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Effects of Increasing the Initial Nitric Acid Concentration from a Maximum of 7.5 to 8.5 M During the Dissolution of Aluminum Spent Nuclear Fuel

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EXECUTIVE SUMMARY

H-Canyon is blending solutions from the dissolution of High Flux Isotope Reactor (HFIR) and Material Test Reactor (MTR) fuels with Target Residue Material (TRM) to prepare feed solution for the 1st Cycle of solvent extraction. The initial acid concentration for HFIR fuel dissolution is limited to 7.5 M by the flowsheet; however, an increase in the initial concentration is desirable to more easily achieve the target acidity for solvent extraction using the current blending strategy. To provide flexibility in batching the highly enriched uranium (HEU) solutions, the Savannah River National Laboratory (SRNL) was requested to evaluate the potential for increasing the maximum HNO_3 concentration for HFIR fuel dissolution from 7.5 to 8.5 M. In response to this request, a literature review was performed to evaluate the impact of a higher starting HNO_3 concentration on the dissolution of aluminum spent nuclear fuels (ASNF) including both HFIR and MTR fuels.

The dissolution rates of U-Al and Al alloys peak in the range of 4 to 7.5 M HNO_3 depending on the Hg concentration and the metallurgical history of the alloy. Less rapid dissolution rates result in lower offgas generation rates; therefore, as the HNO_3 concentration increases beyond the value where the maximum rate is observed the offgas generation rate will decrease. Flowsheet development work for both HFIR and MTR fuels showed that a decrease in the offgas generation rate generally resulted in a decrease in the H_2 generation rate. Hydrogen gas analyses for the dissolution of Al using "low" versus "high" concentrations of HNO_3 show that much lower concentrations of H_2 result if 40 wt % (7.9 M) HNO_3 was used to dissolve Al cladding compared to the use of 10 wt % (1.7 M) HNO_3. Therefore, an increase in the HNO_3 concentration beyond 7.5 M for ASNF dissolution will result in decreases in the dissolution rate and in the offgas and H_2 generation rates.

The lower flammability limit (LFL) of H_2 is a function of H_2, NO, N_2O and air in the dissolver offgas and has been reported at varying values of the NO:N_2O ratio. At the lower NO:N_2O ratio reported, the H_2 LFL exhibits its lowest measured values. However, as the concentration of HNO_3 used in the dissolution increases, the amount of acid consumed also increases resulting in a net increase in the production of NO_2 and NO compared to N_2O. The NO:N_2O ratio will increase moving toward ratios where higher values for the H_2 LFL were measured; therefore, an increase in the initial HNO_3 concentration for ASNF dissolutions would not result in conditions which result in dramatically lower values of the H_2 LFL.

Increasing the initial maximum HNO_3 concentration for ASNF dissolution from 7.5 to 8.5 M will not have an adverse impact on the generation rate of H_2 or the H_2 LFL and can be performed with insignificant impact on the dissolution process. Increasing the HNO_3 concentration from 7.5 to 8.5 M should also result in a proportional increase in the final concentration following the dissolution.

TABLE OF CONTENTS

LIST OF FIGURES....vii

LIST OF ABBREVIATIONS....viii

1.0 Introduction....1

2.0 Quality Assurance....1

3.0 Results and Discussion....1

4.0 Conclusions....8

5.0 References....9

LIST OF FIGURES

Figure 1. Rate of U-Al Alloy Dissolution as a Function of Nitric Acid Concentration 2

Figure 2. Dissolution of U-Al Alloys in HNO_3 3

Figure 3. Offgas and H_2 Generation Rates from the Dissolution of an Al-1100 Alloy Coupon Used for the HFIR and MTR Fuel Flowsheet Development 4

Figure 4. LFL for Air, H_2, NO, NO_2 Mixtures 6

Figure 5. Offgas Characterization During Al-1100 Alloy Dissolution.. 7

Figure 6. Measured NO:N_2O Ratio During Al-1100 Alloy Dissolution... 7

LIST OF ABBREVIATIONS

ASNF	aluminum spent nuclear fuel
HEU	highly enriched uranium
HFIR	High Flux Isotope Reactor
LFL	lower flammability limit
MTR	Material Test Reactor
SRNL	Savannah River National Laboratory
TRM	Target Residue Material

1.0 Introduction

Aluminum spent nuclear fuels (ASNF) are dissolved in the H-Canyon facility. High Flux Isotope Reactor (HFIR) fuel is currently dissolved in the 6.4D dissolver and Material Test Reactor (MTR) fuels are dissolved in the 6.1D dissolver. The flowsheets for the dissolution processes specify the use of an initial HNO_3 concentration in the dissolving solution which is typically between 5 and 7.5 M, depending upon the amount of U and Al which must be dissolved.[1,2] Completion of a HFIR or MTR fuel batch requires the successive dissolution of multiple cores or multiple L-Bundle charges, respectively, resulting in a final solution containing greater than 0.5 M HNO_3 to guard against the solution becoming acid deficient with the potential to precipitate fissile material. Once a fuel batch is dissolved, the solution is combined with other sources of highly enriched uranium (HEU) to prepare feed solution for the 1st Cycle of solvent extraction.

Currently the dissolved HFIR and MTR fuels are combined with Target Residue Material (TRM) which is shipped to H-Canyon. The acid concentration of the feed solution for the 1st Cycle mixer-settlers must be in the 1-2 M range.[3] When batching the HEU solutions for subsequent purification, the desire is to add as little HNO_3 as possible to adjust the acidity of the 1st Cycle feed. Based on recent blend strategies that prepare solution for Head End processing using one batch of MTR fuel plus one-half batch of HFIR fuel plus TRM, the final acidity of the solution containing the HFIR fuel needs to be between 1.0 and 1.3 M. However, based on the existing HFIR flowsheet which limits the acid concentration to a maximum of 7.5 M,[1] the actual terminal acid concentration is only slightly above 1.0 M.

To provide flexibility in the batching of HEU materials for U recovery, H-Canyon Engineering has requested that the Savannah River National Laboratory (SRNL) evaluate the potential for increasing the maximum HNO_3 concentration for ASNF fuel dissolution from 7.5 to 8.5 M. In response to this request, a literature review was performed to evaluate the impact of a higher starting HNO_3 concentration on the dissolution of ASNF. Of primary concern was the potential for the increase in the dissolution rate of Al and a concurrent increase in the H_2 gas generation rate; although, the impact of increasing the initial acid concentration on the lower flammability limit (LFL) of H_2 was also evaluated. The results from the literature review and the conclusions reached are discussed in the following sections of the report.

2.0 Quality Assurance

A Functional Classification of Safety Significant was applied to this work. To match the functional classification, this report received technical review by design verification. Requirements for performing reviews of technical reports and the extent of review are established in manual E7, 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

For the development of the HFIR and MTR fuel dissolution flowsheets, the offgas and H_2 generation rates in the H-Canyon dissolvers were bounded by the dissolution of an Al-1100 alloy.[1,2] The laboratory experiments used to define the flowsheets were performed using 7 M HNO_3 with the addition of a small amount (0.002 to 0.004 M) of Hg to catalyze the Al dissolution. The use of solutions containing acid concentrations significantly higher were not investigated based on existing H-Canyon operating history. However, a considerable amount of information is available in the literature on the dissolution of U-Al alloys containing low concentrations of U using solutions with a wide range of HNO_3 concentrations. Burns and Holm performed a series of experiments in which a U-Al alloy containing 92.5 wt % Al and 7.5 wt % U was dissolved in 0 to 9 M HNO_3 using 0.002 M Hg at the boiling points of the solutions.[4] Results obtained from these experiments confirmed expectations that during dissolution, the U-Al alloy behaved much like Al alone.

The experimental data from Burns and Holm (Figure 1) show there is an optimum HNO_3 concentration for a given $Al(NO_3)_3$ concentration which maximizes the dissolution rate. Wymer and Blanco performed similar experiments in which they measured the initial dissolution rate of extruded and cast U-Al alloys with U concentrations which ranged from 5 to 15 wt % (Figure 2).[5] The same general trends in the data were observed. As the HNO_3 concentration increased, the dissolution rate increased to a maximum value which was dependent upon the concentration of Hg and the metallurgical treatment of the U-Al alloy (i.e., extruded versus cast) and then decreased significantly at higher acid concentrations.

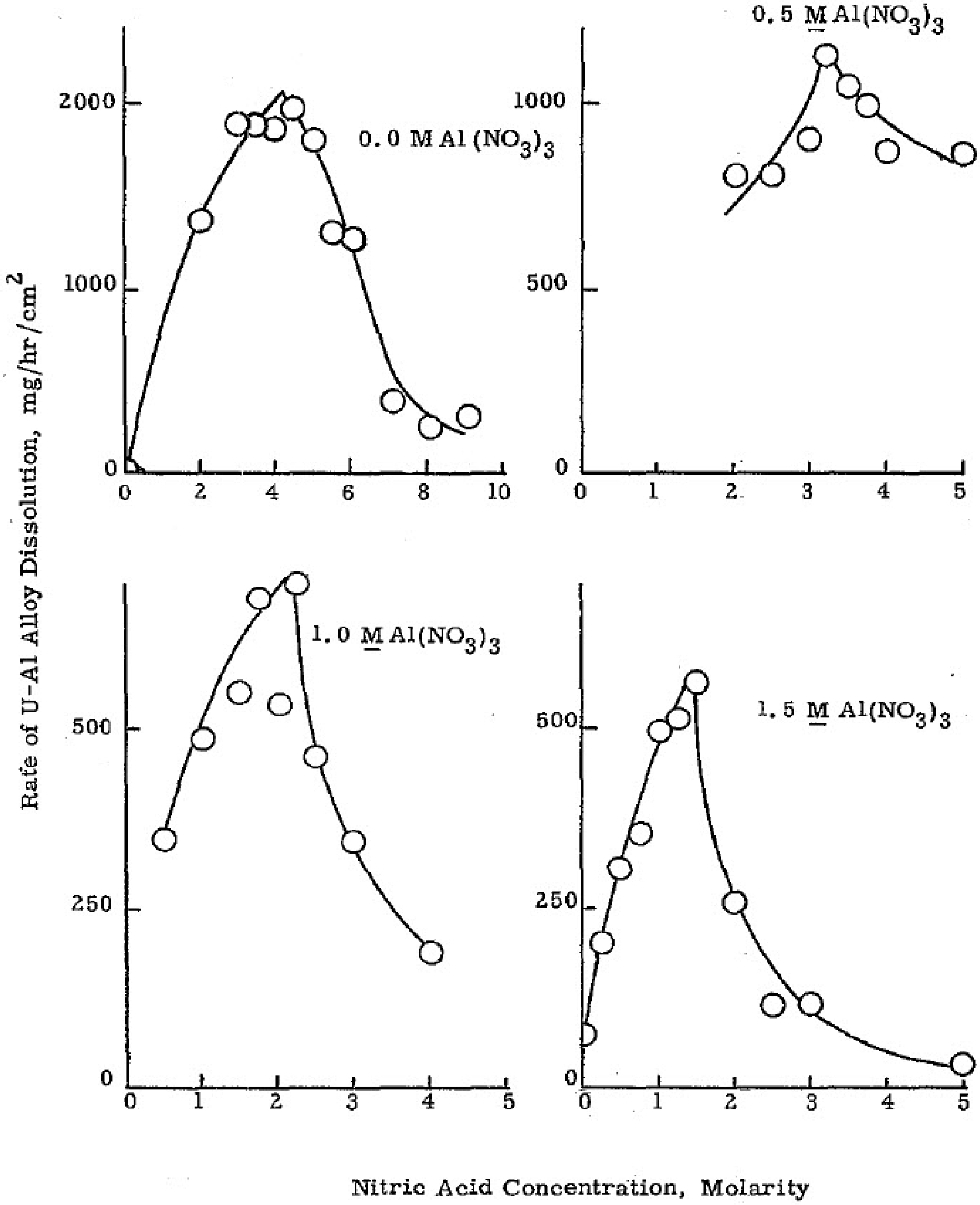


Figure 1. Rate of U-Al Alloy Dissolution as a Function of Nitric Acid Concentration

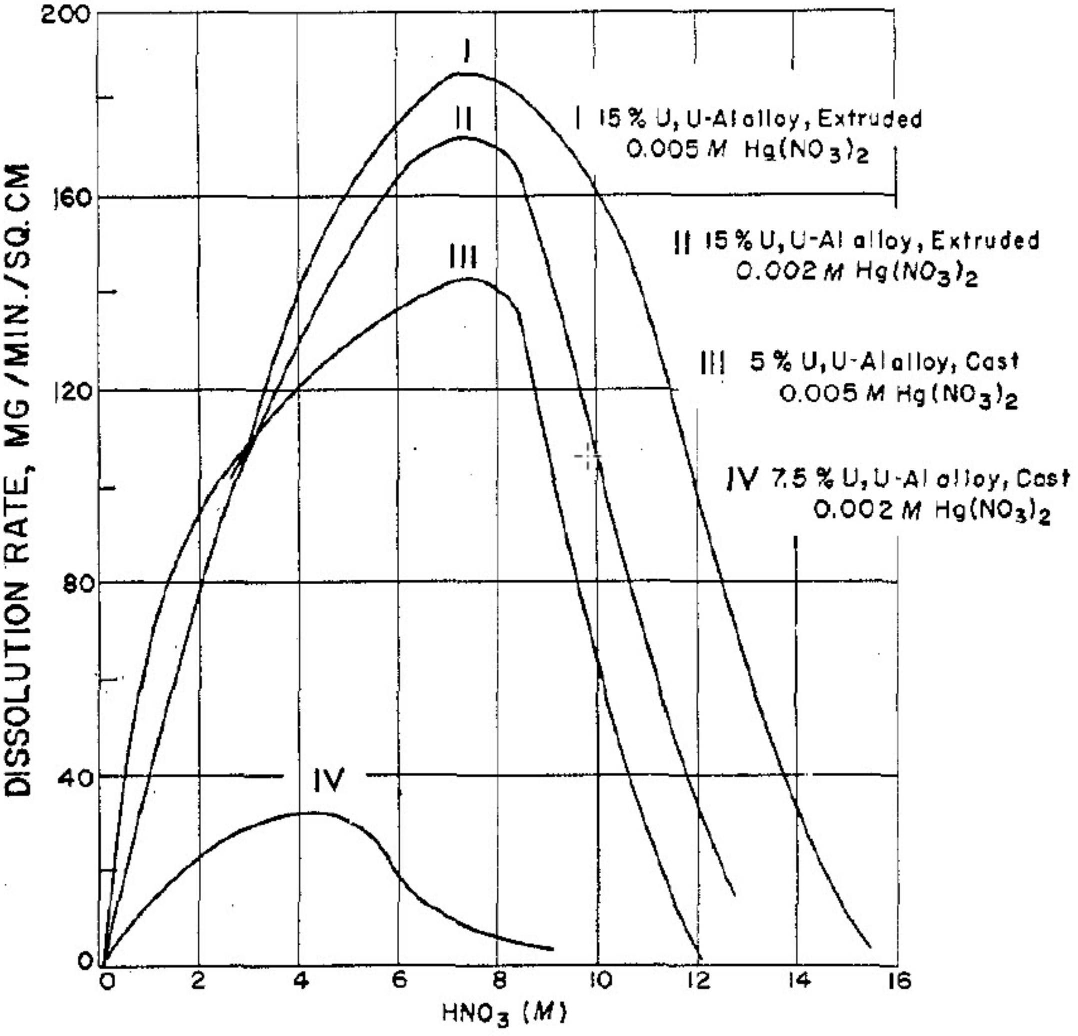


Figure 2. Dissolution of U-Al Alloys in HNO_3

The maximum in the dissolution rate over the range of HNO_3 concentrations shown in Figure 1 and Figure 2 can be explained by considering the catalytic role which Hg plays in the dissolution of Al. At the start of an Al (or U-Al alloy) dissolution, free Hg which has a transient lifetime in HNO_3 solutions, amalgamates with the surface of the Al which is passivated with an oxide film during this initial induction period of the reaction. The amalgamated surface area then reacts vigorously with HNO_3, leading to the production of more metallic Hg which causes further amalgamation. This process continues until a balance is reached between the reduction of Hg by the dissolving Al (or its alloys) and the dissolution of metallic Hg by the HNO_3. The maxima shown in Figure 1 and Figure 2 are evidence that the amalgamated Al dissolves at rates which increase with the HNO_3 concentration up to the point where the amount of amalgamation drops due to the oxidation rate of the free Hg increasing more rapidly than the overall rate of Al dissolution and Hg reduction. The declining dissolution rates continue as the HNO_3 concentration increases and the solution becomes more highly oxidizing leading to the passivation of the surface by the acid.[4,5]

The maximum dissolution rate of Al (and U-Al alloys) occurs at a HNO_3 concentration which is a function of the Hg and $Al(NO_3)_3$ concentrations in the dissolving solution. Other factors such as the metallurgical treatment of the alloys can also influence the concentration where the maximum rate occurs.[4,5] In the experiments performed by Burns and Holm (Figure 1), a Hg concentration of 0.002 M was used during the dissolutions of U-Al alloy wafers cut from fuel elements. In the absence of $Al(NO_3)_3$, the maximum dissolution rate occurred at nominally 4 M HNO_3 and began to decrease with increasing acid concentrations. The data in Figure 1 also show that the HNO_3 concentration where the maximum dissolution rate occurs decreased with increasing $Al(NO_3)_3$ concentrations. The HNO_3 concentration where the maximum rate of dissolution was observed by Wymer and Blanco (Figure 2) for cast and extruded U-Al alloys using 0.002 and 0.005 M Hg was between 7 and 7.5 M HNO_3 except for experiments in which cast 7.5 wt % U-Al alloy samples were dissolved using 0.002 M Hg. The dissolution rate peaked at nominally 4 M HNO_3; however, the metallurgical history of the samples was different from the other cast samples as the cast rod was cut into wafers which primarily exposed the two circular faces to the dissolving solution.

The dissolution rates for U-Al alloys reproduced from the literature (Figure 1 and Figure 2) clearly show that the peak rates occur in the range of 4 to 7.5 M HNO_3 depending on the Hg concentration and the metallurgical history of the alloy. The same trend should also hold true for the Al-1100 alloy coupons used to provide a bounding value for the offgas generation rate during the dissolution of HFIR and MTR fuels. This conclusion is based on the observation by Burns and Holm that during the dissolution of U-Al alloys with low concentrations of U, the alloys behaved much like Al alone.[4] Less rapid dissolution rates are consistent with lower offgas generation rates;[6] therefore, as the HNO_3 concentration increases beyond the value where the maximum rate is observed during the dissolution of an Al-1100 alloy coupon (or HFIR and MTR fuel), the offgas generation rate will decrease. The flowsheet development work for the dissolution of HFIR and MTR fuels shows that a decrease in the offgas generation rate generally results in a decrease in the H_2 generation rate.[1,2] Offgas and H_2 generation rates for dissolution of an Al-1100 alloy coupon used for both the HFIR and MTR fuel dissolution flowsheet development are plotted on Figure 3. The shape of the curve for the H_2 generation rate is very similar to the curve for the offgas generation rate data showing a decrease in the production rate generally at the same Al concentration where the offgas generation rate decreases.

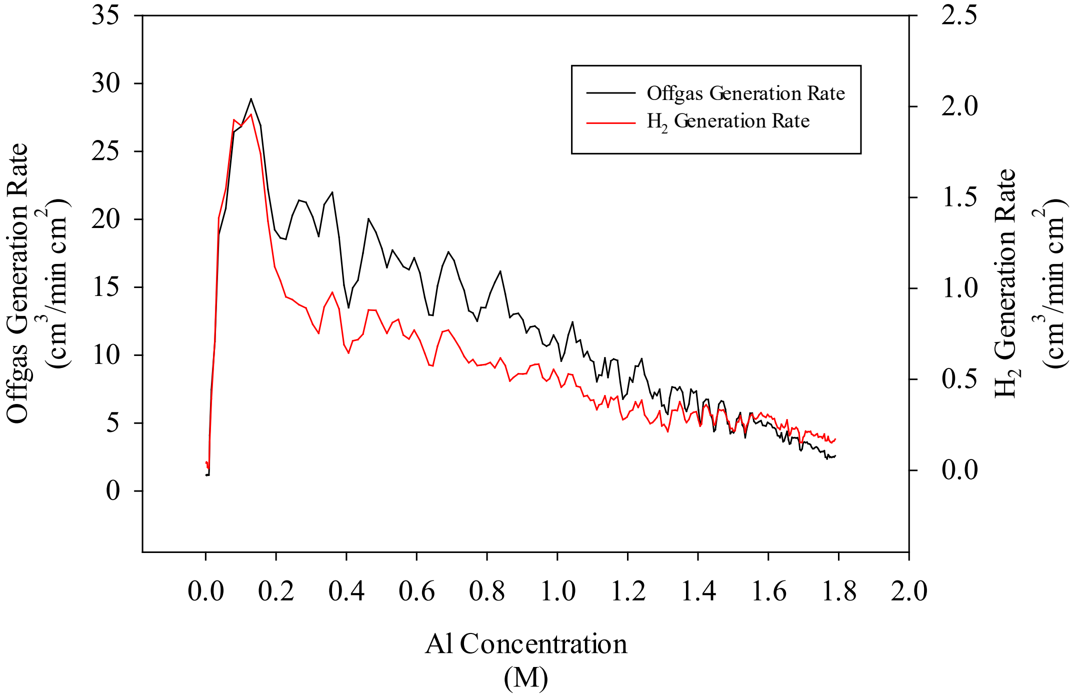


Figure 3. Offgas and H_2 Generation Rates from the Dissolution of an Al-1100 Alloy Coupon Used for the HFIR and MTR Fuel Flowsheet Development

Hydrogen gas analyses have also been performed to compare the concentration in the offgas from Al dissolutions for “low” versus “high” concentrations of HNO_3. During the early development of flowsheets for the removal of Al cladding from targets used to produce Pu, an observation was made that much lower concentrations of H_2 result if 40 wt % (7.9 M) HNO_3 is used during the cladding removal compared to the use of 10 wt % (1.7 M) HNO_3.[7] The decrease in H_2 generation with increasing HNO_3 concentration is consistent with the dissolution mechanism of the amalgamated Al shifting away from a typical metal/acid reaction toward increased production of nitrogen oxides by nitrate (NO_3^-) oxidation.[8,9]

The data from previous work show that an increase in the initial HNO_3 concentration above 7.5 M for a HFIR or MTR fuel dissolution will result in decreases in the dissolution rate and offgas and H_2 generation rates. However, an evaluation of the change in the lower flammability limit (LFL) of H_2 is also needed to ensure that the LFL is not dramatically reduced due to the use of a higher acid concentration during a dissolution. Lower flammability limit data reported by Scott et al.[10] for air, H_2, NO, and N_2O mixtures were used to calculate the LFL for comparison to the H_2 concentrations calculated for the dissolution of HFIR and MTR fuel in an H-Canyon dissolver. Three data sets for NO:N_2O ratios of 2.57, 1.00, and 0.33 (Figure 4) were used for the calculations based on the measured value of the NO:N_2O ratio.[1,**Error! Bookmark not defined.**]

In laboratory dissolution experiments using Al-1100 alloy coupons to bound the offgas generation rate for the dissolution of spent nuclear fuel in the H-Canyon dissolvers,[1,2] the predominate gas species were nitrogen oxides (e.g., NO, N_2O, and NO_2). The composition of the offgas for increasing Al concentrations measured in the previous work during the dissolution of the Al-1100 alloy coupon which was used to define both the HFIR and MTR dissolution flowsheets is shown in Figure 5. In the experiment, the Hg was not added until the dissolving solution boiled for 45 min which reduces both the offgas and H_2 generation rates by passivating the surface of the coupon (and ASNF during an H-Canyon dissolution). The NO:N_2O ratio measured during the experiment is shown in Figure 6.

Aluminum and HNO_3 can react in multiple proportions forming the reaction products given by equations 1-5.

$$\mathrm{Al + 6HNO_3 \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O} \tag{1}$$

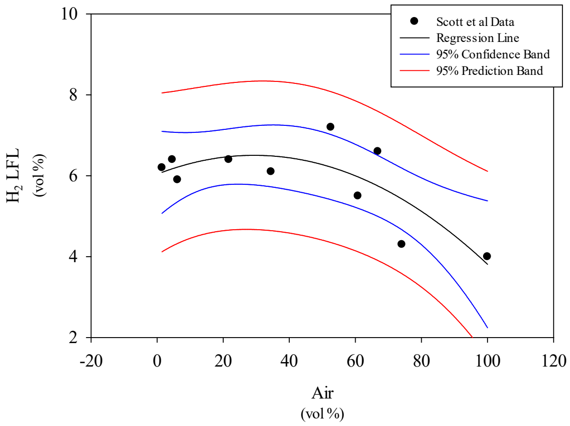
$$\mathrm{Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + 2H_2O} \tag{2}$$

$$\mathrm{8Al + 30HNO_3 \rightarrow 8Al(NO_3)_3 + 3N_2O + 15H_2O} \tag{3}$$

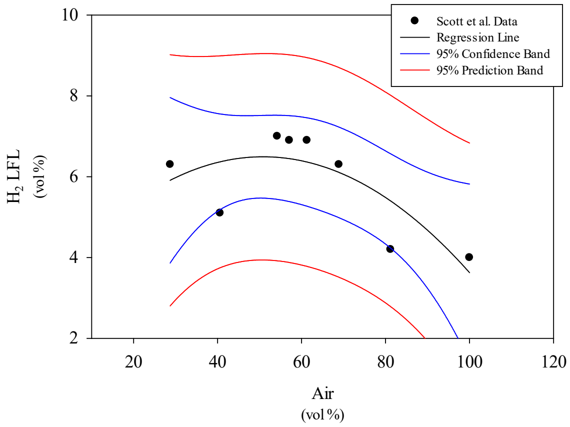
$$\mathrm{10Al + 36HNO_3 \rightarrow 10Al(NO_3)_3 + 3N_2 + 18H_2O} \tag{4}$$

$$\mathrm{2Al + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2} \tag{5}$$

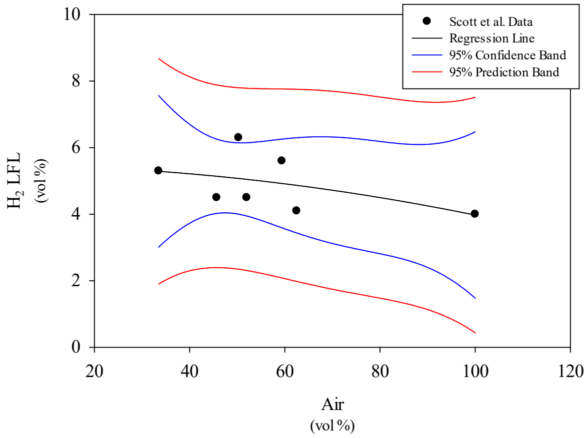
All of these reactions occur to some extent as illustrated by the offgas characterization for the dissolution experiment shown in Figure 5.[1,2] However, as the concentration of HNO_3 in the dissolving solution decreases, the Al dissolution shifts toward the reactions which consume the least acid (i.e., progressing from Equation 1 to Equation 5).[11] The reverse of this observation is also true which implies that at higher HNO_3 concentrations, Al dissolution shifts toward reactions which maximize acid consumption. Therefore, if the initial HNO_3 concentration for a HFIR or MTR fuel dissolution is increased from 7.5 M to a value between 7.5 and 8.5 M, the increased acidity will result in a net increase in the production of NO_2 and NO compared to N_2O. The NO:N_2O ratio will increase moving toward ratios where higher values for the H_2 LFL were measured by Scott and Zabetakis (Figure 4).[10] Therefore, an increase in the initial HNO_3 concentration for HFIR or MTR fuel dissolutions would not result in conditions which result in dramatically lower values of the H_2 LFL. The increase in the HNO_3 concentration from 7.5 to 8.5 M should also result in a proportional increase in the final HNO_3 concentration following fuel dissolutions since a significant portion of the NO_2 gas is absorbed in the condenser and converted back to HNO_3.[3]



NO:N_2O = 2.57



NO:N_2O = 1.00



NO:N_2O = 0.33

Figure 4. LFL for Air, H_2, NO, NO_2 Mixtures

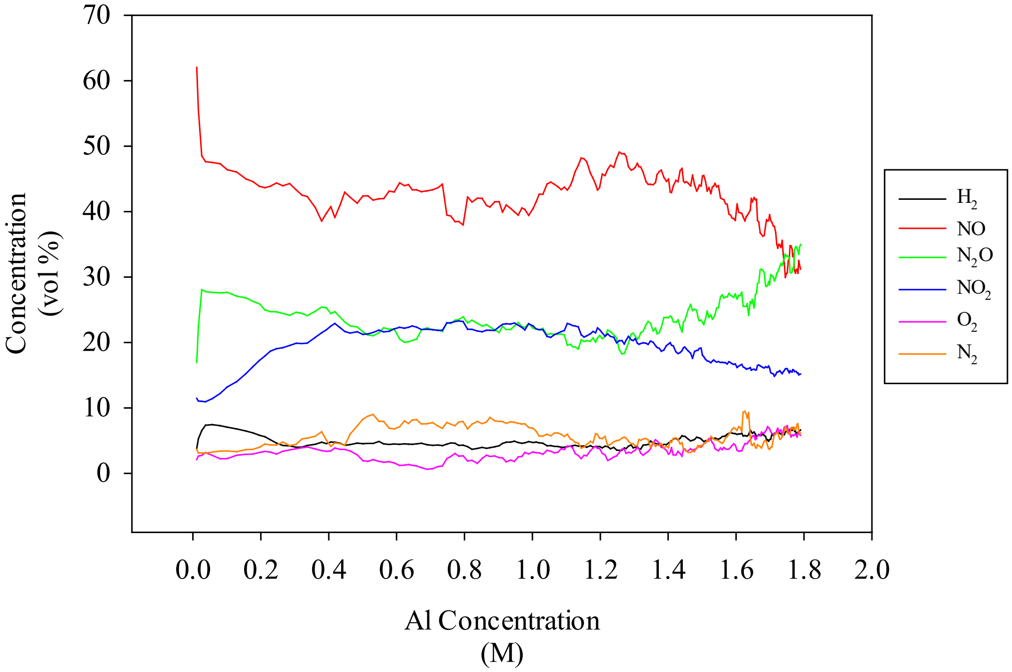


Figure 5. Offgas Characterization During Al-1100 Alloy Dissolution

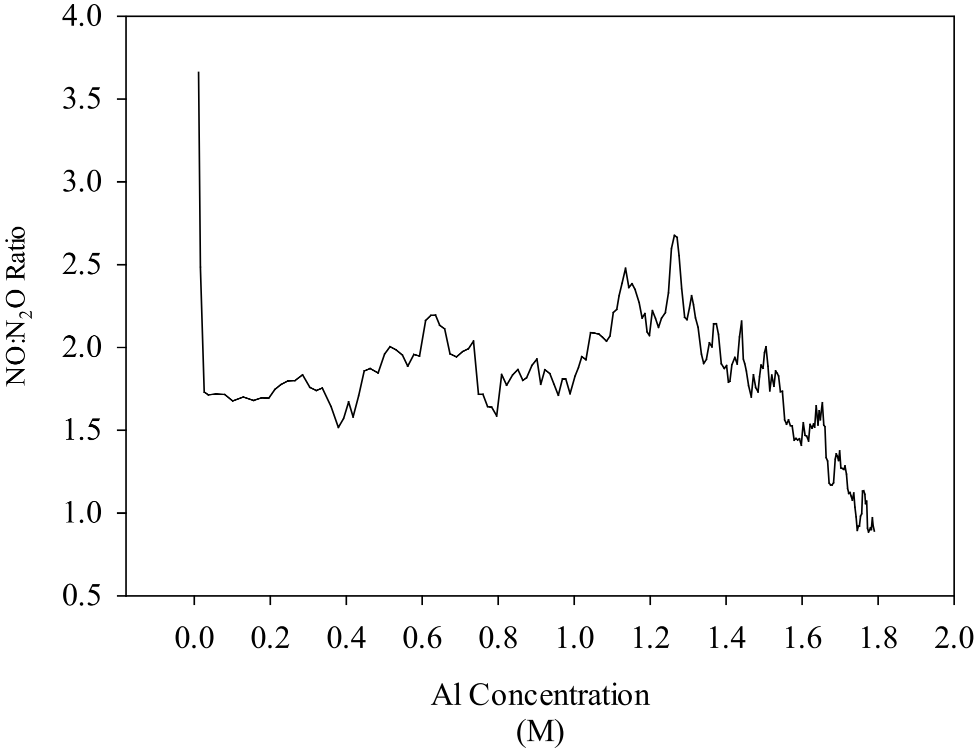


Figure 6. Measured NO:N_2O Ratio During Al-1100 Alloy Dissolution

4.0 Conclusions

A review of the literature on the dissolution of U-Al alloys showed that peak dissolution rates occur in the range of 4 to 7.5 M HNO_3 depending on the Hg concentration and the metallurgical history of the alloy. The same trend also holds for Al alloys like the materials used to provide bounding values for the offgas generation rate during the dissolution of HFIR and MTR fuels. Less rapid dissolution rates result in lower offgas generation rates; therefore, as the HNO_3 concentration increases beyond the value where the maximum Al dissolution rate is observed, the offgas generation rate will decrease. Data from the development of dissolution flowsheets for HFIR and MTR fuels showed that a decrease in the offgas generation rate generally resulted in a decrease in the H_2 generation rate. Hydrogen gas analyses available from literature for the dissolution of Al using “low” versus “high” concentrations of HNO_3 show that much lower concentrations of H_2 result if 40 wt % (7.9 M) HNO_3 was used to dissolve Al cladding compared to the use of 10 wt % (1.7 M) HNO_3. Therefore, an increase in the HNO_3 concentration beyond 7.5 M for ASNF dissolution will result in decreases in the offgas and H_2 generation rates.

The effect of increasing the HNO_3 concentration on the H_2 LFL was also evaluated to ensure that the LFL is not dramatically reduced due to the use of a higher acid concentration during a HFIR or MTR fuel dissolution. The LFL, a function of the concentrations of H_2, NO, N_2O, and air in the dissolver offgas, is reported at varying values of the NO:N_2O ratio. At the lowest NO:N_2O ratio reported, the H_2 LFL exhibits its lowest measured values. Aluminum and HNO_3 can react in multiple proportion forming reaction products which maximize or minimize the amount of acid consumed in the reaction. As the concentration of HNO_3 used in the dissolution increases, the maximum amount of acid is consumed resulting in a net increase in the production of NO_2 and NO compared to N_2O. The NO:N_2O ratio will increase moving toward ratios where higher values for the H_2 LFL were measured; therefore, an increase in the initial HNO_3 concentration for HFIR or MTR fuel dissolutions would not result in conditions which result in dramatically lower values of the H_2 LFL.

Increasing the initial maximum HNO_3 concentration for ASNF dissolution from 7.5 to 8.5 M will not have an adverse impact on the generation rate of H_2 or the H_2 LFL and can be performed with insignificant impact on the dissolution process. Increasing the HNO_3 concentration from 7.5 to 8.5 M should also result in a proportional increase in the final concentration following the dissolution.

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