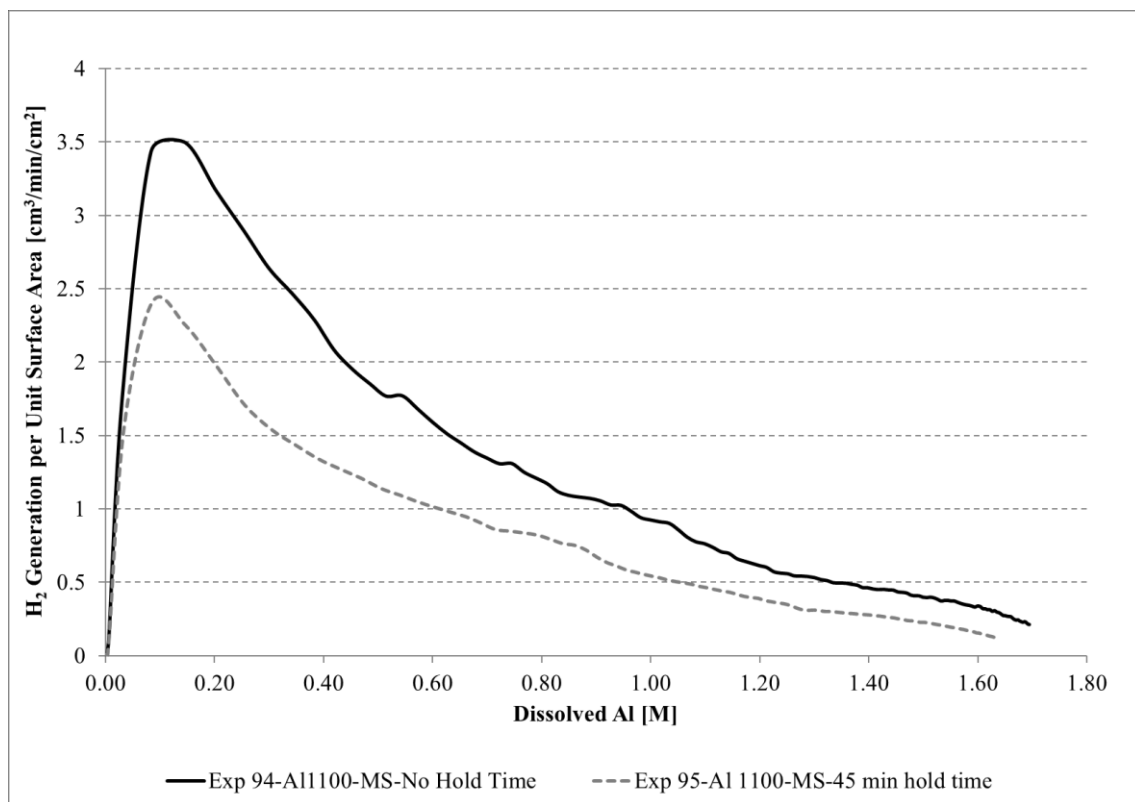


Fig. 5. Effect of Hold Time on H₂ Generation Rate

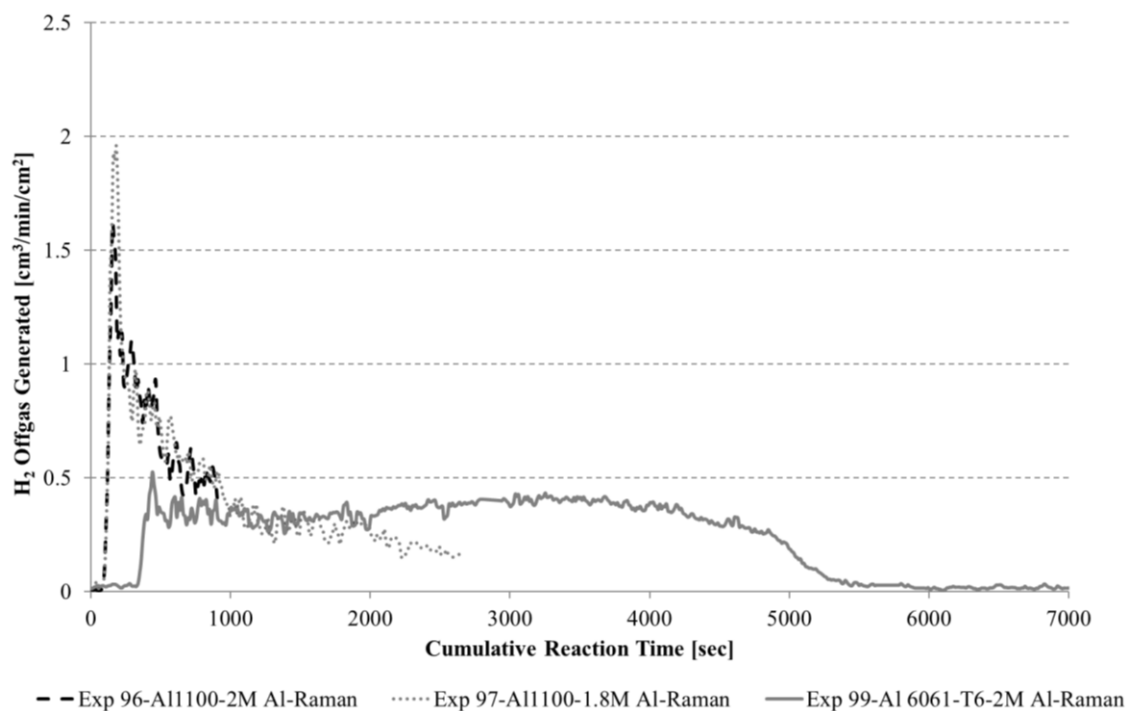


Fig. 6. H₂ Generation Rate for Experiments Targeting High Concentrations of Al

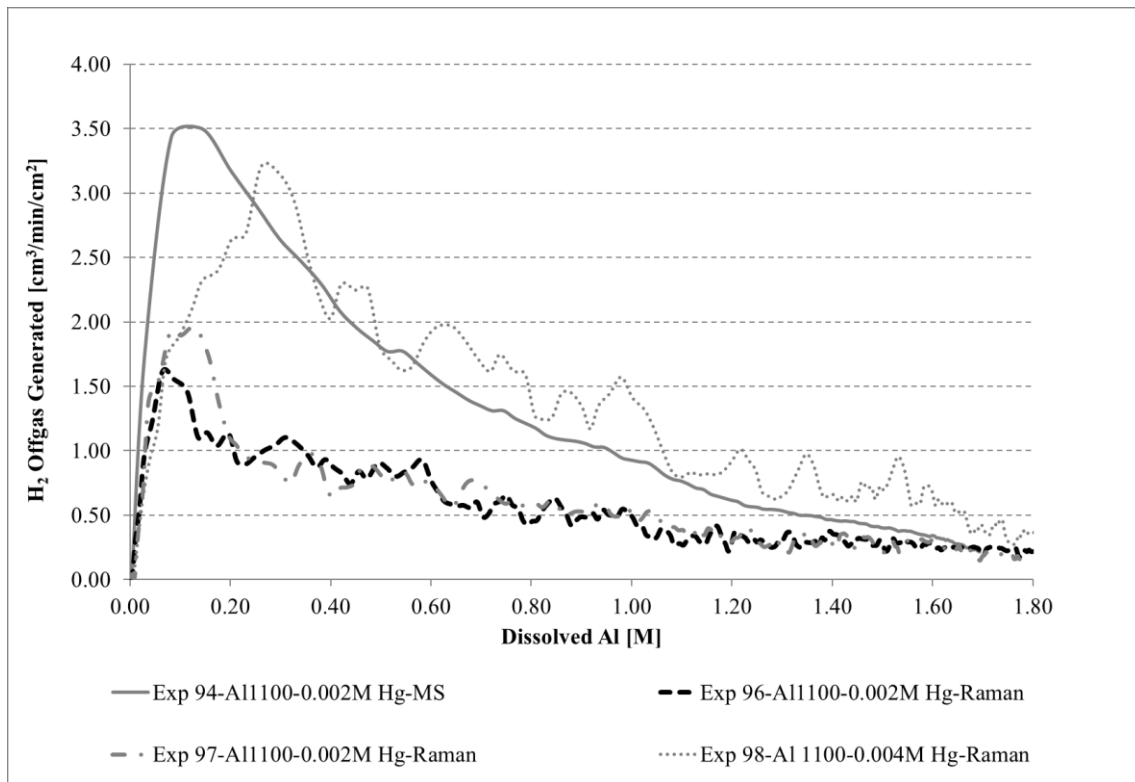


Fig. 7. H_2 Generation Rate from the Dissolution of Al 1100 Alloy

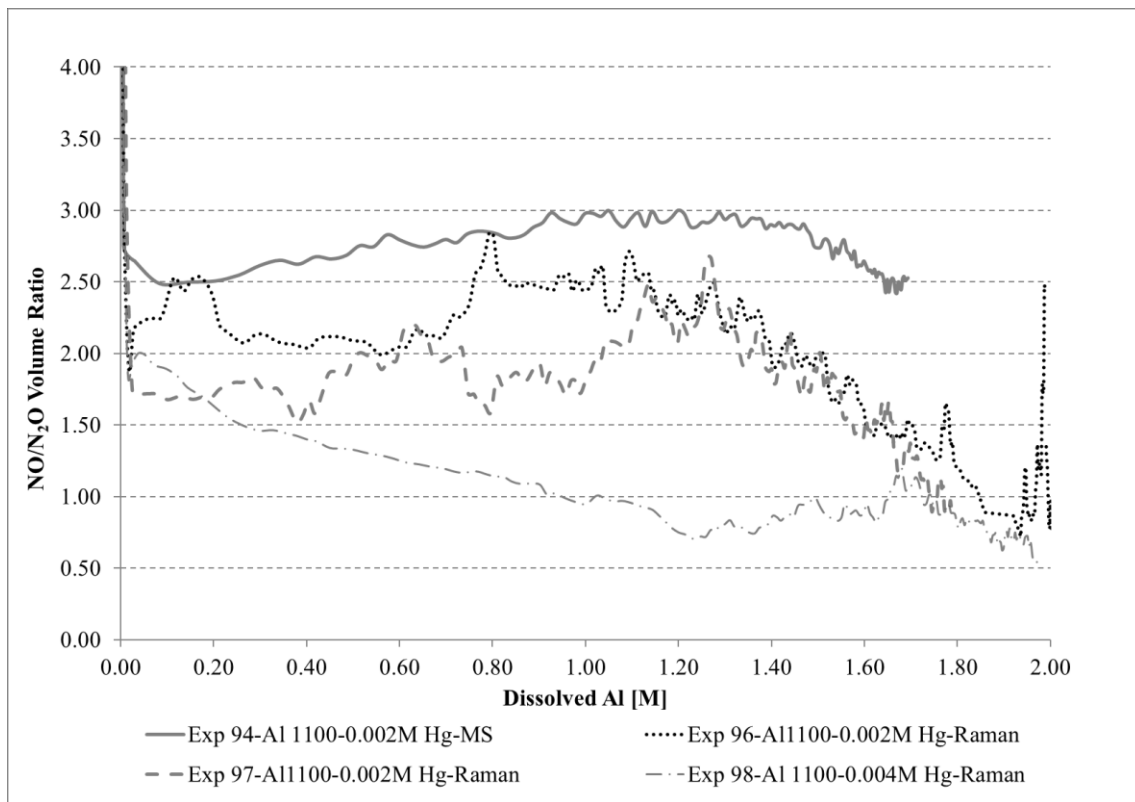


Fig. 8. NO: N_2O Volume Ratio from the Dissolution of Al 1100 Alloy

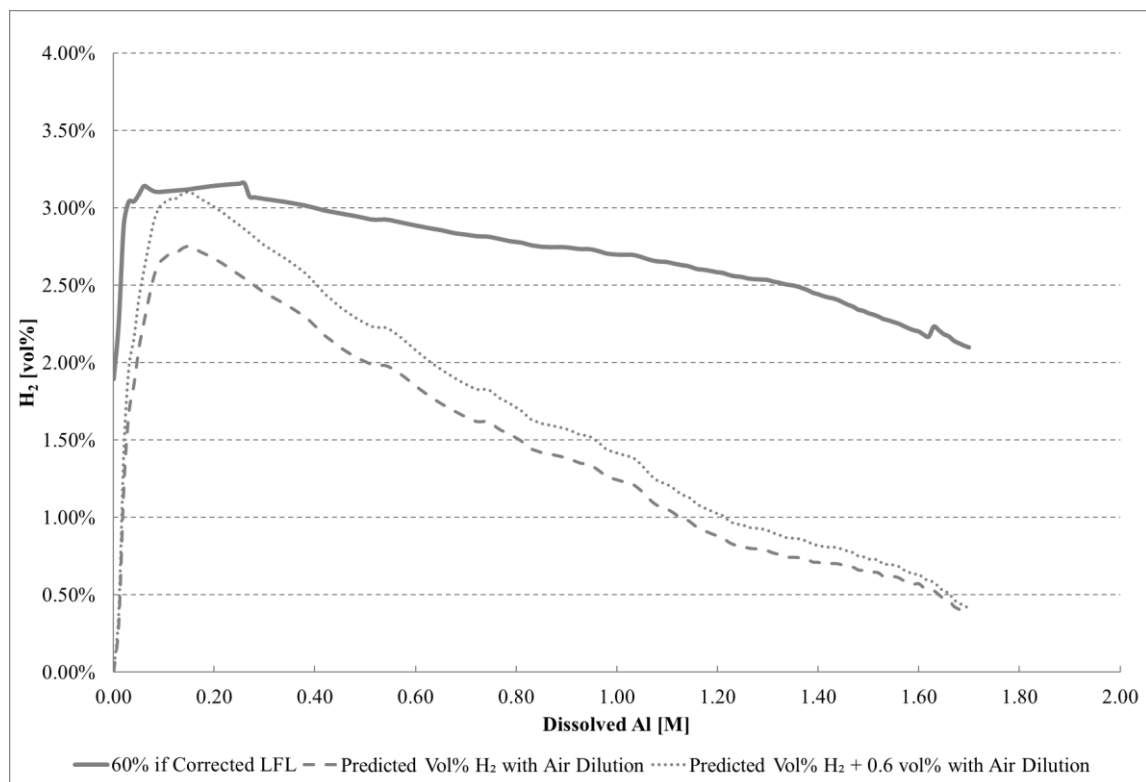


Fig. 9. H_2 LFL Comparison for Exp. 94 – 7 M HNO_3 , 0.002 M Hg, and No Hold Time

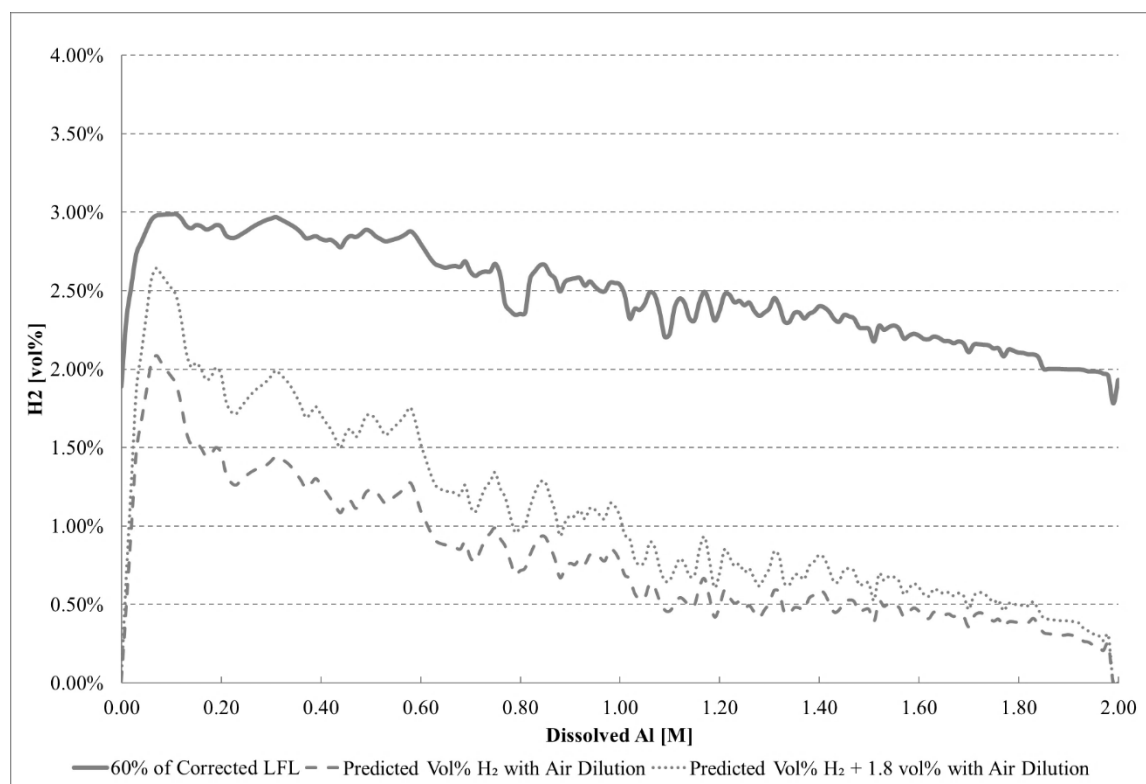


Fig. 10. H_2 LFL Comparison for Exp. 96 – 7 M HNO_3 , 0.002 M Hg, and 45 min Hold Time

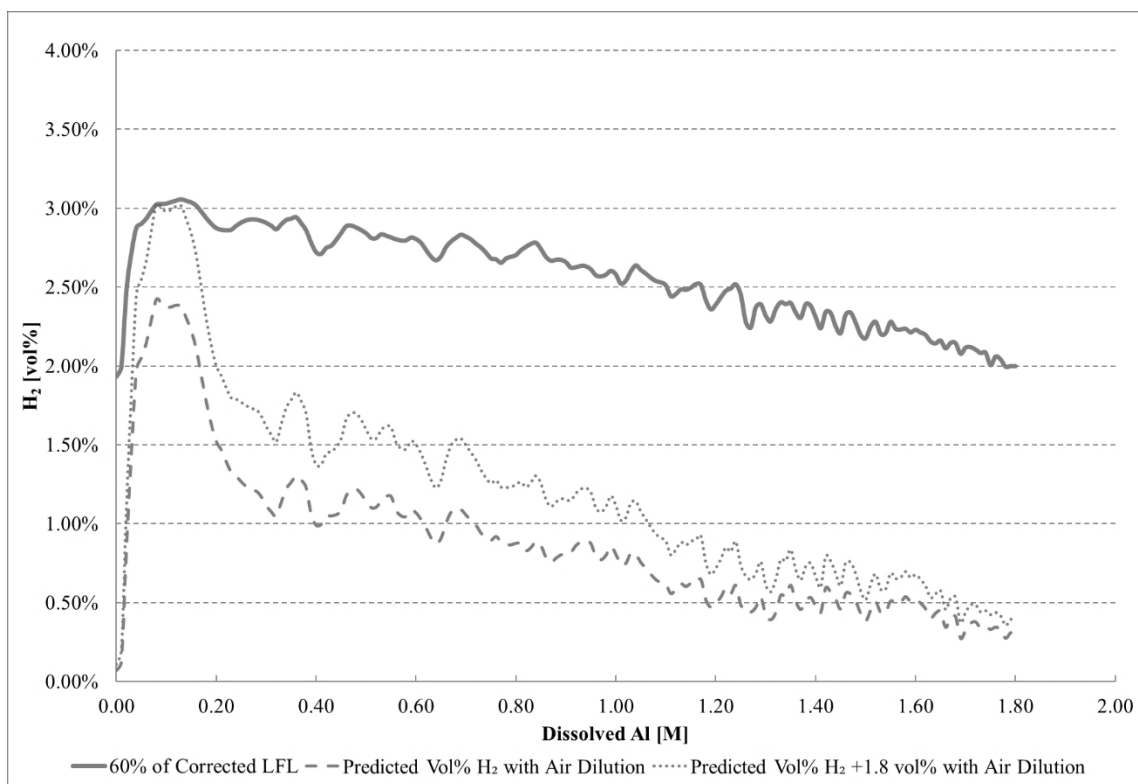


Fig. 11. H₂ LFL Comparison for Exp. 97 – 7 M HNO₃, 0.002 M Hg, and 45 min Hold Time

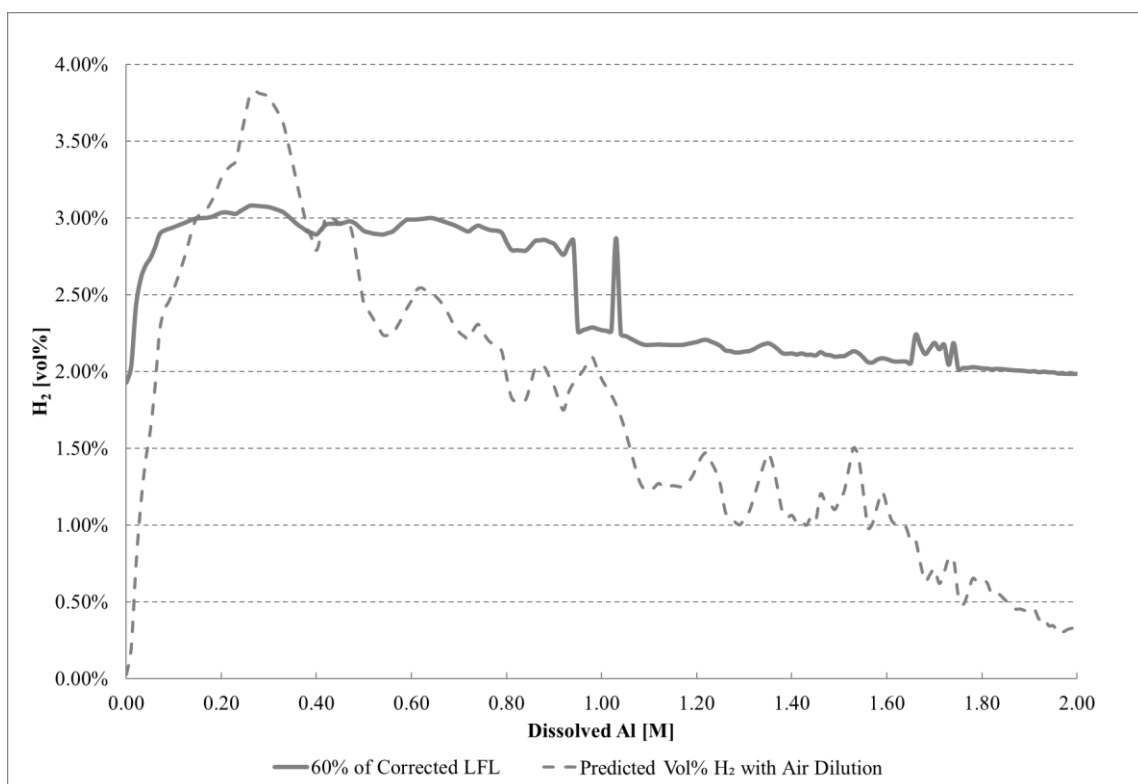


Fig. 12. H₂ LFL Comparison for Exp. 98 – 7 M HNO₃, 0.004 M Hg, and 45 min Hold Time

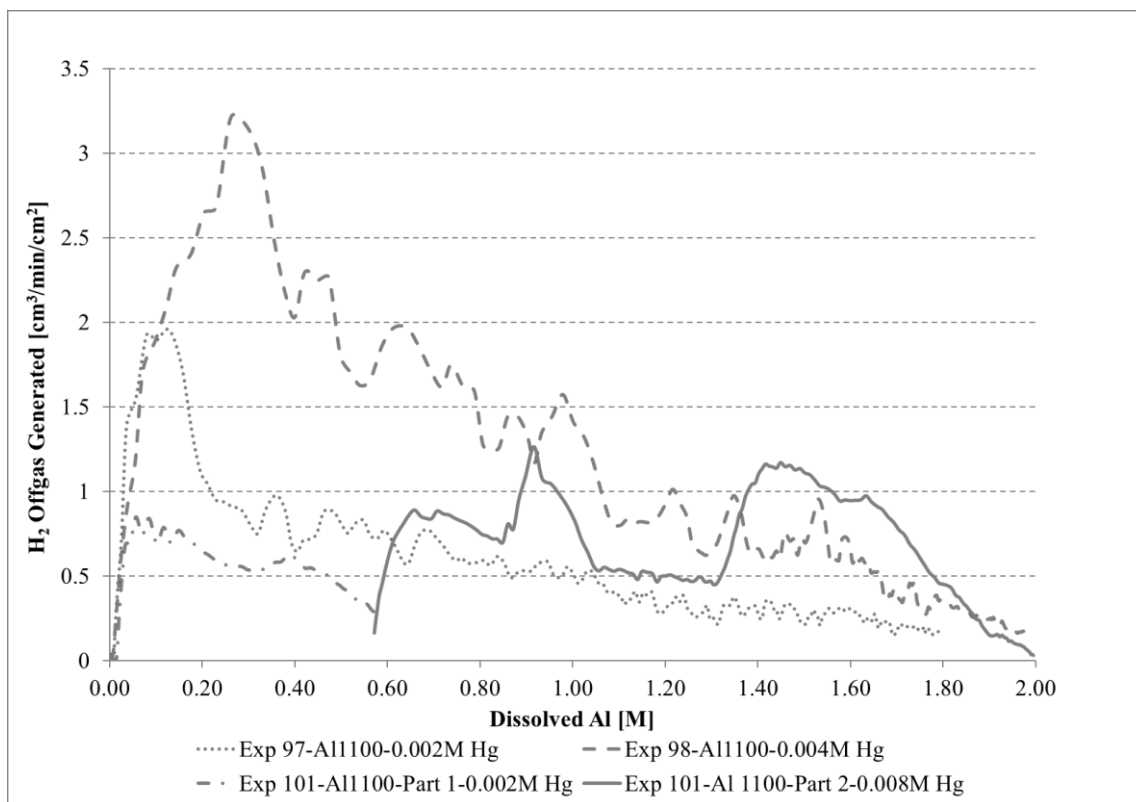


Fig. 13. Effect of Adding Additional Hg During Al 1100 Alloy Dissolution

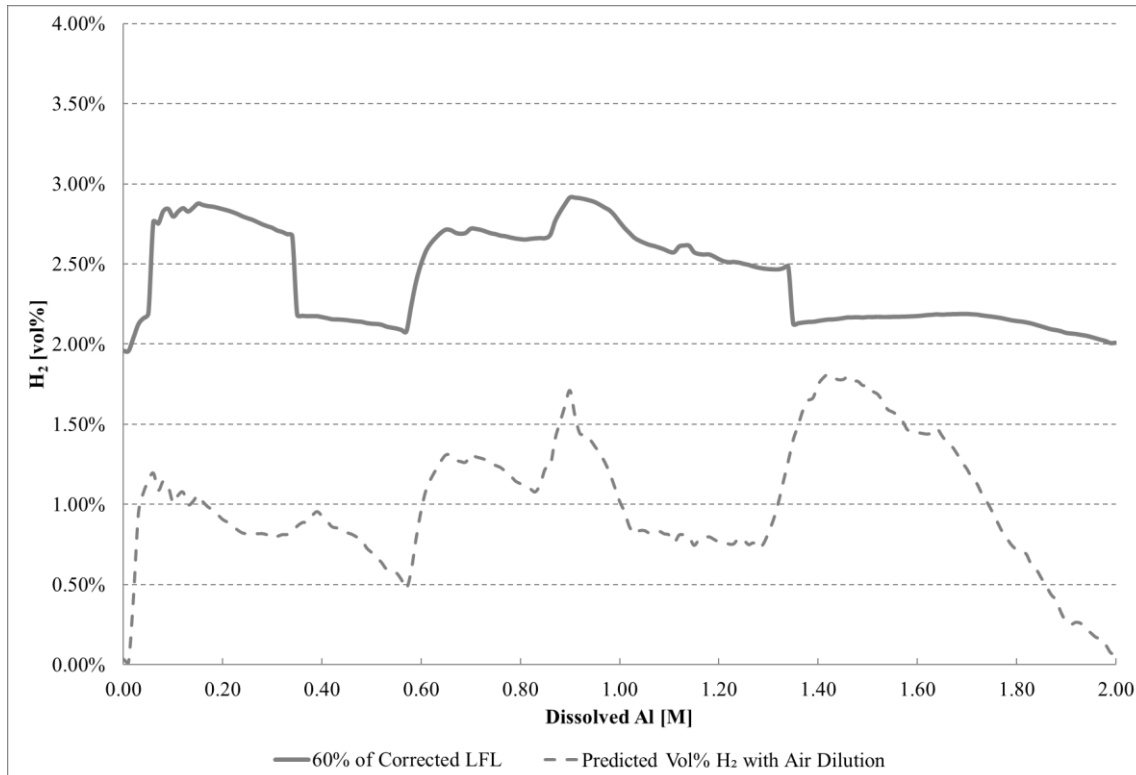


Fig. 14. H_2 LFL Comparison for Exp. 101 – 7 M HNO_3 and 0.002 to 0.008 M Hg at 1.3 M Al