SRNL-STI-2010-00005
Revision 2

Keywords: *MURR Fuel, H-Canyon, Aluminum Dissolution, Off-site Fuel*

Retention: *Permanent*

Dissolution of Irradiated MURR Fuel Assemblies

E.A. Kyser

June 2010

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

REVIEWS AND APPROVALS

AUTHORS:

original approved by E. A. Kyser on 6/17/10

E. A. Kyser, Separations and Actinide Science Programs Date

TECHNICAL REVIEW:

original approved by G. F. Kessinger on 6/17/10

G. F. Kessinger, Separations and Actinide Science Programs Date

original approved by James E. Laurinat on 6//21/10

J. E. Laurinat, Process Modeling and Computational Sciences Date

APPROVAL:

original approved by Samuel. D. Fink on 7/21/2010

S. D. Fink, Manager Date
Separations and Actinide Science Programs

original approved by Sharon L. Marra on 7/26/10

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

original approved by W. G. Dyer on 8/2/2010

W. G. Dyer, Manager Date
H-Canyon Technical Support

Table of Contents

Table of Contents v
Table of Figures: vi
Table of Tables: vi
SUMMARY 7
INTRODUCTION 8
BACKGROUND 8
- MURR Fuel Description and History: 8
- Dissolution History: 10
- Dissolution Chemistry- Aluminum Clad Uranium-Aluminum Alloy Fuel: 11
- Effect of Nitric Acid and Aluminum Nitrate Concentration: 12
- Effect of Catalyst Concentration: 13
- Effect of Rate of Catalyst Addition: 14
- Effect of Surface Area- Geometry: 15
- Effect of Radiation Dose: 16
- Hydrogen Evolution: 18
- Off-gas Composition: 18
- Aluminum Solubility: 19
- Nuclear Poison: 19
- Multiple Charge Dissolution: 20
- Idealized Dissolution Model: 20

Downstream Processing 21
- Head End Operation: 21
- Solvent Extraction: 21

DISCUSSION 22
- Required Purge Rate as a Function of Off-gas Rate: 22
- Determination of Peak Off-gas Rate: 22
- Off-gas rate scaled by surface area: 24
- General Discussion: 25

CONCLUSIONS 26
RECOMMENDATIONS 27
- PROCESS IMPROVEMENTS 28

ACKNOWLEDGEMENTS 28
REFERENCES 28
APPENDIX 31
- Calculation A - Estimated Off-gas from Historical Dissolution of MURR Fuel 32
- Calculation B - Predicted Off-gas from Future Dissolution of MURR Fuel 33
- Calculation C - Predicted Off-gas from Dissolution of MURR Fuel – Second Charge 34

Table of Figures:

Figure 1. Three-Dimensional Sketch of MURR Fuel Assembly. ……... 9
Figure 2. Top View Schematic of a MURR Fuel Assembly. ……….. 9
Figure 3. Sketch of Dissolver Pot Showing Fuel Insert and Coils. ………………….……………. 10
Figure 4. Sketch of Insert Port and Condenser on Top of Dissolver. ……………….……………. 10
Figure 5. Details of the Ten-Well Insert. ……………………….. 10
Figure 6. Effect of Nitric Acid Concentration on the Dissolving Rate of Unirradiated Aluminum -16 wt % Uranium Alloy. ……………………………………..... 13
Figure 7. Effect of Aluminum Nitrate Concentration on the Dissolution Rate Characteristics of Fuel Elements – 16 wt % Uranium Alloy. ……………………………..13
Figure 8. Effect of Aluminum Dissolution and Nitric Acid Consumption on the Dissolution Rate. ……….……………………………………………………………. 13
Figure 9. Effect of Mercury Concentration on the Dissolving Rate of Unirradiated Aluminum - 16 wt % Uranium Alloy. ……….………………………….. 14
Figure 10. Effect of Irradiation on Initial Dissolving Rate of Mark VI Tube in 6 M HNO_3. ...……. 16
Figure 11. Flammability of the Hydrogen-Nitric oxide-Nitrous oxide-Air System at 28 °C. ……. 17
Figure 12. Limits of Flammability:
a) The System H_2-NO-Air at 28 °C and 1 atm Pressure. ..……………………………… 17
b) The System H_2-NO-N_2O-Air at 28 °C and 1 atm Pressure (NO/N_2O =2.57). ……….. 17
Figure 13. Off-gas Concentrations Observed during the Dissolution of Aluminum Clad Fuel. ..… 18
Figure 14. Solubility of Aluminum Nitrate in Nitric Acid Solutions as a Function of Temperature. ……………………………………….…………………... 19
Figure 15. Idealized Dissolving Process. ………………………………………………….…..... 20
Figure 16. Capacity of Dissolver Jet. ………………………………………………….......... 23

Table of Tables:

Table 1. History of Dissolution of MURR Fuel in H-Canyon. ………………………..………. 11
Table 2. Effect of the Number of Bundles Charged on the Aluminum and Uranium Concentrations. ……………………………………………………………. 19
Table 3. Effect of Purge Rate Dilution on Off-Gas Composition (40 scfm minimum purge rate). ..22
Table 4. Pilot Scale Dissolution Rate Data with Peak Rates. …………………………………….. 24
Table 5. Estimated Off-gas Rates from Historical MURR Dissolution. …………………………… 32
Table 6. Estimated Off-gas Rates for Proposed Future MURR Dissolution. ……………………… 33
Table 7. Estimated Off-gas Rates for a Six-Bundle Second Charge MURR Dissolution (Assumes 0.3 M Al present from the initial charge). ..…………….. 34
Table 8. Effect of Soluble Aluminum on the Number of Bundles in a Second Dissolution Charge. 34
Table 9. LFL Data at NO/N_2O Ratio Equal to 2.57. ……………………………………………… 35

Dissolution of Irradiated MURR Fuel Assemblies

by

Edward A. Kyser

Savannah River National Laboratory
Environmental and Chemical Technology Directorate

June 17, 2010

SUMMARY

A literature survey on the dissolution of spent nuclear fuel from the University of Missouri Research Reactor (MURR) has been performed. This survey encompassed both internal and external literature sources for the dissolution of aluminum-clad uranium alloy fuels. The most limiting aspect of dissolution in the current facility configuration involves issues related to the control of the flammability of the off-gas from this process. The primary conclusion of this work is that based on past dissolution of this fuel in H-Canyon, four bundles of this fuel (initial charge) may be safely dissolved in a nitric acid flowsheet catalyzed with 0.002 M mercuric nitrate using a 40 scfm purge to control off-gas flammability. The initial charge may be followed by a second charge of up to five bundles to the same dissolver batch depending on volume and concentration constraints. The safety of this flowsheet relies on composite lower flammability limits (LFL) estimated from prior literature, pilot-scale work on the dissolution of site fuels, and the proposed processing flowsheet. Equipment modifications or improved LFL data offer the potential for improved processing rates. The fuel charging sequence, as well as the acid and catalyst concentrations, will control the dissolution rate during the initial portion of the cycle. These parameters directly impact the hydrogen and off-gas generation and, along with the purge flowrate determine the number of bundles that may be charged. The calculation approach within provides Engineering a means to determine optimal charging patterns. Downstream processing of this material should be similar to that of recent processing of site fuels requiring only minor adjustments of the existing flowsheet parameters.

INTRODUCTION

H-Canyon is preparing to resume processing of off-site aluminum-clad spent nuclear fuel (SNF)[1]. The Savannah River Site (SRS) has historically received aluminum-clad fuel from research reactors and processed these fuels in H-Canyon. Currently SRS receives these fuel assemblies from off-site sources and stores them in the L-Area basin as bundles of assemblies. The upcoming SNF campaign is projected to involve ~19,500 assemblies from numerous off-site sources and is projected to require nine years to complete. The bundles of assemblies will be removed from L-Area basin, transported to H-Area for dissolution and processed to recover the uranium and discard the aluminum and fission products. The highly enriched uranium that is recovered will be blended with natural uranium to produce a low-enriched uranium (LEU) product.

H-Canyon will receive SNF in the railroad tunnel and charge the material to the ten-well insert in the 6.1D or 6.4D dissolvers. During past campaigns, this fuel type was dissolved by a mercury-catalyzed, nitric acid flowsheet, and the same technique is planned for the upcoming campaign. The dissolution will include the addition of boron or gadolinium as a nuclear poison. After dissolution, the solution will be processed through Head End and centrifuged to remove particulate matter. After Head End treatment, the uranium will be recovered and purified by solvent extraction processing (First and Second Uranium cycles) and the waste will be processed for transfer to the Tank Farm. The relatively high aluminum content of the fuels (~90 wt %) results in the downstream processing being limited by issues of aluminum solubility.

H-Canyon Engineering requested that Savannah River National Laboratory (SRNL) utilize existing literature to determine the flowsheet parameters necessary to dissolve and process these fuels safely and efficiently.[1] H-Canyon's long history of processing SRS fuels is the basis for much of the applicable literature. Since the late 1960s, H-Canyon has processed various off-site spent fuels by similar dissolution flowsheets as that used for the SRS fuels. In the 1970s, a ten-well dissolver insert[2,3] was built specifically for controlling the geometry of most off-site fuels during dissolution. Pickett[4] prepared a listing of the offsite fuels processed between 1976 and 2001 and basic parameters of the dissolution flowsheet.

The initial fuel type planned for processing is irradiated spent fuel assemblies from the University of Missouri Research Reactor (MURR). This report focuses only on that fuel, although some of the results of this investigation will be applicable to other fuel types as well. This report primarily addresses fuel dissolution because customization of the flowsheet is required to control the dissolution rate. Once the fuel dissolution is complete, most downstream process steps will be maintained within historical operating parameters for uranium-aluminum alloy fuel.

BACKGROUND

MURR Fuel Description and History:

MURR fuel originates from the University of Missouri Research Reactor Center in Columbia, Missouri. MURR began operation in the fall of 1966.[5] MURR's flux-trap type reactor has been a primary research source almost since its startup. Originally licensed to operate at 5 MW in 1966, the reactor was upgraded to 10 MW in 1974. The reactor's core contains a fuel region of a fixed geometry consisting of eight fuel assemblies having identical physical dimensions placed vertically around an annulus between two cylindrical aluminum reactor pressure vessels. Each fuel assembly is comprised of 24 circumferential plates containing ~93% enriched uranium (pre-irradiation) alloyed with aluminum (see Figures 1 and 2).[1,6] Each assembly weighs ~6250 g (containing ~5419 g aluminum and ~831 g uranium or ~13 wt % uranium). The curved parallel plates are 0.05 in. (1.27 mm) thick with a 0.08 in. (2.032 mm) spacing oriented vertically.[7] Each plate weighs from 80 to 175 g (with 21 to 49 g of uranium) and is clad with 0.015 in. (0.381 mm) of aluminum. The fuel plates are supported along

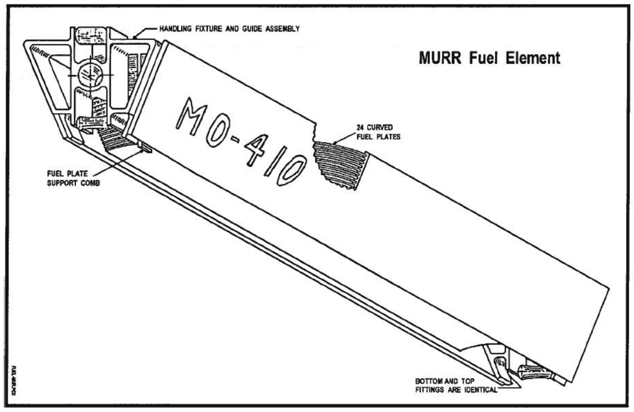

Figure 1. Three-Dimensional Sketch of MURR Fuel Assembly.

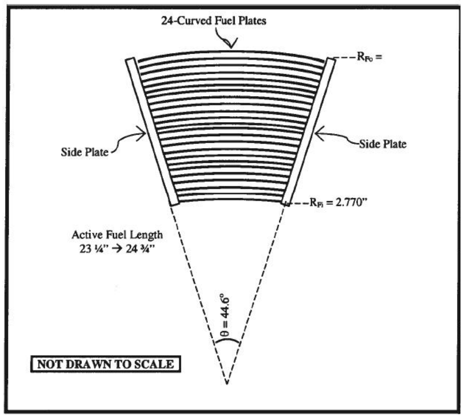

Figure 2. Top View Schematic of a MURR Fuel Assembly.

the vertical edge by slotted aluminum side plates (see Figures 1 and 2). The fuel plates are permanently fastened into the side plates. The assemblies were manufactured with a handling fixture and guide assembly at each end but much of this hardware was removed after receipt at SRS.[8] The removal of this hardware left some assemblies trimmed to 29 in. and others trimmed to 27 in. in length due to variations in the trimming method. This trimming removed the stainless-steel rollers that are not compatible with the H-Canyon dissolution process along with some excess aluminum material.

Assemblies[9,10] are typically irradiated to 20 to 25% burn-up, reducing the ^{235}U content from ~774 g to ~600 g (+/-20 g). Reports show each assembly contains approximately ~1.3 g of plutonium and probably <0.7 g ^{237}Np. Some older reports show the plutonium content at zero and 5 to 6 g of ^{237}Np.

For ease of handling after receipt and trimming at SRS, four assemblies were stacked vertically in a 5 in. outer diameter aluminum tube (0.052 in. wall thickness) generally referred to as a "L-bundle" (containing ~6.8 kg of aluminum[11]). Bundles containing the spent fuel will be removed from storage in L-Area basin and transported by railroad cask car to H-Canyon. H-Canyon will charge fuel bundles to the 6.1D or 6.4D dissolvers utilizing a ten-well insert to control the physical configuration of the material during dissolution. This insert is designed to be installed in the insert port of the dissolver in place of the rectangular insert used for dissolving bundles of site fuel. The ten-well insert[2] is a 2x5 array of 18-foot deep cylindrical wells constructed of 304L stainless steel. Each well is 5.5 in. inner diameter with perforations (1 in. holes) to permit circulation of the dissolvent. Details on the dissolver and ten-well insert configuration are included as Figures 3, 4 and 5. For efficient processing of MURR fuel it is desired to charge five to ten bundles at a time to the dissolver, but limited dissolution data on high surface area fuel may restrict the amount of fuel charged at one time due to either the hydrogen or total gas generation rates. Multiple charges of fuel to the same dissolver solution are desirable for waste management and process efficiency purposes.

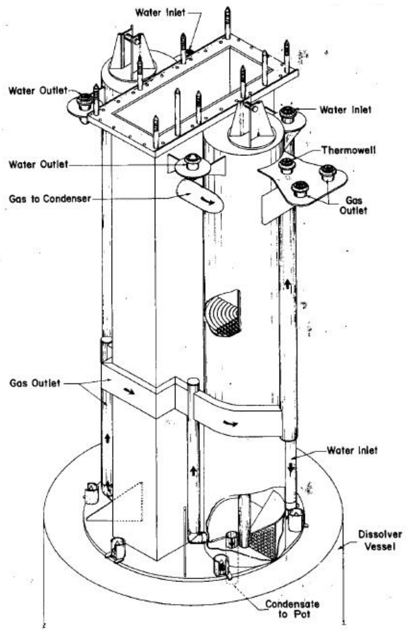

Figure 3. Sketch of Insert Port and Condenser on Top of Dissolver.

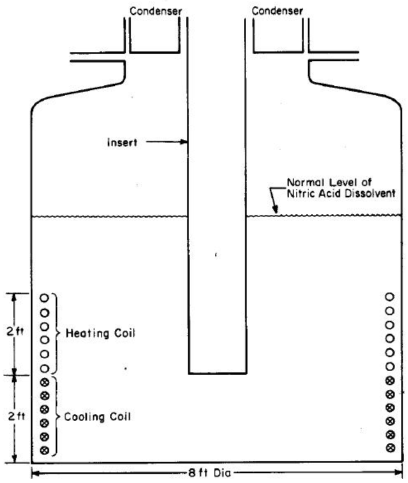

Figure 4. Sketch of Dissolver Pot Showing Fuel Insert and Coils.

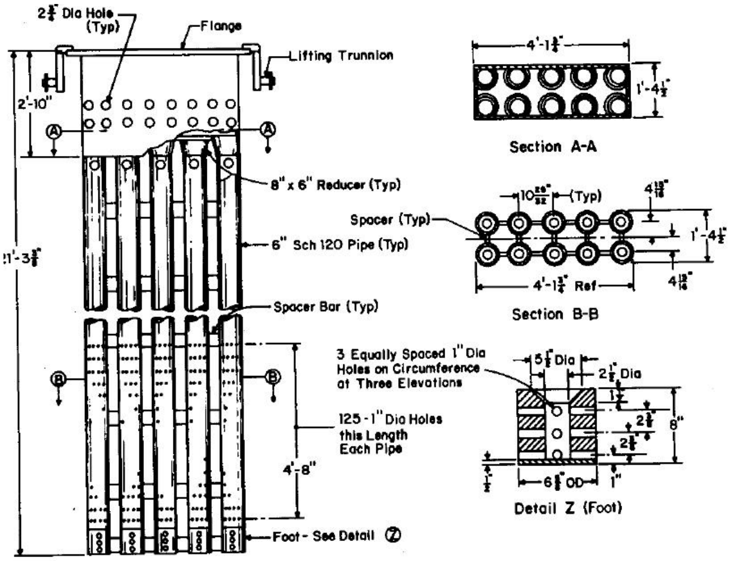

Figure 5. Details of the Ten-Well Insert.

Dissolution History:

H-Canyon has processed various aluminum-uranium fuels since the 1950s using a mercury-catalyzed nitric acid dissolution flowsheet. Starting in the mid 1960s, H-Canyon processed fuels from a number of research reactors. MURR fuel processing (initially from the original 5 MW configuration) started in 1970. Pickett[4] compiled a listing of all fuel processed in H-Canyon from 1976 to 2001 along with process conditions. Some details on fuels processed prior to 1976 were available in monthly reports.[12,13] Table 1 lists the available information from Pickett's listing and monthly reports for dissolver charges containing MURR fuel. Thirteen batches containing only MURR fuel assemblies were processed between 1970 and 1987; another four batches consisted of a mixture of fuel assemblies including some MURR assemblies. Several of the earlier batches included multiple charges of fuel to the same dissolver batch, but most of the batches consisted of a single charge of six fuel bundles dissolved in 1.7 to 2.4 M nitric acid using 0.004 to 0.007 M mercury catalyst. The use of multiple dissolver charges in the same batch was developed and used to a limited extent with several types of fuel.[14] The main limitation on multiple-charge dissolution was the reduced dissolution rate of the successive charges due to the effect of dissolved aluminum from the previous charge(s). For nuclear safety reasons, the initial charge had to be verified (typically by physical probing) to have completely dissolved (within acceptable limits) prior to the introduction of the next charge. Most MURR fuel batches appear to have been refluxed from 20 to 29 hours although several of the initial dissolutions were refluxed for less than 12 hours. Unfortunately, very little information is available that describes the steps used to control the dissolution rate of the higher surface area MURR fuel. Based on the amounts of uranium and aluminum reported, there were probably only two assemblies per bundle whereas current fuel bundles typically contain four MURR assemblies. Past processing of MURR was not optimized to allow processing for either uranium or aluminum limitations. The volume of liquid charged to the dissolver limits fuel submergence (and thus the surface area of the fuel available for dissolution) to less than two assemblies per bundle at a time.

Table 1. History of Dissolution of MURR Fuel in H-Canyon.

Date in 8.3	Run #/Tank		Fuel Type	RBOF Tubes	Aluminum kg/charge	^{235}U g	Volume L[b]	HNO_3 M[b]	Hg M	Reflux h
12/15/1987	12HD-3	6.1D	ORR/MURR/UVA	2,6,1[a]	173.89					
12/8/1987	12HD-1	6.1D	ORR/MURR	2,5[a]	138.32					
4/2/1987	3HD-11	6.1D	MURR	6	96.36					
3/22/1987	3HD-9	6.1D	MURR	6	96.36					
3/17/1985	2HD-18	6.1D	MURR	6	103.2	9420	7500	2.43	0.007	24
2/25/1985	2HD-14	6.1D	MURR	6	103.2	9420	7500	2.43	0.007	29
7/7/1981	7HD-3	6.4D	MURR	6	99.4	7122	12500	1.45		
7/1/1981	7HD-1	6.4D	MURR	6	99.4	7122	12500	1.45		
7/21/1980	7HD-4	6.4D	MURR/converter plate	3,1[a]	52[c]		13000	1.1	0.004	20
7/16/1980	7HD-2	6.4D	MURR	6	102	9420	13000	1.7	0.004	20
7/15/1980	7HD-1	6.4D	MURR	6	102	9420	13000	1.7	0.004	20
7/2/1980	6HD-12	6.4D	MURR	6	102	9420	13000	1.7	0.004	20
6/29/1980	6HD-10	6.4D	MURR	6	102	9420	13000	1.7	0.004	20
3/16/1977	3HD-9	6.4D	MkXX/MURR/ORNL	5,1,1[a,d]	150.83					
1/15/1977	1HD-5	6.4D	MURR	6	102.18	9240	6500	2.8		21
Mar-1971			MURR	9[e]		5859			0.0025	12-20
Nov-1970			MURR	7[f]		9114			0.0025	8

[a] Number of each type of fuel tube, single charge.
[b] Initial values.
[c] Monthly report states 59.4 kg Al.
[d] Two charges.
[e] Probably three charges
[f] One bundle per quadrant, two charges.

Thus the resulting generation of off-gas per bundle from future processing will be similar to that in the past when processed under similar conditions.

Dissolution Chemistry- Aluminum Clad Uranium-Aluminum Alloy Fuel:

The mercury catalyzed dissolution of aluminum in nitric acid has been studied numerous times, particularly by researchers at SRS,[15] Oak Ridge National Laboratory (ORNL),[16] and Idaho National Laboratory (INL).[17,18] An oxide coating that forms on the aluminum requires the use of a mercury catalyst to achieve sufficiently rapid dissolution rates in nitric acid. Mercuric nitrate, at concentrations ranging from 0.001 to 0.02 M, was used during previous SRS H-Canyon fuel campaigns.[19]

Aluminum and nitric acid react to form a variety of reaction products (as shown in reactions 1-10 listed below). Literature reports that all these reactions occur to some extent, as evidenced by the various gaseous reaction products found in the dissolver off-gas during dissolution. Long[20] reports that as the concentration of the reacting acid decreases, the dissolution shifts toward reactions that consume less acid. Furthermore, he states that hydrogen evolution is relatively low at greater than 1 M nitric acid and that hydrogen evolution can be appreciable under acid deficient conditions (<0.1 M) but quantitative data are not provided. Similar statements are made by other authors in the literature, but these statements appear contradictory to the observations of Caracciolo[21] during SRS pilot-scale dissolution work. Caracciolo measured hydrogen in the off-gas from the dissolution of full-scale unirradiated fuel tubes and found that the highest concentrations of hydrogen occurred during the initial phase of dissolution (when the acid was still relatively high, ~5-6M, seemingly in conflict with Long's statements). Because Caracciolo[21] measured hydrogen under realistic conditions for the mercury-catalyzed nitric acid dissolution of aluminum, one must consider the generation of hydrogen during the initial portion of the dissolution cycle when the dissolution rates are the highest as a credible safety concern.

On the other hand, dissolution of aluminum under acid deficient conditions (<0.1 M HNO_3) results in significant amounts of hydrogen generation.[16,20] Aluminum metal dissolves at a significant rate in aluminum nitrate solutions in the presence of mercury catalyst and generates hydrogen at higher concentrations than when significant nitric acid is present.[16] For this reason the amount of acid charged to each dissolver batch is matched with the amount of metal to be dissolved so that excess acid remains unconsumed at the end of the dissolution cycle. By charging appropriate amounts of metal fuel and acid to the dissolver, a nitric acid solution of uranium and aluminum can be generated that is acceptable as a solvent extraction feedstock (of ~0.5 M HNO_3 and 1.5 M $Al(NO_3)_3$) with minimal adjustment.

(1) $Al_{(s)} + 6\ HNO_3 \rightarrow Al(NO_3)_3 + 3\ NO_{2\ (g)} + 3\ H_2O$
(2) $Al_{(s)} + 4\ HNO_3 \rightarrow Al(NO_3)_3 + NO_{(g)} + 2\ H_2O$
(3) $Al_{(s)} + 3.75\ HNO_3 \rightarrow Al(NO_3)_3 + 0.375\ N_2O_{(g)} + 1.875\ H_2O$
(4) $Al_{(s)} + 3.6\ HNO_3 \rightarrow Al(NO_3)_3 + 0.3\ N_{2\ (g)} + 1.8\ H_2O$
(5) $Al_{(s)} + 3\ HNO_3 \rightarrow Al(NO_3)_3 + 1.5\ H_{2\ (g)}$

(6) $2\ NO + HNO_3 + H_2O \leftrightarrow 3\ HNO_2$
(7) $NO_{(g)} + \frac{1}{2}\ O_{2\ (g)} \leftrightarrow NO_{2\ (g)}$
(8) $3\ NO_{(g)} \leftrightarrow N_2O_{(g)} + NO_{2\ (g)}$
(9) $2\ NO_{2\ (g)} \leftrightarrow N_2O_{4\ (g)}$
(10) $NO_{(g)} + NO_{2\ (g)} \leftrightarrow N_2O_{3\ (g)}$

At nitric acid concentrations around 4 M the overall reaction stoichiometry is approximately that of reactions 11 and 12. The heat of dissolution is approximately 190 kcal/mol Al (with water as a gaseous product).[15]

(11) $Al_{(s)} + 3.75\ HNO_3 \rightarrow Al(NO_3)_3 + 0.225\ NO_{(g)} + 0.15\ N_2O_{(g)} + 0.1125\ N_{2(g)} + 1.875\ H_2O_{(g)}$

(12) $U_{(s)} + 4\ HNO_3 \leftrightarrow UO_2(NO_3)_2 + 2\ NO_{(g)} + 2\ H_2O$

Effect of Nitric Acid and Aluminum Nitrate Concentration:
Schlea[15] reports that the dissolution rate of uranium-aluminum alloy fuels is essentially a linear function of the dissociated nitric acid ("free acid") concentration. He also includes a viscosity factor to include a mass transfer hindrance which is also a function of the nitric acid and aluminum nitrate concentrations. Note that the concentration of dissociated nitric acid is a function of both nitric acid and aluminum nitrate concentrations, which makes the effect of nitric acid concentration on dissolution rate more complicated than it first appears. Since the concentrations of both nitric acid and aluminum nitrate change dramatically during the course of a dissolution cycle and both affect the effectiveness of the catalyst, the net effect on overall dissolution is significant.

Schlea correlated his laboratory dissolution data using equation 13.
(13) $r = k[Hg]\alpha[HNO_3]/\mu$
k = 1400 for unirradiated Al-16 wt % U alloy vs 280 for irradiated Al-16 wt % U alloy
α = disassociation factor for nitric acid
μ = solution viscosity

Figure 6 is a graph from Schlea's report[15] showing dissolution rates between 10 to 100 mg/min/cm^2 as a function of dissociated nitric acid concentration. Figure 7 is a graph Caracciolo's pilot-scale dissolution work[21] showing the dissolution rate dropping as the aluminum nitrate concentration increases. Figure 8 shows a comparison of Caracciolo's data to Schlea's dissolution correlation (eq. 13) for unir-

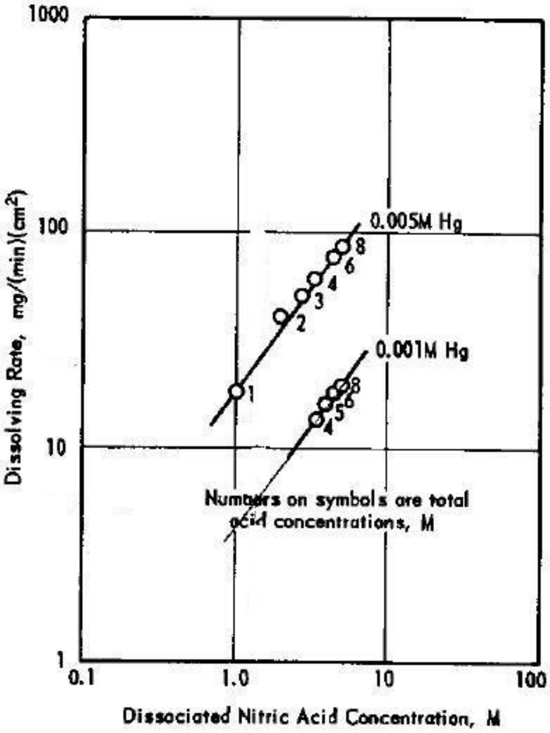

Figure 6. Effect of Nitric Acid Concentration on the Dissolution Rate of Unirradiated Aluminum - 16 wt % Uranium Alloy.

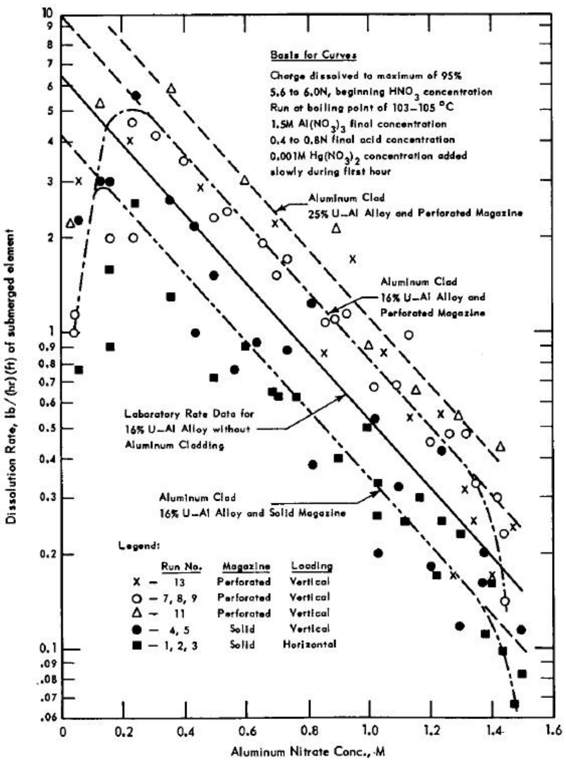

Figure 7. Effect of Aluminum Nitrate Concentration on the Dissolution Rate Characteristics of Fuel Elements (Aluminum - 16 wt % Uranium Alloy).

radiated aluminum-clad fuel. To compare these data, they were converted to consistent units and the Schlea data was calculated assuming an initial solution consisting of 5.6 M HNO_3 and 0.001 M catalyst with consumption of 3.75 moles of nitric acid for each mole of aluminum dissolved. Figures 7 and 8 show the dissolution rate at 0.3 M Al to be ~50% of the rate extrapolated to 0 M Al.

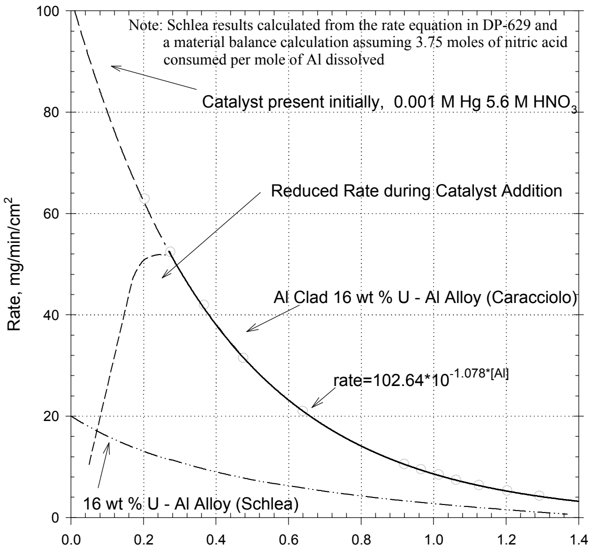

Figure 8. Effect of Aluminum Dissolution and Nitric Acid Consumption on the Dissolution Rate.

Rice[22] generally agreed with Schlea on the effect of nitric acid and aluminum concentration; however, he points out that the actual mechanism is complex and that significant changes in conditions can shift the specific reaction step that limits the overall reaction rate.

Effect of Catalyst Concentration:

The catalytic behavior of mercury involves the cyclic redox of mercury/mercuric ion along with the formation of a mercury-aluminum amalgam. The physical characteristics (i.e. extrusion process vs casting) and history of the aluminum (including radiation dose) affect the formation of the amalgam, and thus the dissolution rate.[15] Wymer[16] reported that the dissolution rate of uranium-aluminum alloy was not affected by increases in the mercuric ion concentration

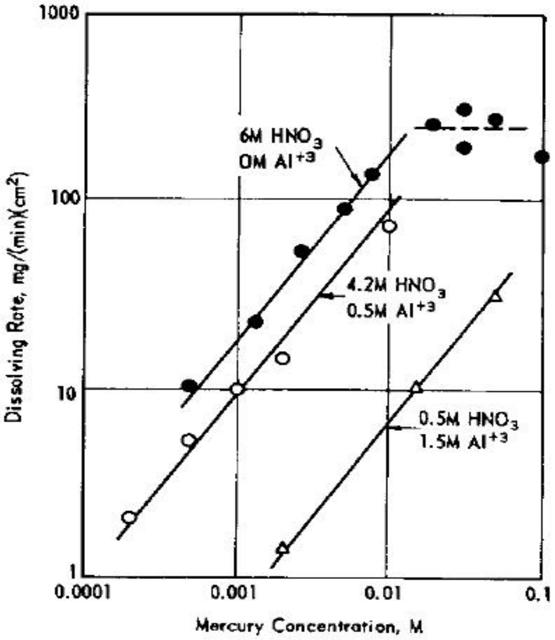

Figure 9. Effect of Mercury Concentration on the Dissolving Rate of Unirradiated Aluminum – 16 wt % Uranium Alloy.

above 0.005 M Hg. His work showed the dissolution rate was linear with respect to mercury concentration below this concentration but this threshold is likely affected by the specific alloy(s) tested. Schlea[15] also reported the dissolution rate to be linear function of mercury concentration in solutions ranging between 0 M Al/6 M HNO_3 to 1.5 M Al/0.5 M HNO_3 (see Figure 9). Schlea specifically indicated a maximum dissolution rate of ~250 mg/min/cm^2 which he attributed to the boiling characteristics at the reacting metal surfaces. At the heat flux associated with this rate, he surmised that the aluminum surface is blanketed by a film of vapor which limits the amount of dissolver solution in contact with the reacting metal surface. The effect of such a limitation explains the dissolution rate plateau observed at high concentrations of mercury. Rice[22] and Long[20] both report the dissolution rate to be less than first order with respect to mercury concentration. Rice reports (with limited data) the dissolution of pure aluminum to be zero order with respect to catalyst concentration for low nitric acid concentrations and 0.3 to 0.65 order for higher nitric acid concentrations. Long[20] reports the dissolution rate to vary as the cube root of mercury concentration below 0.005 M but cited continuous dissolution work by Boeglin[17] that is not directly comparable to other data from batch dissolution. In pilot scale tests, Caracciolo[21] reported a single comparison for aluminum-25 wt % U fuel where the dissolution rate increased ~70% when the catalyst concentration doubled from 0.001 to 0.002 M. This author recommends relying heavily on the results of Schlea and assuming that the dissolution rate is approximately linear with catalyst concentration; however, this recommendation should be used with appropriate caution as other researchers suggest that it could overstate the effect.

Perkins[23] found that catalyst requirements for decladding aluminum-clad thoria targets were inversely proportional to the total nitrate concentration. He noted process spills that had occurred in H-Canyon due to the unexpected high reaction rates when the catalyst concentration was increased at the same time that the nitric acid concentration was decreased. He concluded the total nitrate concentration caused more rapid oxidation of "free" (elemental) mercury at higher nitrate concentrations, decreasing the amount of mercury available for forming an amalgam on the surface of the aluminum, which subsequently limits the reaction rate.

Effect of Rate of Catalyst Addition:
A detailed description of historical catalyst addition protocols during H-Canyon plant operations is not available. In the pilot scale work by Caracciolo,[21] several different methods were used, but generally catalyst solution was added over ~40 min to achieve a concentration of 0.001 or 0.002 M mercury. In a 1970 monthly report, observation was made that during the processing of High Flux Isotope Reactor (HFIR) fuel the off-gas iodine reactor exceeded temperature limits.[12] The cause of this event was traced to the high rate of catalyst addition and a suspected surge of NO generation from the resulting high dissolution rate. Based on this event, the catalyst addition rate was modified to extend the catalyst addition time to avoid reoccurrence. In the mid-1980s, Gray[24] suggested a reduction in the catalyst concentration (from 0.02 M to 0.002 M Hg) as well as a change in the addition method. Gray proposed that a small amount of mercury catalyst be added prior to the start of the dissolution

heating cycle and the dissolver be heated with steam to a temperature of ~50-70 °C. At that point, he found (in laboratory tests) that the heat of reaction from the dissolution was sufficient to raise the dissolver temperature to boiling. After the reaction subsided, the reaction rate would decrease sufficiently requiring steam heating to maintain the dissolver temperature until the completion of the dissolution cycle. He believed that this approach would improve control of the dissolution reaction and significantly reduce the potential for over-pressurization of the dissolver. Both of these recommendations were tested under the control of a Test Authorization in 1985.[25] As a result of that testing, H-Canyon reduced the amount of catalyst routinely used from 0.02 M to 0.002 M Hg, but decided to retain the existing method of catalyst addition over time after the dissolver solution was heated to boiling temperatures. Current equipment for addition of catalyst probably allows for better control of the addition rate (< 10 lb solution/min) with the use of a control valve (as compared to dissolutions performed in the 1970s). Procedural controls on dissolver vacuum, pressure drop in the condenser and foam level were used to monitor the dissolution rate and the associated off-gas rate. The minimum dissolver purge-gas flowrate limits the potential hydrogen concentration in the off-gas system based on estimated off-gas rates. This system includes an interlock to shut down the dissolver steam in the event of low purge-gas flow but does not currently have the capability for off-gas flowrate measurement.

Effect of Surface Area- Geometry:

Implicit in the discussion of mercury-catalyzed nitric acid aluminum fuel dissolution is the assumption that the dissolution rate is proportional to the exposed surface area. However, under conditions that produce high reaction rates, the portion of the surface that is exposed to solution depends on complex three-phase turbulent heat and mass transfer phenomena. The replenishment of the acid and mercury at the reacting surface must occur at the same time as the off-gases are removed and the heat of dissolution dissipated. An additional gas barrier is created due to the local vaporization of water (since the bulk solution is already at or near the boiling point). The mercury-catalyzed dissolution of aluminum metal creates a gas blanket near vertical metal surfaces that limits the mass transfer of fresh acid reactant to the surface thus limiting the dissolution rate. This phenomenon was observed by Wymer,[16] Schlea[15] and others. Caracciolo[21] also found this phenomenon limited the effective surface area of SRS tubular fuel to the outside surface of the fuel tubes during dissolution, and concluded that the outside surface area of the outer tube controlled the dissolution rate. The configuration of the MURR fuel in the bundle is assumed to limit dissolution rate in a similar manner during the initial period of the dissolution cycle until the side plates of the fuel either dissolve or separate from the fuel plates.

Rice[22] investigated the dissolution of aluminum in nitric acid for geometries where the surface area/volume ratio (S/V, cm^2/cm^3) varied from 12 (shot, slab) to 200 (wire) to 3845 (powder) cm^2/cm^3. For the materials tested, he found the conventional dissolution rate (mg Al/min/cm^2) declined appreciably as the S/V ratio increased (~87 mg Al/min/cm^2 for shot/slab, 16 mg Al/min/cm^2 for 0.5-mm wire and 0.6 mg Al/min/cm^2 for powder). Rice suggests that the overall rate was controlled by a "solid-state" phenomena unrelated to the liquid-solid interface and describes the primary means by which mercury promotes aluminum dissolution is by making aluminum available to nitric acid by converting it to a more reactive form. A comparison between the S/V ratio of MURR fuel and those materials that Rice tested shows MURR at the low end of the scale (~15 cm^2/cm^3). Rice measured dissolution rates comparable to those reported by Schlea[15] for materials with similar S/V ratios. Compared to the SRS fuels that Caracciolo tested, bundled MURR fuel has a significantly higher total surface area per unit length (~500 cm^2/cm for MURR vs ~45 cm^2/cm for Caracciolo).

While consideration of the Rice paper indicates that the dissolution rate would not scale proportionally to the S/V ratio for very high values, MURR fuel is actually on the low end of the scale for the materials that Rice tested, and thus the initial dissolution rate may not be affected by the phenomena that Rice observed. However the solution mass transfer limitations reported by Caracciolo[21] should be expected to be a significant factor in limiting the peak dissolution rate for the MURR fuel.

Effect of Radiation Dose:
Each of the MURR fuel assemblies has a documented radiation history. Typically, eight assemblies were irradiated for 120 days at 1200 MWD (megawatt-days) or up to 150 MWD per assembly.[7] In practice, individual assemblies were cycled in and out of the core a number of times until they were discharged with burn-up typically around 130 to 140 MWD per assembly. For bundles of MURR fuel, the bundle itself is anticipated to behave as unirradiated aluminum (alloy 6063-T6 or 6061-T6). The actual MURR assembly is composed of parts fabricated from various alloys of aluminum and a uranium aluminide (mostly UAl_3) meat.[5] Stainless steel hardware was removed by L-Area personnel, along with some of the aluminum from the end fittings; however, the remaining side plates of the MURR fuel assembly are composed of irradiated aluminum (alloy 6061-T6 or T651). Other minor parts could include the aluminum end fittings, comb and comb pin (alloys 6061-T6, T651, or 4043). The actual fuel plates are composed of a uranium aluminide fuel meat clad in aluminum (believed to be the 6061 alloy).[26]

Much of the available experimental results regarding aluminum fuel dissolution address unirradiated aluminum or aluminum-uranium alloys. Limited data exist indicating a reduction in the dissolution rate due to increasing radiation dose. Specific information on the dissolution of uranium aluminide fuel is not available but this same fuel configuration has been successfully dissolved in the past in H-Canyon.

Schlea[15] observed the dissolution rate of irradiated fuel (~25 % burn-up, 200 day cooled) was about 20% of the rate of unirradiated alloy (i.e. factor of five lower). Hyder[39] cites other data attributed to Schlea showing irradiation effects to be somewhat less (i.e. factor of three lower) (see Figure 10) but there is no indication on the amount of burn-up. Vague statements in SRS monthly reports suggest that the catalyst concentration was probably adjusted to increase the dissolution rate on fuel charges expected to have slower dissolution rates due to higher burn-up.[27,28,29] The description of the effect indicates radiation exposure causes a change in the hardness of the materials which reduces the dissolution rate. Since variation on dissolution rate is observed for a number of factors tied to metallurgical history (e.g.., fabrication process (i.e. extruded vs cast), alloy type, and tempering) it is not surprising the radiation dose also affects dissolution rate. It might be expected that radiation damage would enhance the dissolution rate due to imperfections created in the structure but at the levels normally encountered any such effect appears to be overwhelmed by the hardening effect. Specific information on radiation dose effects on the dissolution of uranium aluminide fuel is not available; however, entries in the monthly reports during the mid-1980s show this fuel configuration was successfully dissolved in H-Canyon without any indication of difficulty.

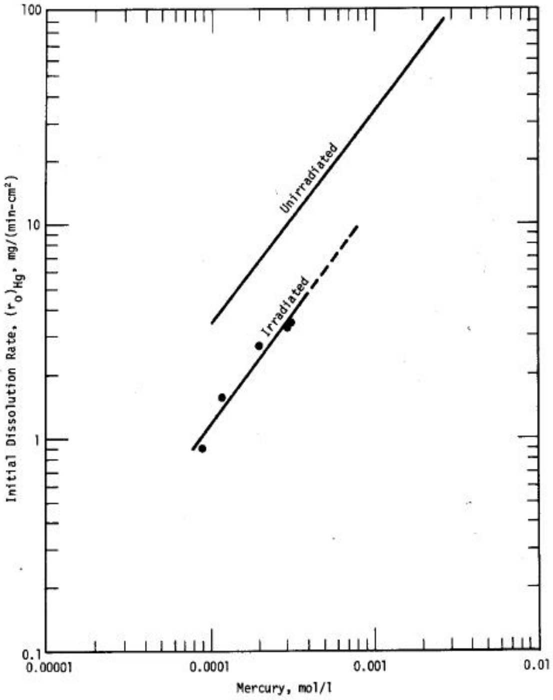

Figure 10. Effect of Irradiation on Initial Dissolving Rate of Mark VI Tube in 6 M HNO_3.

Hydrogen LFL:

Hydrogen forms flammable mixtures at ambient temperatures and pressures with oxygen, air and the gaseous oxides of nitrogen.[30] The lower flammability limit (LFL) for hydrogen (25 °C, 1 atm) is reported to be 4.0 vol % in air or oxygen, 3 vol % in N_2O and 6.6 vol % in NO.[30] In the presence of oxygen or air, nitric oxide (NO) reacts with oxygen to form nitrogen dioxide (NO_2). (This reaction appears to have little impact on the LFL but complicates the measurement of the composition.) The literature shows that in mixtures of these gases the presence of nitric oxide increases the nonflammable region whereas nitrous oxide (N_2O) increases the flammable region. In the absence of nitrous oxide the LFL of certain H_2-NO-air mixtures has been measured as high as ~17.3 vol % (see Figures 11 and 12a), but when such mixtures contain a ratio of NO/N_2O equal to 2.57 the highest LFL measured is ~6.83 vol % (see Figure 12b).[31] Le Chatelier's mixture rule assumes that mixtures of gases at the limit of flammability in the common component, when combined in any proportion, will form a new mixture at the flammable limit for that composition. It is convenient to consider LFL data from this system in terms of deviations from this ideal behavior. Large positive deviations (~300%) from ideal behavior were observed to occur in the plane (see Figure 12a) representing the H_2-NO-air (no N_2O) indicating a smaller range of flammability. Over the region of data below an NO/N_2O ratio equal to 2.57 the deviations from the ideal mixing rule approach 50% (which is still a significant increase). The lack of data for higher NO/N_2O volume ratios causes difficulty in determining an appropriate method of modeling the LFL due to the significant changes that occur as the NO/ N_2O ratio approaches infinity. The uncertainty in LFL estimates in this region is significantly higher.

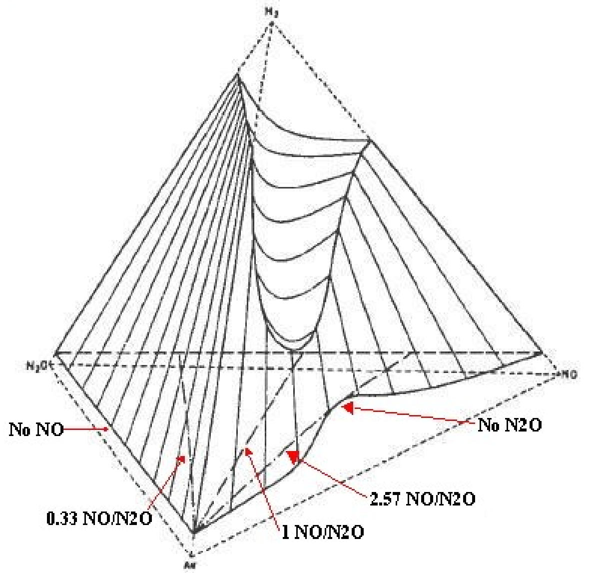

Figure 11. Flammability of the Hydrogen-Nitric oxide-Nitrous oxide-Air System at 28 °C.

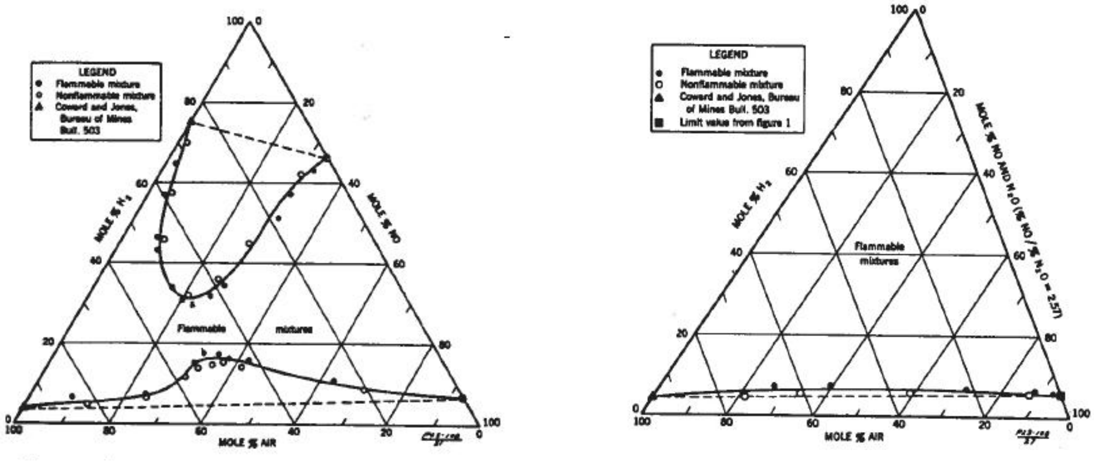

Figure 12. Limits of Flammability: a) The System H_2-NO-Air at 28 °C and 1 atm Pressure, b) The System H_2-NO-N_2O-Air at 28 °C and 1 atm Pressure (NO/N_2O =2.57).

A calculation by Weitz,[32] uses an off-gas specific LFL that takes credit for the increase in the LFL as oxides of nitrogen replace air in a mixture. A mathematical model (using a linear interpolation method) was used to obtain LFL values at the compositions of interest. As part of the current effort, it was recognized that the existing model was not appropriate for use for MURR fuel dissolution. An alternative approach using Scott's data[31] at NO/N_2O equal to 2.57 will be used. Because of the lack of understanding of the effect of small concentrations of N_2O on the LFL of this system, the lack of LFL data in the region above an NO/N_2O ratio of 2.57 limits the accuracy of predictions in this region but the use of the NO/N_2O equal to 2.57 data bounds the LFL value since higher ratios involve lower concentrations of N_2O and thereby increase the LFL value. As will be discussed later in this report, this region is of interest for the dissolution of aluminum-clad fuel and the generation of additional LFL data might show that a higher value for the LFL (with an increased region of safe operation) is appropriate.

Hydrogen Evolution:
The basis used for hydrogen flammability control for recent site fuels is based on calculations by Weitz.[32,33] This calculation cites the available literature on hydrogen generation from mercury catalyzed dissolution of aluminum-alloy fuel in nitric acid. An important reference for these calculations is the pilot-scale work of Caracciolo[21] which shows that potentially flammable concentrations of hydrogen are produced during the initial 2 to 3 hours of the dissolution cycle (Figure 13) and shows that the NO/N_2O ratio varied from 2.75 to 5.4 over the course of the dissolution. Weitz concluded that during the initial four hours of dissolution a bounding hydrogen off-gas of 7 mol % (on an air, water and NO_2 free basis) was appropriate based on data from Caracciolo and other sources. He calculated peak off-gas rates for site fuels based on the Caracciolo's data which were scaled by the exposed surface area of the fuel. Ultimately, Weitz used these combined calculations to determine purge rate required to dilute the dissolution off-gas to below 60 vol % of the calculated off-gas specific LFL. Weitz's methodology was generally followed in the calculations included in the appendix of this report utilizing the LFL data of Scott[31] as previously discussed.

Off-gas Composition:
Weitz[32] looked at literature values for the off-gas composition from the dissolution of aluminum because that composition is needed to calculate an off-gas specific LFL. Analytical determination of the nitrogen dioxide and nitrogen in the off-gas is difficult and dilution with air further complicates the interpretation of those results. Much of the nitrogen dioxide is disdissolved in the condensate and is not found in the downstream samples, and. although nitrogen is reportedly produced, the actual yield of nitrogen is not typically reported due to the contamination with air. Weitz selected an assumed dissolution off-gas composition of 7.0 vol % H_2, 71.38 vol % NO and 21.62 vol % N_2O on an air, water and nitrogen dioxide-free basis. He essentially considered nitrogen, nitrogen dioxide and water to act as diluents for the purposes of LFL estimation. It must be recognized that the NO/N_2O ratio has some significance on the LFL. This ratio does

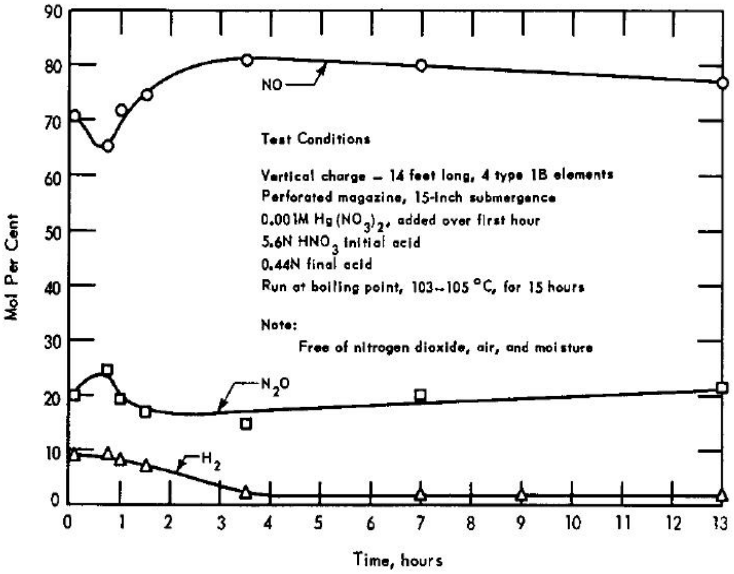

Figure 13. Off-gas Concentrations Observed during the Dissolution of Aluminum Clad Fuel.

not remain constant over the course of a dissolution cycle. The NO/N_2O ratio for the assumed composition is 3.3 but inspection of data in Figure 13 shows that this ratio varied from 2.75 to 5.4 over time and was the lowest in the initial hour when the hydrogen concentration was highest. Lower ratios imply lower composite LFL values so the use of Scott's data[31] at an NO/N_2O ratio of 2.57 provides bounding estimates for the LFL for the current system.

Aluminum Solubility:

Aluminum nitrate has a modest solubility in nitric acid solutions that varies with the nitric acid concentration and temperature (see Figure 14). Due to the large amount of aluminum involved with processing aluminum-clad fuels, aluminum nitrate solubility limits the amount of fuel that can be dissolved in a single dissolver batch without forming solids. Aluminum nitrate solubility also limits the downstream concentration of the aluminum-bearing solutions by evaporation. Aluminum solubility has historically been factored into the size of the fuel charge to the dissolver batch to avoid solubility issues and provide a feedstock to the downstream solvent extraction process that was typically 1-2 M aluminum nitrate and 0.5 M nitric acid.[34] Table 2 shows the effect of the number of bundles charged on the final aluminum and ^{235}U concentrations for 7500 and 13000 L dissolver batches. A minimum limit of 0.3 M nitric acid concentration was observed to avoid the precipitation of aluminum, uranium or plutonium as well as to limit the evolution of hydrogen during dissolution.[35]

Nuclear Poison:

Boron (added as boric acid) was used as a nuclear poison during dissolution of four batches of Sterling Forest Oxide fuel (SFO) and one batch of a mixture of SFO and WPI/OSU fuel in H-Canyon dissolvers in the 1990s. The resulting solutions of SFO were found to contain solids composed of aluminum and boron.[36,37] The mixed-fuel solution did not contain solids. Pickett analyzed the solutions and found that both alu-

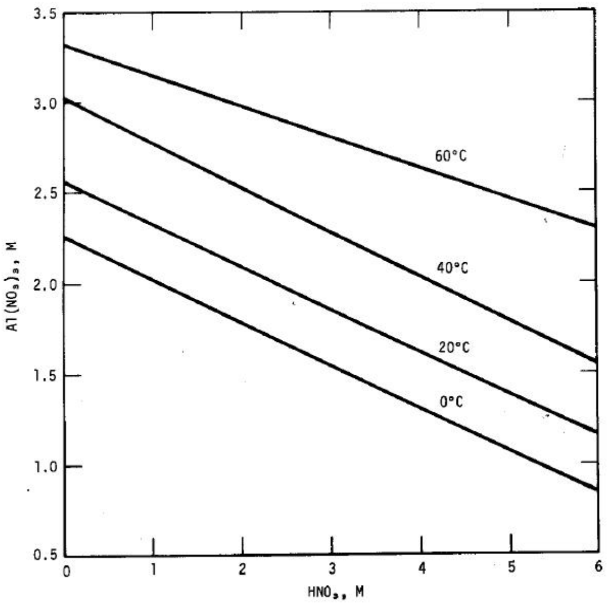

Figure 14. Solubility of Aluminum Nitrate in Nitric Acid Solutions as a Function of Temperature

Table 2. Effect of the Number of Bundles Charged on the Aluminum and Uranium Concentrations.

Vol L	Bundles	Al kg [a]	U kg	Al M	^{235}U g/L	^{235}U g/L [b]	HNO_3 M [c]
7500	1	28.5	3.3	0.14	0.41	0.33	1.04
7500	2	56.9	6.6	0.28	0.82	0.66	1.57
7500	3	85.4	10.0	0.42	1.24	0.99	2.11
7500	4	114	13.3	0.56	1.65	1.32	2.64
7500	5	142	16.6	0.70	2.06	1.65	3.18
7500	8	228	26.6	1.13	3.30	2.64	4.78
7500	9	256	29.9	1.27	3.71	2.97	5.32
7500	10	285	33.2	1.41	4.12	3.30	5.85
13000	1	28.5	3.3	0.08	0.24	0.19	0.81
13000	2	56.9	6.6	0.16	0.48	0.38	1.12
13000	3	85.4	10.0	0.24	0.71	0.57	1.43
13000	4	114	13.3	0.32	0.95	0.76	1.74
13000	5	142	16.6	0.41	1.19	0.95	2.04
13000	7	199	23.3	0.57	1.66	1.33	2.66
13000	9	256	29.9	0.73	2.14	1.71	3.28
13000	10	285	33.2	0.81	2.38	1.90	3.59
13000	11	313	36.6	0.89	2.62	2.09	3.90
13000	12	342	39.9	0.97	2.85	2.28	4.21
13000	13	370	43.2	1.06	3.09	2.47	4.51
13000	14	399	46.5	1.14	3.33	2.66	4.82
13000	15	427	49.9	1.22	3.57	2.85	5.13
13000	16	456	53.2	1.30	3.80	3.04	5.44

[a] Assumes 6.8 kg Al/bundle + 5.418 kg Al/assembly, 4 assemblies/bundle.

[b] Post irradiation values assuming 20% burn-up of ^{235}U.

[c] Initial acid: 0.5 M excess acid, 3.75 moles of acid consumed per mole of Al, 4 moles of acid consumed per mole of U.

minum and boron to be within their solubility ranges for the individual binary systems (of aluminum nitrate–nitric acid and boric acid-nitric acid). He found that the solution of 5 g B/L (as boric acid), 1.5 M Al and 2 M HNO_3 to form solids. Since the solubility limit for boric acid with aluminum was exceeded in the SFO solutions (5 g B/L), but not in the mixed-fuel solution (2.5 g B/L) he concluded that the solubility limit was in that concentration range. Herman[38] performed experiments in which the nitric acid and Al concentrations were varied over the expected concentration range of solutions during dissolution with either boron (as boric acid) or gadolinium at 2 g/L. Those tests showed that boric acid solids precipitated from 3 g B/L solution across the range of aluminum and nitric acid concentrations after 12 days. No solids were observed after eight weeks of testing for similar samples with 2 g/L gadolinium or boron (as boric acid).

Multiple Charge Dissolution:
Normal practice in H Canyon was to charge the dissolver batch with sufficient acid and fuel to result in dissolver product with acceptable fissile concentration and ~1.5 M aluminum nitrate and 0.5 M nitric acid concentrations. In some cases, sufficient fuel could not be added in a single charge to attain those conditions and additional charges were introduced to a single dissolver batch.[14] There is a possibility that with multiple charges, that excessive reactivity (off-gas) might be encountered in a second charge if the initial fuel charge were too small to put sufficient aluminum into solution to limit the reaction rate. The full concentration of catalyst is available as the dissolver is heated for the second charge. This risk will be reduced if the initial charge contains sufficient aluminum to make the dissolver at least 0.3 M aluminum (which should limit the peak rate to the peak rate in the initial charge (see Figures 7 and 8). Five fuel bundles dissolved into 13000L results in a 0.41 M Al solution (see Table 2) which reduces the dissolution rate an additional 30% (Figure 8). Dissolution of the same quantity of fuel into a larger volume of solution will provide less reduction in dissolution rate and will limit the second charge to a smaller number of bundles.

Idealized Dissolution Model:
Fuel and nitric acid solution are initially added to the dissolver vessel. Nitric acid solution is heated to boiling and after the initial reaction subsides, a 4.7 wt % mercuric nitrate and 47.7 wt % nitric acid solution is added at a rate that controls the dissolution rate and maintains (along with the vacuum capability of the off-gas system) the dissolver at a pressure below atmospheric.[39]. During this period of the dissolution cycle, the heat of dissolution may be sufficient to keep the dissolver at temperature without additional steam heat. The initial mercury-catalyzed dissolution of aluminum is vigorous and is accompanied by rapid off-gas rate and foaming. As the dissolution proceeds, the nitric acid concentration decreases and the aluminum nitrate concentration increases. These concentration changes tend to suppress the dissolution rate (as well as the off-gas rate and foaming).

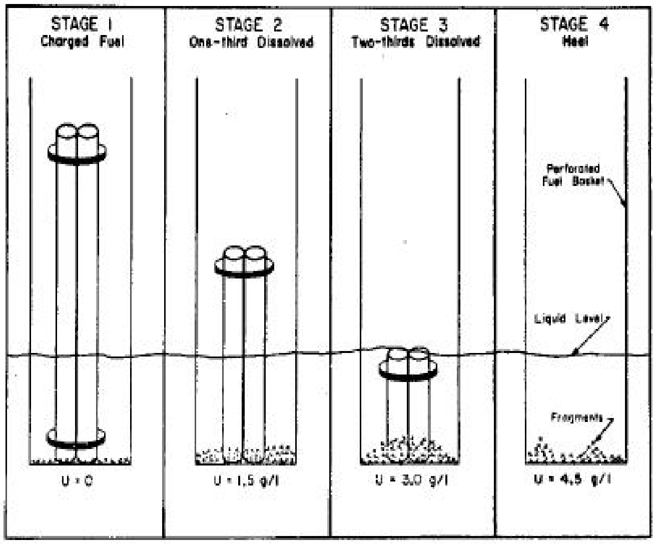

Figure 15. Idealized Dissolving Process.

Initially the nitric acid primarily attacks the outer surface of the bundle, which is quickly consumed (estimated at 10 min at a rate of 35 mg/min/cm^2) allowing an additional section of the bundle to slide into the solution until it rests on the vertically stacked fuel assemblies. As the nitric acid completes the dissolution of the submerged portion of the bundles, sufficient acid is transferred to attack the outer surfaces of the submerged assemblies. First the submerged outer portions of aluminum side plates and outer cladding surfaces dissolve until the internal portions of the fuel assembly are exposed. As the submerged portion of the fuel assemblies dissolve, the assemblies become weak and eventually collapse, allowing the non-submerged portion (both the bundle and upper fuel assemblies) to slide into the nitric acid solution (exposing additional surface area) until all the fuel is submerged. The fuel insert is designed to physically contain most un-dissolved fuel fragments and plates until they are dissolved, although the 1-in. holes in the sides of the insert tubes could allow small fragments to escape from the insert. Studies with various site fuels found that tubular fuels retained sufficient structure such that collapse did not occur until ~89 % of the submerged fuel was dissolved.[40,41] MURR fuel, stacked as individual 27 to 29 inch long assemblies, will probably collapse somewhat earlier and as the end plates are consumed the individual fuel plates will be released and may move to allow the assembly above to partially slide down the insert tube. Figure 15 is an illustration of this process with tubular fuel.

At the end of the predetermined boiling period (probably 24 to 72 hours) the dissolver is cooled to less than 60 °C and dissolver insert is probed mechanically to measure the height of the metal heel in the insert. Historically a maximum fragment height limit was established by nuclear safety studies that limited the amount of fragments allowed in the well for the next charge.

Downstream Processing

Head End Operation:

During normal operation with site fuel, the dissolver solution is sent to the Head End process for clarification via gelatin addition and centrifugation. The MURR spent fuel is fabricated with 6000 series aluminum alloy as is the case for SRS fuel. The gelatin strike would be expected to have a limited capacity for silicon (the principal impurity targeted for removal), but since MURR fuel should have same type and similar concentrations of impurities as SRS fuels this operation should be controlled within the existing parameters. The permanganate strike has historically been performed to remove zirconium and niobium fission products from shorter-cooled fuels. The permanganate strike has not been performed recently as no short-cooled fuels have been processed since the SRS reactors were deactivated but if zirconium or niobium fission products are observed to cause dose issues then it may be desirable to reinstitute this step in the future. MURR fuel assemblies are expected to be sufficiently cooled that a permanganate strike should not be necessary.

Solvent Extraction:

During normal HM solvent extraction operation the dissolver solution is adjusted to provide concentrations of uranium, aluminum nitrate and nitric acid within the existing limits of the Double Contingency Analysis (DCA) technical standard prior to feeding to the process. Historically, offsite fuel was co-processed with site fuel to allow dilution of the offsite fuel aluminum (offsite fuels generally have a higher aluminum to uranium ratio). During the upcoming campaign, offsite fuels will not be co-processed with other fuels containing higher uranium concentrations; therefore, the dissolution product from the upcoming campaign will have the same aluminum concentrations used in past operation, but will tend to have a lower uranium-aluminum ratio. The normal solvent extraction flowsheet can be used for the offsite fuels so long as the aluminum and acid concentrations are within the existing DCA and process limits. Gadolinium used as a nuclear poison during dissolution should be removed with a DF similar to those observed for other rare earth ions already present in irradiated fuel solutions. Due to the concentration of gadolinium nitrate used and the specification for blended fuel product, the DF for gadolinium must be $>10^6$ which should be feasible in the process. Hudlow[42] reported that acceptable product purity was been demonstrated in recent campaigns using both gadolinium nitrate and boric acid. Gadolinium nitrate was used during the EU-Pu campaign and boric acid is being used in the U-Mo campaign. The concentrations of gadolinium and boron used during these campaigns are significantly higher than the expected concentrations to be used during the MURR processing, and no issues with product purity due to inadequate DF in the solvent extraction cycles have been reported. It is expected that either gadolinium nitrate or boric acid will be removed to acceptable levels without changes to the solvent extraction process. However, due to the consequences of producing uranium that is out of specification on either of these poisons, it is recommended to perform analyses during the initial operations to confirm that adequate DF is obtained by the process.

Once operations have started, consideration could be given to reducing the solvent flow rate (1AX) relative to the feed flow rate (1AF) within existing DCA limits due to the lower uranium concentration. Changes in the 1AX and 1AF flowrates would also require corresponding changes in other cold feed streams to ensure compliance with the existing DCA limits as well. Changes beyond the existing limits should be considered a process change and should only be performed after appropriate process modeling and review by SRNL.

DISCUSSION

Required Purge Rate as a Function of Off-gas Rate:

H-Canyon has historically operated this process by establishing a minimum purge rate for dilution of the off-gas from the dissolution process. Because of the iodine reactor in the off-gas stream that is heated to 200 °C, the basis of minimum purge rate is set at 60% of the LFL at 200 °C. Temperature attenuation of the LFL from 28 to 200 °C is performed using a formula taken from the literature and described in a report by Dyer.[43] Various temperature coefficients are reported in the literature but the value of 0.0011 for hydrogen in air[44,45] appears to be the most appropriate for the assumed gas mixture. Table 3 shows the calculated dilution effect that a 40 scfm purge has on the assumed off-gas composition at various peak off-gas rates. The LFL is estimated using the NO/N_2O ratio =2.57 data from Scott[31] (numerical values for curve from Scott's data included as Table 9 in the Appendix). These values for the LFL are assumed to be applicable anywhere in the region of NO/N_2O ratio of 2 to 5. Keeping the peak off-gas flowrate below 34.37 scfm will maintain conditions in the iodine reactor below 60% of the LFL.

Table 3. Effect of Purge Rate Dilution on Off-Gas Composition (40 scfm minimum purge rate).

Peak Off-gas Rate scfm	H_2 scfm	NO scfm	N_2O scfm	H_2 Diluted	NO Diluted	N_2O Diluted	Air Diluted	LFL 28 °C	60% LFL 200 °C	LFL Margin
20	1.4	14.3	4.3	2.3%	23.8%	7.2%	66.7%	6.20%	3.0%	0.7%
30	2.1	21.4	6.5	3.0%	30.6%	9.3%	57.1%	6.58%	3.2%	0.2%
34.37	2.4	24.5	7.4	3.2%	33.0%	10.0%	53.8%	6.65%	3.2%	0.0001%
40	2.8	28.6	8.6	3.5%	35.7%	10.8%	50.0%	6.70%	3.3%	-0.2%
50	3.5	35.7	10.8	3.9%	39.7%	12.0%	44.4%	6.83%	3.3%	-0.6%
60	4.2	42.8	13.0	4.2%	42.8%	13.0%	40.0%	6.80%	3.3%	-0.9%
70	4.9	50.0	15.1	4.5%	45.4%	13.8%	36.4%	6.76%	3.3%	-1.2%
80	5.6	57.1	17.3	4.7%	47.6%	14.4%	33.3%	6.71%	3.3%	-1.4%
90	6.3	64.2	19.5	4.8%	49.4%	15.0%	30.8%	6.67%	3.2%	-1.6%
100	7.0	71.4	21.6	5.0%	51.0%	15.4%	28.6%	6.63%	3.2%	-1.8%
130	9.1	92.8	28.1	5.4%	54.6%	16.5%	23.5%	6.53%	3.2%	-2.2%
150	10.5	107.1	32.4	5.5%	56.4%	17.1%	21.1%	6.44%	3.1%	-2.4%
200	14.0	142.8	43.2	5.8%	59.5%	18.0%	16.7%	6.25%	3.0%	-2.8%

Note: Off-gas assumed to be generated at 7.0 % H_2, 71.4% NO, and 21.6% N_2O on an air and water free basis (NO/N_2O=3.3).
LFL conservatively estimated from NO/N_2O=2.57 data. Actual value is likely a larger value.
Temperature correction of LFL calculated as LFL corrected = LFL* (1-0.0011* (28- t)), t = °C.

Determination of Peak Off-gas Rate:

Literature[21] indicates that the formation of gas between closely space parallel surfaces limits mass transfer of fresh nitric acid and catalyst to the surfaces of the fuel plates and thus restricts the reaction to the outer, more accessible, surfaces. These mass transfer limitations for MURR fuels (which has vertical parallel plates spaced ~2 mm apart) are hypothesized to be similar to those observed by Caracciolo[21] for concentric fuel tubes (~9.7 mm apart).. If so, then the dissolution rate for the MURR fuel may also empirically scale with the outer area of the side plates and the largest and smallest fuel plates (see Figure 2), as observed in other fuels. Schlea[15] noticed an extreme version of similar phenomena when he observed a limit on the dissolution rate of 250 mg/min/cm^2 attributed to the ability to transfer heat from the fuel surface into the boiling dissolver solution. In the confined spaces between fuel tubes or plates, the mass transfer limitations that hinder the introduction of fresh reactants may severely limit the reaction at those inner surfaces. After the bundle and end plates are dissolved the fuel assembly will lose its tight configuration and allow reactants better access to the inner surfaces of the fuel. The aluminum that is dissolved prior to this point will then suppress the dissolution rate.

H-Canyon repeatedly processed MURR fuel but only minimal process details are available (see Table 1). For most batches, a single charge of six bundles (probably with two assemblies per bundle or 12 assemblies per dissolver batch) was charged to 1.1 to 2.43 M nitric acid. Sufficient acid was used to produce a 0.5 M nitric acid solution after dissolution. Details on the catalyst addition in the past H-Canyon MURR campaigns are limited, but it is assumed that the mercuric nitrate was added over a period of time after the solution had heated to a boil as was the standard practice at that time[24,25]. Mercuric ion concentrations in the 0.004 to 0.007 M range were used to dissolve the MURR fuel typically in less than 24 hours. In March 1985, at the same time that H-Canyon was testing dissolution of site fuels (MK-16B and MK-22) with reduced mercury concentrations (from 0.020 M down to 0.002 M), two batches of MURR fuel were processed at 0.007 M mercury.[25,47] Fuel submergence (which limits the exposed surface area) is determined by solution volume and the configuration of the insert in the dissolver. The insert and dissolver configuration are essentially unchanged from the mid 1980s. Note that a standard fuel submergence of 54 in. cannot completely submerge the second MURR assembly in a bundle as two assemblies end-to-end are at least 54-58 in. long. For conservativeness in estimating maximum off-gas rates, a reduced submergence of 47 in. is assumed for the past MURR dissolutions based on the reported dissolver volume and discussions with plant personnel.[46] Past experience with the dissolution of a single charge of six bundles (submerging at least the equivalent of 10.5 full assemblies) indicates that it took 24 hours to complete the dissolution (with 0.007 M catalyst).[47] The vacuum to the dissolvers was provided by a jet that had a capacity limitation of ~220 scfm[48] (see Figure 16) providing a bounding total flow from the dissolvers. In 1985, the control requirement was a purge of > 27 scfm to maintain the hydrogen off-gas at less than 4 vol %.[49,50] (The current hydrogen controls are more complex and a higher purge rate is re-

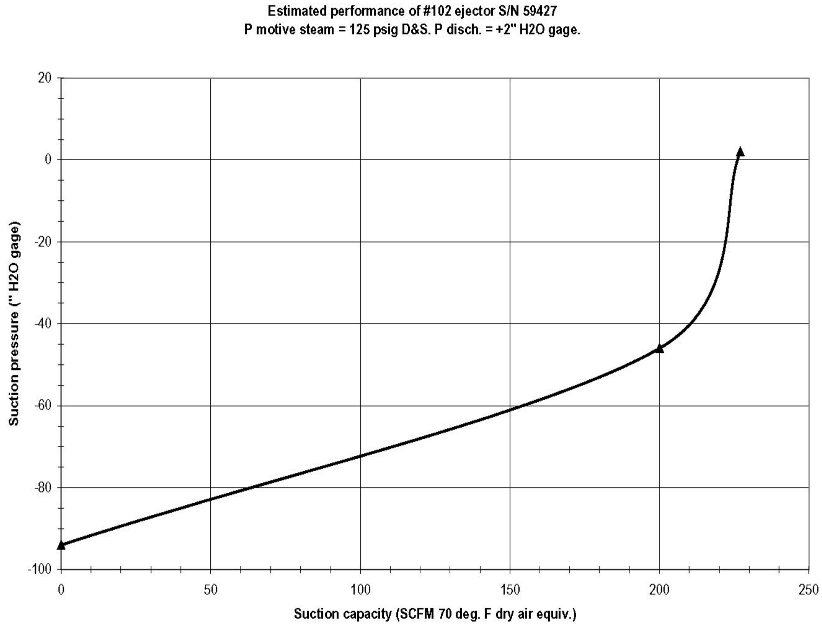

Figure 16. Capacity of 200 scfm Dissolver Jet.

quired.) The actual operating purge rate was thought to be 1.5 times the limit or ~40 scfm. There is no indication in the monthly reports related to excessive reactivity when MURR fuel was processed. All evidence from past processing of MURR fuel indicates that it was processed without any difficulties caused by excessive off-gas evolution (that would accompany a high dissolution rate caused by large effective surface area). It is possible that those operating the process may have made adjustments to either the catalyst addition or the dissolver vacuum to keep the process within the operating limits.

Off-gas rate scaled by surface area:
Alternatively, the peak off-gas rate can be estimated based on the pilot-plant work of Caracciolo and scaled based on submerged surface area (see Table 4) using a similar basis to that previously used by Weitz.[32,33] Discounting the low data from Test 10, peak off-gas rates were calculated that ranged from 0.203 to 0.676 scfm/ft^2 of submerged outer fuel area (corrected to 0.001 M Hg). Previously, Weitz[32] used a peak value of 0.347 scfm/ft^2 based on a peak gas generation rate of 18 scfm/min. After calculation of the submerged surface area of the MURR fuel bundles, the peak off-gas rate from the pilot-scale work[21] can then be used to estimate the peak off-gas rate for MURR bundles. Laurinat[8] calculated surface area for the MURR assemblies and bundles from which the surface area per linear foot of submerged fuel was computed.

Table 4. Pilot Scale Dissolution Rate Data with Peak Rates.

	Solid Magazine			Perforated Magazine						
Test #	4	5	6	7	8	9	10	11	12	13
Type	1A	1A	1B	1A	1A	1A	1A	1B	1B	II assembly
Weight, lb	88	83.5	88	132	147.8	135	85.5	93	88	128.5
Length, ft	14	13	13.5	14	7.5	14.3	13.5	14	13.4	11.2
Number	4	4	4	6	12	6	4	4	4	4
Submergence, in	15	15	15	35	35	35	15	15	15	15
Vol, gal	245	245	230	385	400	385	230	230	230	333
Hg, M	0.002[a]	0.001	0.001	0.003[b]	0.001	0.001	0.0025[c]	0.001	0.002	0.001
Hg addition rate,mol/min	0.039	0.0144	0.0174	0.03	0.028	0.028	0.0164	0.0174	0.031	0.03
Est. Hg addition. time, min	24	64	50	49	54	52	133	50	56	42.
Reflux Time, h	39	32.5	16	5.3	5	18.3	31	15	7	22
Peak Off-gas scfm[d]	3	5	3.2	9.8	18	7	1.7	4.4	6.5	
Peak rate, lb/h	28		38	96	112	67		32.7	43	24
Ave Rate, lb/h	2.32	2.6	4.62	15.4	28.7	15.6		7.6	12.5	4.64
Ave Rate/ft, lb/h/ft	0.386	0.433	0.77	0.853	0.87	0.865		1.26	2.09	0.774
Total Area, ft^2/ft	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.42
Outer Area, ft^2/ft	0.778	0.778	0.778	0.778	0.778	0.778	0.778	0.778	0.778	0.793
Peak Rate lb/h/ft	4.7	0.0	6.3	5.3	3.4	3.7		5.4	7.2	4.0
Peak rate/Ave Rate	12.1		8.2	6.2	3.9	4.3		4.3	3.4	5.2
Ave Rate/Ave Rate/ft	6.01	6.00	6.00	18.05	32.99	18.03		6.03	5.98	5.99
Total length, ft	5	5	5	17.5	35	17.5		5	5	5
Peak Off-gas/Peak rate	0.107		0.084	0.102	0.161	0.104		0.135	0.151	
Ave Rate lb/h/ft^2	0.26	0.29	0.52	0.58	0.59	0.58		0.85	1.41	0.55
Mg/min/cm^2	2.1	2.4	4.2	4.7	4.8	4.8		6.9	11.5	4.4
Peak lb/h/ft^2	3.15		4.28	3.59	2.29	2.51		3.66	4.86	2.82
Mg/min/cm^2	25.6		34.9	29.3	18.7	20.4		29.8	39.6	23.0
Peak Off-gas scfm/ft^2	0.405	0.676	0.432	0.378	0.347	0.270	0.230	0.595	0.878	
Hg corrected[e] Peak scfm/ft^2	0.203	0.676	0.432	0.378	0.347	0.270	0.092	0.595	0.439	

[a] Run 4: Hg added in 2 increments one at the beginning and the second at 24 hr.

[b] Run 7: Hg added in 3 increments over initial 4 hours. Assume peak rate occurred during first addition or 0.001 M Hg.

[c] Run 10: Two of the elements charged were only ~50% dissolved after 24 hours while other two were completely dissolved.

[d] Gas reference conditions 60°F, 1 atm.

[e] Peak rate corrected to 0.001 M Hg.

Note: All rate data calculated based on total submerged area rather than outer submerged area.

Calculation A, as presented in the Appendix, was used to estimate the peak off-gas rates for the MURR processing performed in the past. This calculation clearly shows that the peak off-gas rate does not scale with the total surface area of the fuel because it would exceed the capacity of the exhaust system. These results are consistent with the hypothesis that only the outer surface of the bundle or the outer surface of the MURR assemblies contributes significantly to the dissolution (and off-gas) rate.

Calculation B, as presented in the Appendix, estimates the peak off-gas rate for MURR processing under conditions proposed for the future. This calculation looks only at the outer surfaces of the bundle and the MURR assemblies as separate items. The off-gas from dissolution of the bundle is the larger value at 30.9 scfm compared with 14.1 scfm for dissolution of the outer MURR surfaces. Comparison of these values with Table 3 shows that 40 scfm should be adequate to dilute the off-gas from four bundles of MURR to below 60% of a 200 °C LFL.

Calculation C, as presented in the Appendix, estimates the peak off-gas for a second charge of MURR bundles under conditions proposed in the future. As in Calculation B, this calculation only looks at the outer surfaces of the bundle and the MURR assemblies as separate items. This calculation credits the effect of the previous dissolution of five bundles for changes in the nitric acid and aluminum concentrations which will reduce the off-gas rate. An aluminum concentration of 0.32 M is credited with reducing the reaction rate by ~12% over the peak rate estimated from Caracciolo's work,[21] offsetting the increase in surface area from additional bundles and the reality that the catalyst is already present in the solution from the initial charge. The amount of aluminum in the initial charge and the total solution volume in the dissolve is credited, so any decrease in the amount of aluminum in the initial charge or increase in the solution volume over that assumed will change this result. Calculation C shows that the off-gas from the dissolution of five bundles of MURR will result in 34.37 scfm based on the outer surface (crediting the rate reduction from 0.316 M Al). Comparison of this value with Table 3 shows that a 40 scfm purge should be adequate to dilute the off-gas from five bundles of MURR to below 60% of the LFL. Calculation C also provides Table 8 which shows the number of bundles in a second charged based on the amount of aluminum credited. A modest increase in the purge rate would allow more flexibility for variation in the dissolver volume or could allow an additional bundle(s) in the second charge.

General Discussion:

Fundamentally, the dissolution rate is controlled by the concentrations of nitric acid, mercury catalyst, dissolved aluminum, and the effective submerged surface area. Initial nitric acid concentration should be a function of the moles of aluminum and uranium metal to be dissolved while arriving at a terminal nitric acid concentration of ~0.5 M nitric acid after the complete dissolution of the last charge (assuming 3.75 mole of nitric acid consumed per mole of aluminum dissolved and 4 mole of nitric acid consumed per mole of uranium dissolved). The concentration of aluminum at the beginning of each dissolver batch is assumed to be minimal (due only to aluminum in the heel of the previous batch). It is assumed that the maximum dissolution rate (where the purge requirements are the highest) will occur early in the initial dissolver charge (as the catalyst addition is completed), and will be primarily determined by the amount of catalyst present, the nitric acid concentration and the effective surface area of the fuel bundles. This assumption is consistent with the data of Caracciolo.[21] The metered addition of mercury catalyst as a function of time allows significant aluminum to dissolve into solution prior to the catalyst addition being completed, thus it lowers the peak off-gas rate. Depending on the dissolution rate during catalyst addition and the length of time taken to add the catalyst, sufficient aluminum will dissolve to control the dissolution rate during the middle stage of the dissolution of the initial charge. Historically, a tank of aluminum nitrate solution was available as a "Dissolver Drown" tank to be used to quench the dissolution reaction in the event that the dissolution reaction could not be controlled by other means. However, there is no indication that this method was ever used to quench the dissolution reaction. It is recommended that this method be considered as a potential method of terminating an overly-reactive dissolution.

Initial dissolution rates of no more than 35 mg/min/cm^2 (0.033 kg/min/ft^2) are estimated from the data of Schlea[15] and Caracciolo[21] for this flowsheet (0.002 M catalyst). This rate appears to be a reasonable value for the early dissolution rate of the unirradiated aluminum bundle and would result in the dissolution of 0.19 kg/min/bundle from the outer area of the bundle. The bundle is not irradiated, but MURR fuel assemblies are irradiated and the effect of irradiation on the dissolution rate has been reported to reduce the dissolution rate by a factor of 3 to 5.[15,39] Based on experience with the previous dissolution batches of MURR fuel, it is likely that observed rates during the upcoming campaign will accordingly be significantly slower than predicted by these estimated rates. It is likely that additional mercury may be needed during a second charge of the dissolver batch to keep the dissolution rate from falling precipitously. A mercury catalyst concentration of up to 0.007 M has been used in the past and may be required during the upcoming campaign to maintain a sufficiently rapid dissolution rate at the end of the dissolution batch. A second catalyst addition would be reserved until after the start of a second charge, when sufficient aluminum had been dissolved to limit the flammability issues. The aluminum concentration necessary to limit the rate is dependent on the amount of additional catalyst proposed. Based on descriptions in monthly reports from the late 1950s and early 1960s, the mercury concentration was increased over several years to increase the rate of fuel processing through H-Canyon. A similar approach may be employed in the upcoming campaign as a flowsheet revision. The lack of off-gas rate measurements is a significant limitation, since this lack of information creates the need to rely on calculations (which tend to be very conservative) and indirect observations of reactivity (such as foam level, dissolver vacuum, condenser pressure drop). An off-gas measurement would provide better information on the rate of dissolution that is occurring both for protection of the LFL limit as well as for completion of the dissolution of the remaining fuel when the aluminum concentration has slowed the rate.

CONCLUSIONS

MURR fuel was processed in H-Canyon in batches of up to six bundles, during the 1970's and 1980's. Dissolver batches of this fuel were processed in a 24-hour reflux cycle with 0.007 M Hg catalyst without indication of process upsets even though this fuel type has a relatively high surface area. Phenomena such as the formation of gas-film barriers and reduced surface activity from radiation and other factors decrease the observed dissolution rate to much lower than expected for the total submerged surface area of the fuel. The mercury catalyst addition rate was used to limit the peak dissolution rate by slowly introducing the catalyst after the dissolver reached the target temperature (i.e., boiling). A similar flowsheet should be used for the upcoming campaign. The amount of catalyst used on the initial batches should be limited to the recently used reduced catalyst level of 0.002 M Hg. Higher catalyst concentrations should be considered only if shown to be necessary to achieve reasonable dissolution rates, as excessive dissolution rate will impact the off-gas flammability. The number of bundles initially charged will need to be limited based on the amount of expected off-gas and the available purge rates. A second charge may be dissolved in the same dissolver batch, but careful consideration of the expected dissolution rate and flammable gas formation is needed (based on the nitric acid, aluminum and mercury catalyst concentrations). Values for the LFL should be estimated directly from the data of Scott[31] at the NO/N_2O volume ratio of 2.57 rather than using previous models.

Preparing solutions from dissolution which meet the historical requirements for First Uranium Cycle processing requires no particular changes in downstream processes. MURR fuel has a uranium content that is similar to historical SRS fuels and little adjustment should be required if sufficient fuel is fed in a second charge to the dissolver batch. Evaporation of 1AW solutions to concentrate them prior to disposal should pose aluminum solubility issues similar to historical operations when aluminum clad fuel was processed.

RECOMMENDATIONS

Based on the review of the pertinent literature, the following recommendations are made regarding the processing of irradiated MURR fuel.

- The number of fuel bundles initially charged shall be limited based on the amount of expected off-gas and the available purge rates. Calculations show that up to four bundles containing 20 assemblies may be charged with a dissolver purge rate of 40 scfm in either dissolver with a submergence of no more than 54 in.
- Multiple charges of fuel will be necessary to operate the process efficiently since off-gas flammability issues will limit the amount of fuel in the first charge of each batch. With 0.316 M Al in solution, up to five bundles of MURR fuel may be dissolved as a second charge to the dissolution batch based on off-gas generation rates. Since the mercury catalyst will already be present in the solution, the reaction will become vigorous at a lower temperature than the initial charge. The heating period of the dissolution of the second charge should be monitored closely.
- The amount of catalyst added to the dissolver batch should be limited to the reduced catalyst concentration of 0.002 M mercury that has been recently used.
- Catalyst should be added slowly due to concerns about excessive off-gas generation. A catalyst solution composed of 4.7 wt % $Hg(NO_3)_2$ and 47 wt % HNO_3 has been used in the past. Historically, catalyst addition has occurred after the solution was heated to a boil and then added over about a one-hour time period. The catalyst addition rate should be determined such that the catalyst addition occurs in no less than one hour. Addition over a longer time period reduces the peak off-gas rate and reduces the off-gas flammability issues.
- The beginning nitric acid concentration should be determined by the amount of aluminum and uranium to be dissolved so ~0.5 M nitric acid will remain after the completion of the dissolution of the last charge.
- The existing minimum limit of 0.3 M nitric acid concentration should continue to be observed. This limit is credited to avoid precipitation of aluminum, uranium, and plutonium as well as to limit the generation of hydrogen from dissolution in an acid-deficient condition.
- Either boric acid or gadolinium nitrate may be used as a nuclear safety poison. Concentrations of up to 2 g/L of B or Gd in surrogate dissolver solutions have been observed to be stable from precipitation.
- It is expected that dissolver reflux times of 72 hours per charge may be required for the initial charge to a dissolver batch. The second charge will require a longer reflux time.

There should be limited need to adjust downstream processes since MURR fuel has a uranium content that is similar to historically-processed fuels. Depending on the total amount of fuel charged to a batch, the uranium concentration may be lower than the normal operating range.

- Aluminum nitrate solubility is dependent on nitric acid concentration. Aluminum nitrate concentration should be limited to prevent precipitation in dissolving and during evaporation. Existing aluminum nitrate solubility references should be used. In general, final aluminum nitrate concentrations of up to 2 M should not cause precipitation issues.
- A gelatin strike should be performed per the existing procedures.
- A permanganate strike should not be necessary for most fuel (as it will likely be cooled for multiple years prior to processing). If zirconium or niobium fission product levels in the uranium product prove to be a problem at some point, the use of a permanganate strike should be considered.

- Once solvent extraction operations have started, consideration could be given to reducing the solvent flow rate relative to the feed flow rate if the uranium concentration is consistently low. This action would also require corresponding changes in cold stream flow rates as well. If changes are desired outside of the existing DCA limits, then modeling of the process changes should be performed by SRNL to provide a basis for those changes.
- Analysis of the uranium product for the nuclear poison should be done during initial operation to confirm that the DF is adequate.

PROCESS IMPROVEMENTS

- Increasing the purge rate would either provide additional conservatism or allow an increase in the number of bundles charged.
- The installation of off-gas flow instrumentation would allow direct measurement of the peak off-gas from the dissolution process. This information might justify increases in the amount of fuel in a charge.
- The availability of a "Dissolver Drown" tank of aluminum nitrate solution to quench an overly reactive dissolution should be considered.
- Additional catalyst may be necessary to achieve acceptable dissolution rates during the second charge and would reduce the total reflux time for the dissolver batch.
- Additional LFL data in the range of expected off-gas composition would allow for a better prediction of the LFL applicable to this process. A higher value for the LFL might be justified which would increase the number of bundles allowed in a dissolution charge.
- Further investigation of the past solvent extraction performance would be needed to confirm that amount of plutonium in the spent nuclear fuel which would require the re-introduction of reductant to the first uranium cycle scrub stream to achieve purity specifications.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of a wide range of individuals who provided assistance during the compilation of this work. The work benefited from extensive discussions with or assistance provided by Major Thompson, Neal Askew, James Laurinat, Bill Clifton, Frank Weitz, and John Scogin. Significant assistance was also provided by David Herman, Fernando Fondeur, Stephanie Hudlow, Richard Brown, Chuck Goergen, Scott Nagley (B&W Lynchberg), Tony Vinnola (INL) and Kiratadas (Das) Kutikkead (University of Missouri Research Reactor Center).

REFERENCES

[1] W. H. Clifton, "Flowsheet Evaluation for Dissolution of Spent Nuclear Fuel", NMD-HTS-2009-3080, Technical Task Request, Savannah River Nuclear Solutions, Aiken, SC, Oct 21, 2009.
[2] W. C. Perkins, J. L. Forstner, "Nuclear Safety of the Ten-Well Insert for the SRP Fuel Element Dissolver", DP-1429, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, Jun 1977.
[3] R. W. Zeyfang, "Dissolving U-Al Alloy in the 10-Well Insert", DPSOX 8422, Test Authorization 2-844, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, May 30, 1974.
[4] C. E. Pickett, "Off-Site Fuels Dissolved in H-Canyon – 1976-2001", file 221H-LIB-F-20-005, February 15, 2005.
[5] J. C. McKibben, K. Kutikkad, L.P. Foyto, "Current Status of the Missouri University Research Reactor HEU to LEU Conversion Feasibility Study", 2006 International RERTR Meeting, Cape Town, South Africa, Oct 29-November 2, 2006.
[6] R. Street, "University of Missouri at Columbia Test Research Training Reactor 4, MURR UAlx Fuel Element Assembly", Drawing 40907, sheet 1 of 2, EG&G Idaho, Inc, September 7, 1977.

[7] K. Kutikkad, “Declaration for MURR Fuel ID’s MO-421 through MO-428”, Appendix A Agreement Spent Nuclear Fuel Acceptance Criteria, DOESRAA-97-005, Rev 0, July 30, 1997.

[8] J. E. Laurinat, “Calculation of Surface Area for Dissolution of MURR Fuel”, X-CLC-H-00800, Rev 0, Savannah River National Laboratory, Aiken, SC, December 17, 2009.

[9] K. Kutikkad, “Appendix A Agreement: Spent Nuclear Fuel Acceptance Criteria”, DOESRAA-98-0004, Rev. 0, University of Missouri Research Reactor Center, Columbia, MO, February 12, 1998.

[10] K. Kutikkad, “Appendix A Agreement: Spent Nuclear Fuel Acceptance Criteria”, DOESRAAD-05-068, Rev. 0, University of Missouri Research Reactor Center, Columbia, MO, July 25, 2005.

[11] J. Johnston, “Building 105-L Disassembly Area Bundling Tube Structural Aluminum”, Drawing C CS L 0962 Rev 7, United States Department of Energy, Savannah River Site, June 19, 2002.

[12] “Works Technical Department Report for May 1970”, DPSP-70-1-5, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, May 1970.

[13] “Works Technical Department Report for March 1971”, DPSP-71-1-3, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, March 1971.

[14] E. R. Norton, “Sequential Charging of Mark 18 Fuel to Dissolver Solution”, DPSOX 8150, Test Conclusion 2-728, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, February 7, 1973.

[15] C. S. Schlea, “The Dissolution of Uranium-Aluminum Alloy”, DP-629, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, September 1961.

[16] R. G. Wymer, R. E. Blanco, “Uranium-Aluminum Alloy Dissolution”, I&EC, 1957, Vol 49, No 1, pp 59-61.

[17] A. F. Boeglin, J. A. Buckham, L. Chajson, R. B. Lemon, D. M. Paige, C. E. Stoops, “Continuous dissolution of Uranium-Aluminum Reactor Fuels”, AICHE J, 1956, Vol 2, No 2, pp 190-4.

[18] R. D. Fletcher, M. E. Jacobson, H. R. Beard, “Effect of Alloying Constituents on Aluminum Dissolution Rates”, IDO-14606, Phillips Petroleum Company, April 15, 1963.

[19] C. E. Pickett, T. G. Campbell, W. E. Harris, “Mercury Requirement for Separations Processes”, memo to J. S. Evans, OPS-STH-890145, Westinghouse Savannah River Company, Aiken, SC, November 27, 1989.

[20] J. T. Long, “Engineering for Nuclear Fuel Reprocessing”, American Nuclear Society, LaGrange Park, IL, 1978.

[21] V. P. Caracciolo, “Dissolver for Uranium-Aluminum Alloy Tubes”, DP-398, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, September 1959.

[22] R. W. Rice, D. V. Sarode, “Mercury-Catalyzed Dissolution of Aluminum in Nitric Acid”, Ind. Eng. Chem. Res., 2001, Vol. 40, No. 8, pp 1872-1878.

[23] W. C. Perkins, “Catalyst Guidelines for Decladding Thoria Targets”, DPST-69-407, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, June 17, 1969.

[24] J. H. Gray, “A Modified Flowsheet for Mercury-Catalyzed dissolution of Aluminum and Uranium-Aluminum Alloy”, DPST-85-244, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, February 6, 1985.

[25] J. A. Savage, “Modified Flowsheet for Catalyst Addition”, DPSOX 10069, Test Conclusion 2-1094, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, March 24, 1987.

[26]A Vinnola, personal communication, Verbal communication with INL personnel indicates that the endplates are 6061 alloy. INL personnel are providing a documentation of the fuel specifications.

[27] “Progress Report, December 1959, Separations Technology Section”, DPSP 59-1-12-S, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, pg 220-2, December 1959.

[28] “Progress Report, January 1961, Separations Technology Section”, DPSP 61-1-1-S, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, pg 213-4, January 1961.

[29] “Progress Report, January 1967, Separations Technology Section”, DPSP 67-1-1-S-DV, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, pg 212-2, January 1967.

[30] M. G. Zabetakis, “Flammability characteristics of Combustible Gases and Vapors”, Bulletin 627, Bureau of Mines, Department of the Interior, Washington, DC, 1965.

[31] 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, Pittsburg, PA, 1956.

[32] F. R. Weitz, “H-Canyon Dissolver Hydrogen Dilution Calculations using Off-Gas Specific Lower Flammability Limit (LFL)”, X-CLC-H-00473, Westinghouse Savannah River Company, Aiken, SC, October 2, 2003.

[33] F. R. Weitz, “Mark 16B Dissolver Off-Gas Purge Air Rates”, X-CLC-H-00447, Westinghouse Savannah River Company, Aiken, SC, August 6, 2003.

[34] "Feed Adjustment for First Cycle Solvent Extraction", DPSTS-221-H-HM-3.03, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, October 1975.

[35] "Dissolving Enriched Uranium and Plutonium in the Ten-Well Insert", DPSTS-221-H-HM-1.04, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, March 25, 1985.

[36] C. E. Pickett, "Aluminum and Born Solids in SFO First Cycle Feed, NMS-EHA-980072, Westinghouse Savannah River Company, Aiken, SC, May 12, 1998.

[37] C. E. Pickett, "Processing Sterling forest Oxide Without Precipitating Boron-Aluminum Solids., NMS-EHA-2000-00121, Westinghouse Savannah River Company, Aiken, SC, October 23, 2000.

[38] D. T. Herman, "Solubility Testing of Neutron Poisons for Dissolution of High Aluminum Spent Fuel",SRNL-STI-2010-00043, Savannah River National Laboratory, Aiken, SC, February 24, 2010.

[39] M. L. Hyder, et al, "Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant", DP-1500, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, April 1979.[40] E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, June 12, 1972.

[41] V. P. Caracciolo, "Vertical Dissolution of Long Fuel Elements", DPST-58-159, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, May 15, 1958.

[42] S. L. Hudlow, "Gadolinium and Boron Impurity Removal in First Cycle Processing", personal communication, Savannah River Nuclear Solutions, Aiken, SC, December 2009.

[43] W. G. Dyer, J. C. Williams, "Impact of Temperature on Hydrogen Lower Flammability Limit for Separations Facilities", WSRC-TR-2003-00313, Rev 0, Westinghouse Savannah River Company, Aiken, SC, July 2003.

[44] M. Hertzberg, K.L. Cashdollar, "Flammability Behavior and Pressure Development of Hydrogen Mixtures in containment volumes", Vol. 1, Thermal-Hydraulics of Nuclear Reactors, The Second International topical Meeting on Nuclear Reactor Thermal-Hydraulics held at Santa Barbara, CA January 11-14 1983, American Nuclear Society, LaGrange Park, IL, 1983.

[45] G. Ciccarelli, D. Jackson, J. Verreault, "Flammability Limits of NH_3-H_2-N_2-Air Mixtures at Elevated Initial Temperatures", Combustion and Flame, 2006, Vol. 144, pp 53-63.

[46] W. H. Clifton, "Estimated minimum fuel submergence for 6.1D/6.4D dissolvers with 7500L and 13000L solution", personal communication, January 2010.

[47] "Monthly Report Draft, March 1985, Canyons, B-Line and Associated Facilities", DPSPU 85-60-3, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, March 1985.

[48] M. M Jerath, "Capacity of 200 cfm Process Jet Siphon Drawing W157923", email communication, Savannah River Nuclear Solutions, Aiken, SC, Jan 2010.

[49] W. C. Perkins, "Reply to RTA 1115-S, Risk of Hydrogen Deflagration in Dissolvers", DPST-83-943, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, November 28, 1983.

[50] "Dissolving Enriched Uranium and Plutonium in the Ten-Well Insert", DPSTS-221-H-HM-1.04, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, SC, March 25, 1985.

APPENDIX

Calculation A - Estimated Off-gas from Historical Dissolution of MURR Fuel

Problem: What is the effective area for dissolution?
The effective area of dissolution will be limited by limitations in heat and mass transfer. Experimental evidence is scant. Caracciolo[21] reported limitations with concentric SRS fuel tubes. Production dissolutions of MURR in 1980s provide insight, but limited data are available.

Assumptions:
6 MURR bundles charged, 2 assemblies per bundle.
Fuel submergence 47 in. (a low value is conservative in this case)
Mercury catalyst conc. 0.007 M, added over a 1-hour period after dissolver heated to boil.
Peak off-gas rate 0.385 scfm/ft^2 (60°F, 1 atm) based on average of Caracciolo rates[18] scaled to 0.001 M Hg.
Surface area of fuel and bundles from Laurinat.[8]
Dissolution rate scales linearly with catalyst concentration.
Effect of irradiation on dissolution rate to be a factor of five (highest value reported).
No effect of irradiation on dissolution rate of bundle since bundle was not irradiated.
Assume purge rate ~1.5 x of technical standard limit of 27 scfm = 40.5 scfm actual.
Assume effective area constant until peak off-gas rate achieved.
Dissolved vacuum pressure maintained throughout process based on lack of adverse information in monthly reports.
Jet capacity during operation represented by Figure 16 (Vacuum capacity limited to ~ 220 scfm.).

Discussion: Table 5 shows the result of calculation of total off-gas rates based on the Caracciolo's peak off-gas results scaled by surface area and Laurinat's calculation of surface area. Five combinations of effective surface area are calculated based on the combinations that were deemed plausible. The assumption that the effective surface area remains constant until after the peak off-gas rate is achieved is an approximation. Maximum reported effect of irradiation on dissolution rate is assumed, but actual effect could be less. Since the dissolver vacuum system is limited to ~220 scfm, the results from these calculations show that if the total surface area of the MURR assemblies were involved in the dissolution process, the result would be a volume of off-gas far in excess of the vacuum capacity. Past operating experience shows that the dissolver did not pressurize while dissolving MURR fuel, so it is concluded that the surface area that is involved in the dissolution process is more accurately approximated by the outer surface of the fuel and bundle (as compared to the other high surface area alternatives). This conclusion is consistent with Caracciolo's assertion that the dissolution rate scales with the outer areas of the fuel. This phenomenon is likely the result of limitations on the mass transfer of nitric acid and mercury to the metal surface, heat transfer from the surface due to the heat of dissolution, and the large of amount of gas generated at the surface due to reaction off-gases and evaporation.

Conclusion: The inner surfaces of the MURR assembly do not have a significant dissolution rate until the outer portions dissolve. The area of outer surfaces of the fuel and bundle appear to determine the peak off-gas flowrate. The peak dissolution rates for outer bundle and the outer MURR surfaces occur at the different times.

Limitations: The factor of five used for the irradiation effect of dissolution is based on very limited observations and the highest value was conservatively used. Based on the 25% burn-up reported for MURR fuel, a factor of three or maybe less is possibly more realistic but would not change the conclusion. The use of a submergence value of 47 in. reduced the flowrate by ~13% over that calculated from a 54 in. submergence value. The scale-up of the effect of increased catalyst concentration on the peak off-gas rate also introduces an estimated 30% uncertainty.

Table 5. Estimated Off-gas Rates from Historical MURR Dissolution (for 6 bundles).

	Area ft^2/ft	Area ft^2	Total Off-gas scfm
MURR outer	1.159	27.2	55
Bundle outer	1.269	29.8	121
MURR total	13.797	324.2	**215**
Bundle total + MURR outer	3.764	88.5	**220**
Bundle total + MURR total	16.402	385.4	**380**

Note: Assumes 1.5 times 27 scfm for the actual purge rate.

Calculation B - Predicted Off-gas from Future Dissolution of MURR Fuel

Problem: Determine the required purge rate and off-gas specific LFL.
Assumptions:
Four MURR bundles charged at 4 assemblies per bundle.
Fuel submergence 54 in.
Mercury catalyst conc. 0.002 M, added over a 1-hour period after dissolver heated to boil.
Initial acid concentration is no more than 6 M nitric acid.
Peak off-gas rate 0.676 scfm (60°F, 1 atm) based on Test #5 Caracciolo[18] scaled to 0.001 M Hg.
Surface area of fuel and bundles from Laurinat.[8]
Dissolution rate scales linearly with catalyst concentration.
Effect of irradiation on dissolution rate to be a factor of two. (Factor of three is lowest value reported.)
No effect of irradiation on dissolution rate of bundle since bundle was not irradiated.
Appropriate purge rate will be determined but initially will assume existing TSR limit of 40 scfm.
Assume effective area constant until peak off-gas rate achieved.
Jet capacity during operation represented by Figure 16. Shows vacuum dropout at > 220 scfm.

Discussion: Table 6 shows the result of calculation of peak off-gas rates based on the Caracciolo's peak off-gas results scaled by surface area and Laurinat's calculation of surface area. Only two cases of effective surface area are calculated involving the outer areas are included. The assumption that the effective surface area remains constant until after the peak off-gas rate is achieved is an approximation. Minimal effect of irradiation on dissolution rate is assumed. Actual reduction could be greater but data is very limited. Peak off-gas rates from the dissolution of the outer surfaces of 14.1 to 30.9 scfm are calculated using the given assumptions. At the point that the lower portion of the bundle tube is dissolved and the upper portion of the bundle rests on the top of the stack of assemblies, greater than 40% of the bundle tube (> 2.7 kg Al/bundle) will have been dissolved. At the point that the assembly is likely to collapse, ~ 60% of the bundle tube (~4 kg Al/bundle) will have dissolved. This aluminum in solution will suppress the dissolution rate.

Conclusion: A maximum peak off-gas rate of 30.9 scfm was calculated from the dissolution of the outer surface of four bundles.

Limitation: The effective surface area used and the irradiation effect on dissolution are large uncertainties which make large differences in the dissolution rate and the peak off-gas rate. As the fuel assembly collapses, there is potential for additional exposure of surface area to fresh nitric acid solution that could increase the rate depending on the amount of aluminum in solution at this point in the dissolution.

Table 6. Estimated Off-gas Rates for Proposed Future MURR Dissolution (Four bundles).

	Area ft^2/ft	Area ft^2	Peak Off-gas scfm
MURR outer	1.159	20.9	14.1
Bundle outer	1.269	22.8	30.9

Calculation C - Predicted Off-gas from Dissolution of MURR Fuel – Second Charge

Problem: Determine the required purge rate and off-gas specific LFL.
Assumptions:
5 MURR bundles dissolved in first charge at 4 assemblies per bundle.
Aluminum concentration at start of second charge is 0.41 M. (5 bundles dissolved into 13000L, Table 2).
8 MURR bundles charged as a second charge at 4 assemblies per bundle.
Fuel submergence 54 in.
Mercury catalyst conc. 0.002 M, added during initial charge.
Initial acid concentration is 5.6 M HNO_3 prior to initial charge (depleted by first charge to ~4.05 M, Table 2).
Peak off-gas rate 0.676 scfm (60°F, 1 atm) based on Test #5 Caracciolo[18] scaled to 0.001 M Hg.
Surface area of fuel and bundles from Laurinat.[8]
Dissolution rate scales linearly with catalyst concentration.
Effect of irradiation on dissolution rate of MURR assembly was a factor of two. (Factor of three is lowest value reported.)
No effect of irradiation on dissolution rate of bundle since bundle was not irradiated.
Assume effective area constant until peak off-gas rate achieved.
Effect of Al concentration and HNO_3 depletion on off-gas rate scales linearly with Al dissolution rate.
Effect of Al and HNO_3 concentration-
Peak observed dissolution rate is 52.53 mg/min/cm^2 at ~0.27 M Al (end of catalyst addition, Figure 8).
Dissolution rate varies with [Al] defined by curve fit of Caracciolo data (Figure 8)
Rate= $102.64*10^{-1.078*[Al]}$ mg/min/cm^2 for [Hg]=0.001 M.
Reduction in peak dissolution rate is a factor $=52.53/(102.64 * 10^{-1.078*[Al]})$.

Discussion: Table 7 shows the result of calculation of peak off-gas rates based on the Caracciolo's peak off-gas results scaled by surface area and Laurinat's calculation of surface area. The effective surface area calculation for both the outer MURR area and the outer bundle area are shown. The assumption that the effective surface area remains constant is an approximation. The aluminum from the initial charge varies with solution volume. Table 8 shows the effect of aluminum concentration of the number of bundles that can be charged as a second charge while maintaining the peak off-gas rate below 34.37 scfm.

Conclusion: A selection of the number of bundles in the second charge should be made based on the amount of reduction in peak off-gas rate that can be credited from dissolved aluminum based on Table 8. For [Al]=0.32 M, five bundles results in < 34.37 scfm of peak off-gas.

Limitation: The effective surface area involves uncertainties which make large differences in the dissolution rate and the peak off-gas rate. This calculation relies on the aluminum in the initial charge in a minimum of solution volume to offset the effect on the off-gas rate from additional fuel bundles. Variation in actual solution volume will change the aluminum concentration.

Table 7. Estimated Off-gas Rates for a Five-Bundle Second Charge MURR Dissolution (Assumes 0.32 M Al present from the initial charge).

	Area ft^2/ft	Area ft^2	Peak Off-gas scfm
MURR outer	1.159	26.1	15.56
Bundle outer	1.269	28.6	34.07

Table 8. Effect of Soluble Aluminum on the Number of Bundles in a Second Dissolution Charge.

Al M	Al Reduction Factor [a]	Bundles	Peak Off-gas scfm
0.000	0.51	2	30.16
0.111	0.67	3	34.37
0.227	0.90	4	34.37
0.316	1.12	5	34.37
0.390	1.35	6	34.37
0.452	1.57	7	34.37
0.506	1.80	8	34.37
0.553	2.02	9	34.37
0.596	2.25	10	34.37

[a] Effect of aluminum upon dissolution rate is calculated based on a peak rate of 52.53 mg/min/cm^2 and a correlation of the rate from Figure 8 of rate = $102.64*10^{-1.078*[Al]}$ mg/min/cm^2 for [Hg]=0.001 M.

Table 9. LFL Data at NO/N_2O Ratio Equal to 2.57.[31]

	La Chatelier's Rule		
% Air	%H_2[a]	Deviation[b]	LFL
0%	5.62%	0.00%	5.62%
5%	5.53%	0.47%	6.00%
10%	5.45%	0.65%	6.10%
15%	5.37%	0.83%	6.20%
20%	5.28%	1.02%	6.30%
25%	5.20%	1.20%	6.40%
30%	5.11%	1.39%	6.50%
35%	5.03%	1.67%	6.70%
40%	4.94%	1.86%	6.80%
45%	4.86%	1.97%	6.83%
50%	4.78%	1.92%	6.70%
55%	4.69%	1.93%	6.63%
60%	4.61%	1.89%	6.50%
65%	4.52%	1.68%	6.20%
70%	4.44%	1.26%	5.70%
75%	4.35%	1.25%	5.60%
80%	4.27%	0.93%	5.20%
85%	4.19%	0.41%	4.60%
90%	4.10%	0.20%	4.30%
96%	4.00%	0.00%	4.00%

[a] Calculated as by the equation 5.62-(5.62-4)/96 * (% Air).

[b] Determined visually from graph in reference by Scott.

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
A. M. Murray, 773-A
F. M. Pennebaker, 773-42A
S. J. Hensel, 773-42A
W. E. Harris, 704-2H
J. B. Schaade, 704-2H
G. J. Zachman, 225-7H
P. B. Andrews, 704-2H
S. J. Howell, 221-H
J. C. Wallace, 221-H
J. L. O’Conner, 704-2H
C. R. Goergen, 704-2H
W. G. Dyer, 704-2H
P. M. Palmer, 221-H
W. H. Clifton, 704-2H
R. A. Eubanks, 221-H
R. G. Brown, 221-H
J. L. Bodkin, 221-H
C. P. Nguyen, 221-H
S. L. Hudlow, 704-2H
F. R. Weitz, 221-13H
J. R. Lint, 704-185H
M. C. Chandler, 703-H
E. A. Kyser, 773-A
G. F. Kessinger, 773-A
J. H. Scogin, 773-A
M. C. Thompson, 773-A
J. E. Laurinat, 773-A
N. M. Askew, 773-42A
D. T. Herman, 735-11A
F. F. Fondeur, 773-A