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WESTINGHOUSE SAVANNAH RIVER CO. CLOSURE BUSINESS UNIT

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Analysis of Events Associated With First Charge of Desicooler Material

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Initial Issue

Revision History

Rev. 0,

Rev.1

The document was reformatted. Additional description of the applicable Safety Basis controls was added along with justification as to why these controls were maintained. Summary and Conclusion sections were expanded to place more emphasis on the fact that there is no Safety Basis violation and better explain the event. Additional discussion was added to show that the Safety Basis maintains protection of the worker, facility, and public.

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1.0 Summary

HB-Line Scrap Recovery's current mission includes dissolution of uranium-aluminum scrap left over from a U_3O_8 scrap recovery program begun in 1972 with material returned from Rocky Flats and Oak Ridge (Reference 1). This material has been stored in desicooler containers, and is commonly referred to as the "Desicoolers." The Scrap Recovery process includes the dissolution of scrap material and transfer of the resulting solution to H-Canyon for further disposition.

During the first charge of the Desicooler material into the HB-Line dissolvers, the solution heated to boiling without external heat being added. Yellow-colored fumes, which dissipated rapidly, were noted in the glovebox by operators and liquid was noted in the glovebox by operators after dissolver cooldown.

The following Technical Report documents the analysis of this event with respect to potential Safety Basis violation and the Integrated Safety Management System (ISMS) process. Based on this evaluation, it was determined that no Safety Basis controls were violated. Applying the principles of the ISMS, it is recognized that WSRC failed to implement adequate process controls to limit the rate of exothermic reaction in RD-13. This however is not a Safety Basis issue and will be addressed through the ISMS process. Based on the analysis presented, a PISA does not exist and the Safety Basis has shown its ability to protect the worker, the facility and the public.

2.0 Introduction

The HB-Line Scrap Recovery process has a mission to dissolve "scrap" material, uranium and plutonium oxide, in nitric acid. The resulting solution is then transferred to H-Canyon for further processing. HB-Line has a dual train dissolving system. One train consists of a dissolver (RD-13 or RD-14) and a Product Hold Tank (RT-33 or RT-34). Each dissolver is a slab tank with a 30-liter capacity. The dissolution process consists of adding 15 liters of 12 molar nitric acid with a small addition of fluoride to act as a catalyst for the reaction. When combined with about one liter of heel, this results in a total dissolver volume of 16 liters. The material is introduced and the solution is heated. Once dissolution is complete, the cooled solution is transferred to RT-33/34 and transferred to H-Canyon.

On 5/29/03 at approximately 0450 hours HB-Line personnel charged an authorized uranium-aluminum oxide batch of 1457 grams to the RD-13 dissolver. The batch contained approximately 52 % aluminum and 6 % uranium. The batch was the first batch charged from a category of material defined as "Desicooler" material. Desicooler material is a mixture of 1970s uranium-aluminum scrap from a U₃O₈ program originating in Rock Flats and Oak Ridge. The material was charged under current WSRC-RP-2002-00615, "Justification for Continued Operations for Alternate Hydrogen Control for Phase 1 Scrap Recovery Processing".

Shortly after the charge was complete, 0456hrs, operators began to see rises in the liquid level and temperature. At approximately 0500 hrs yellow "smoke" was reported to be in the adjacent glove boxes. Operations responded by notifying Fire Department personnel to report to the facility. The yellow "smoke" was nitrogen oxide fumes. The "smoke" dissipated within 5 minutes. No mitigating actions were needed by Fire Department or Operations personnel to clear the "smoke".

The total rise in temperature in the dissolver liquid was approximately 82 degrees centigrade due to the reaction. The rate of rise in temperature was about 7 degrees centigrade per minute in the dissolver liquid until the material reached boiling of 111 degrees centigrade. The reaction then continued boiling for about 3 minutes and 40 seconds. Immediately after boiling stops the liquid began to cool. Within seven minutes, the liquid quickly dropped from a max of 111 degrees to 80 degrees centigrade. The material then continued to cool to ambient temperatures at a slower rate.

Inspection by operators shortly after the reported reaction revealed liquid on the floor of adjacent glove boxes. About 7 liters was lost from the dissolver during the event. The estimated liquid on the glovebox floor based on visual observation was estimated to be about 3-4 liters. An additional 1-1.5 liters was seen in the Vessel Vent Catch Tank (VVCT). The remaining solution evaporated during the event and collected in the Scrubbers or evaporated into the glovebox and was removed with the nitrogen oxide fumes. All processing was halted until reviews of the reaction were completed by WSRC management and engineering.

A narrative of the time line of the event is attached in Appendix A to this report. The dissolver temperature trace during the event is shown in Appendix B.

3.0 Analysis of Event

The source of heat that caused the dissolver to elevate in temperature was the reaction of the scrap constituents with nitric acid. The principal constituent that would cause a temperature increase is aluminum. Laboratory analysis showed that the can containing 1188.7 grams was 52% aluminum, and 6% uranium. Both of these materials undergo exothermic reactions with nitric acid. This can contained the highest concentration of aluminum in analyzed cans that were authorized to be processed under existing controls (2000 gram charge).

The reactions of aluminum with nitric acid depend on the acid concentration during the reaction. These reactions are shown in Appendix C, and are summarized below.

•	$Al + 6HNO_3 \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O$	Equation 1
•	$Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + 2H_2O$	Equation 2
•	$8Al + 30HNO_3 \rightarrow 8AL(NO)_3 + 3N_2O + 15H_2O$	Equation 3
•	$10\text{Al} + 36\text{HNO}_3 \rightarrow 10\text{Al}(\text{NO}_3)_3 + 3\text{N}_2 + 18\text{H}_2\text{O}$	Equation 4
•	$2Al + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2$	Equation 5

The first reaction is favored at high (generally > 7M) nitric acid concentration, and the last reaction is favored at low (generally less than 1M) nitric acid concentration. Note that all these reactions are with aluminum metal. The energies associated with these reactions are shown in Appendix D. The maximum volume of gas formed is from reaction 1, with three moles of NO₂ formed for each mole of aluminum dissolved.

Also shown in Appendix D are the energies associated with creation of hydrated aluminum nitrate. These energies are all less than the energies associated with the non-hydrated aluminum nitrate.

Further, Appendix D shows the energy associated with uranium metal dissolution. The energy released and gas generation are much less, on a per gram basis, than the energy liberation and gas generation for aluminum.

The dissolver contained about 16 liters of 12M nitric acid. The dissolver weighs about 250 pounds and is constructed from 304L stainless steel (Reference 2). The amount of energy necessary to raise the temperature of the dissolver system under adiabatic conditions can be calculated by knowing the contents of the dissolver, the mass of the dissolver, and the material of construction of the dissolver. The pertinent information is from Reference 3:

Heat capacity of 304L SS: 0.12 cal/gram °C Heat capacity of 12M nitric acid: 0.65 cal/gram - °C Density of 12M nitric acid: 1.33 grams/cc

The dissolvers are slab tanks suspended in wing cabinets. To determine the rates of the chemical reactions, the amount of energy needed to raise the temperature of the system at the rate shown in Appendix B was calculated. The reaction needed to add heat to raise the system temperature and to also make up for heat losses. The heat losses to the atmosphere were calculated, using the methods from Reference 4. The equations used, and the results for forced convection at 10 meters/second, are shown in Appendix F. The assumed flow rate of 10 meters/second is conservative, but was chosen to achieve a conservative result. The maximum heat transfer rate was 28.67 Kcal/minute.

The heat losses were also estimated from the cooldown portion of the curve shown in Appendix B. Much larger heat loss rates were obtained from the cooldown curve than from the theoretical calculation, as discussed below. The maximum heat transfer rate from the cooldown curve is 201 Kcal/minute. Using a theoretical analysis without the benefit of knowing the exact conditions can cause large uncertainties in the calculated heat loss. Conduction to the heater was suspected to contribute to the differences seen. However, the area of actual contact with the heater is limited (the heater transfers energy principally by radiant heat). Because of the level of knowledge with respect to heat transfer impacting factors, and to be conservative with respect to gas generation, the heat loss rates were calculated empirically based on the higher heat loss rates obtained from the cooldown curve.

The heat loss was calculated for the approximately 10 °C intervals where the system was cooling down. The first interval started after the solution temperature had peaked and then fallen to 107.65 °C, and extended to a temperature of 99.54 °C. The rate of heat loss was faster in the second interval than in the first. This behavior suggests the reaction did not terminate immediately, but continued at a reduced rate for a few minutes. Using the higher heat loss rate is conservative for the calculation of gas generation rate because it indicates that the rate of reaction was faster. This in turn means that more Aluminum was reacted. The remaining intervals are about 10°C down to 59.89 °C. Below 59.89 °C, the heat losses are assumed to be negligible.

The heat loss rates are summarized in Table 1 below.

Table 1. Amblent fleat Doss Nates Calculated from Temperature Curve				
Time, hours:	Time in	Temperature,	Temperature	Heat loss rate
minutes	Interval,	°C	Change in	in interval,
:seconds	Minutes		Interval, °C	Kcal/minute
04:49:30		29.40		
	4.67		30.49	Assumed 0
04:54:10		59.89		
	1.87		9.80	31.8
04:56:00		69.69		
	1.33		9.49	59.0
04:57:20		79.18		
	1.16		9.96	123.0
04:58:30		89.14		
	1.16		10.40	201.0
04:59:40		99.54		
	1.5		8.11	201.0*
05:01:10		107.65		

 Table 1: Ambient Heat Loss Rates Calculated from Temperature Curve

*The rate from the lower temperature interval is conservatively assigned to this interval

3.1 Analysis of Temperature Rise During Event

The temperature trace of the dissolver during the event showed a rapid rise in temperature shortly after the material was added to the dissolver. The following analysis will show that the quantity of aluminum in the charge was more than sufficient to generate the temperature rise that was observed and prove that aluminum was the most likely cause of the temperature rise.

The amount of aluminum in Can MC02-181A was about 52%, and the mass charged from that can was about 1188 grams. The resulting aluminum content was 617 grams. The aluminum dissolution reactions are shown as Equations 1 through 5, and also in Appendix C. Uranium dissolution is also exothermic, but it generates significantly less heat per gram than does aluminum, and its contribution is conservatively ignored to demonstrate that the heatup can be explained by dissolution of aluminum alone.

The reaction of aluminum with nitric acid that produces three moles of NO_2 (Equation 1) is the predominant reaction at high nitric acid concentrations. The NO_2 evolved matches the observations of the color of gas reported by the operators in the glovebox, and it generates the minimum amount of heat of the reactions that predominate in the high nitric acid regime. The heat of this reaction is slightly higher when non-hydrated aluminum nitrate is assumed for the reaction product, so the hydrated version of the reaction is chosen for this analysis. The heat of reaction for dissolving aluminum oxide is significantly lower, but no gas is liberated when aluminum oxide is dissolved.

Heat is absorbed by the dissolver itself and by the dissolver solution as heat is generated by the dissolution reaction. The parameters that govern the amount of heat required to raise the temperature are summarized below:

- Nitric acid: Specific Gravity = 1.33 grams/cc, specific heat = 0.64 calories/gram °C, volume = 16.1.1 liters
- **Dissolver**: Material is 304L SS, weight (empty) = 250 pounds, specific heat = 0.12 cal/gram °C

The amount of heat required to elevate the dissolver temperature by one degree Centigrade, before accounting for heat loss, is as follows:

[(16,100*1.33*0.64) + (250*454*0.12)][1] = 27.33E+03 calories/degrees °C

The heat required to heat the solution is shown in Section 3.3. The sum of the heat required to heat the system, plus the heat required to replace ambient heat losses during heatup, is 2.15E+03 + 7.82E+02 Kcal, or a total of 2.932E+03 Kcal. Using the equation with the lowest heat input, dissolving one gram of aluminum generates 7.28 Kcal of heat. The amount of aluminum necessary to explain the heatup is conservatively

 $2.932E+03/7.28 \sim 403$ grams. This is well within the 617 grams of aluminum projected to be in MC02-181A based on laboratory analysis.

The analysis presented above proves that aluminum is the most probable cause of the temperature rise in the dissolver. The amount of energy that could be generated by the dissolution of aluminum explains the rise in temperature that was seen during the event.

3.2 Analysis of RD-13 Pressure Trace During Event

The instrument used for vacuum reading in RD-13 is a Foxboro 823DP Pressure Transmitter with a range of 0-30 in WC calibrated in a range for of 0 to 15 in WC.

The graph of the RD-13 pressure instrument output during the exothermic reaction is included in Appendix E. The time scale has been changed to reflect a 67 minute 30 second correction factor. The actual time of the recorder instrument raw data was found to be ahead of Daylight Savings Time by 67 minutes 30 seconds.

Appendix G, Figure 1 is a graphical representation of RD-13/14 min/max vacuum pressure readings during the reaction. Appendix B indicates the charge of material occurred at 0450 hours. A slight elevation in the vacuum reading occurred at 0450 hrs due to the operator placing a charge beaker over the charge chute and partially blocking purge flow into the charge chute during the addition of material to the dissolver. Approximately 270 seconds after charging the material to the dissolver, vacuum pressure rises from approximately 0.3 in WC to approximately 5 in WC. Almost immediately the pressure indication then changes to a positive pressure reading (outside the calibrated range of 0-15 in WC of vacuum). The instrument then fluctuates from a reading of 2 in WC vacuum to a positive pressure indication. The instrument settles out after approximately 20 minutes to a slight positive pressure reading.

Appendix B illustrates the increase in temperature of RD-13 during the reaction. The graph indicates the initial charge of the material at 0450 hrs and the immediate ramp up in temperature. The beginning temperature was ambient temperature (28.5 degrees centigrade). The high level alarm for RD-13 was received at 0456 hours. The High Level alarm is marked on attachment 2 at a corresponding temperature in the dissolver of ~68.82 degrees centigrade. The first report of gas in the glove box was reported at 0500 hrs, which corresponds, to a temp of 100.0 degrees centigrade.

An evaluation of the RD-13 pressure fluctuations was performed by Systems Engineering and the conclusion is that RD-13 pressure instrument readings were a were a result of localized pressure transients inside the instrument sensing line for the RD-13 pressure instrument. The localized pressure transients were a result of foam/bubbles rising in the vessel vent system piping and entering the sensing line. The basis of the conclusion is based on the following:

1. Past dissolver pressure recordings show any change in pressure in one vessel causes proportional pressure variances in the other vessel. A review of the RD-14 instrument output during the incident shows no corresponding fluctuation of the vessel vent system pressure occurred.

A test of was performed using RD-14 while RD-14 dissolver vessel was in DEINVENTORY MODE. RD-14 charge chute was partially blocked with the charge beaker. The resulting blockage was to simulate a blocked vent path for RD-14 and see the trend for RD-13 corresponding pressure trace. The test was performed using calibrated RD-13 and RD-14 pressure instrumentation. The purpose of the test was to document what the system response would when a dissolver charge chute was blocked and unblocked. The result is an almost instantaneous response on RD-13 vacuum readings on initial blockage and unblockage. If the RD-13 pressure recording on Appendix E is real, then an expected corresponding system pressure spike would have been observed on the RD-14 pressure recording. That effect was not recorded during the 5/29/03 exothermic reaction. What was recorded was a slight increase in vacuum pressure normally observed during normal dissolution boiling temperatures.

On 5/27/03 a normal pressure curve (both charge chutes removed) was recorded for RD-13 and RD-13. RD-14 was brought to boiling using heat was generated using the dissolver heater block. The heatup was for post maintenance testing of RD-14 dissolver after replacement of the dissolver unit. The graph indicates a similar increase of RD-13 vacuum pressure as observed in RD-14 during the RD-13 5/29/03 exothermic reaction. This can be explained by higher vapor pressures observed in the on-line condenser reducing vacuum slightly on the on-line dissolver and increasing vacuum slightly on the off-line dissolver. The same trace is observed in RD-14 during RD-13 rapid rise in temperature and boiling on 5/29/03.

2. It is known from past events that foam/bubbles produces higher differential pressure indications in differential pressure instruments. H-Area Outside Facilities has experienced similar incidents in the GP evaporator. Essentially the foam in the GP evaporator caused higher differential pressure readings and subsequently shutdown the evaporator unexpectedly (Reference 8).

3. The calibration of the RD-13 vacuum instrumentation after the exothermic reaction found the as-found condition out-of-calibration. The resulting magnitude of the out-of-calibration discrepancy would have shifted the vacuum readings by 0.9 in WC (more negative) if the correction for the calibration was applied during the transient.

3.3 Analysis of Available Purge During the Event

The bases of the HB-Line JCO for Alternate Hydrogen Control assume that 20 cfm of purge air is available for dilution of hydrogen. Based on analysis of existing data

(temperature, pressure, etc.), the ability of the purge system to supply 20 cfm was not compromised. However, there is one potential mechanism that could have temporarily interrupted purge flow. This mechanism is discussed in Section 3.6.

The temperature data from the event was used to calculate bounding gas generation rates. The amount of heat that needed to be added to the solution to raise the temperature accordingly, plus the heat that needed to be added to the solution to replace ambient heat losses was determined. The reaction that provides the largest gas generation rate for the lowest amount of heat generated is the hydrated reaction that produces three moles of NO₂, per Appendix D. This reaction produces 7.28 Kcal of energy per mole of aluminum metal reacted. This is the principal reaction expected at the high nitric acid concentrations before the concentration in the dissolver is depleted.

As discussed earlier, the heat losses during the reaction were evaluated from the cooldown curve. These are added to the heat inputs needed to raise the system temperature. The reaction that generates three moles of gas per mole of aluminum dissolved was conservatively chosen to be used in this evaluation.

Time,	Temperature,	Heat Loss,	Heat input	Heat input	Gas
hours:min:	DegC	Kcal/minute	from heat	to make up	generated,
seconds		from cooldown	capacity,	for losses,	CFM at
		data	Kcal	Kcal	87 degC
04:49:30	29.4				
		0.0	8.37E+02	0.00E+00	2.85
04:54:10	59.89				
		31.8	2.69E+02	5.95E+01	2.80
04:56:00	69.69				
		59.0	2.61E+02	7.85E+01	4.06
04:57:20	79.18				
		123.0	2.73E+02	1.43E+02	5.71
04:58:30	89.14				
		201.0	2.85E+02	2.33E+02	7.12
04:59:40	99.54				
		179.0	2.23E+02	2.69E+02	5.21
05:01:10	107.65				
TOTAL			2.15E+03	7.82E+02	

 Table 2: Gas Generated with Conservative Reaction Chosen

The applicable glovebox exhaust fan continued to operate as normal during this event. The actual flow through the charge chute with a glovebox exhaust fan operating has been tested and shown to be 30 cfm at 72 °F and one atmosphere. The credit taken in the JCO for hydrogen calculations is 20 cfm. If the reaction was creating a peak of about 7 cfm of gas, the actual flow could be lowered to 23 cfm. This is still higher than the 20 cfm credited in the JCO. Additionally, the 30 cfm was measured with the scrubber off. Per Reference 5, the vacuum at the outlet of the vessel vent catch tank (53PG) is 9.0 inches vacuum with both the glovebox exhaust fan and the scrubber operating, and 6.5 inches vacuum with the scrubber not operating. The scrubber was operating during this event. This provides additional flow not credited in the 30 cfm at one atmosphere and 72 °F credited.

3.4 Analysis of Worst Case Analysis of Gas Generation Rate During Event

Since nitrogen oxide fumes were observed in the charge chute glovebox, it was postulated that enough gas was generated to overcome the 20 cfm of purge that is required by the bases of the HB-Line JCO. The following analysis shows that the worst case chemistry (with respect to total gas generation) could not overcome the 20 cfm of purge.

The aluminum consumed during system heatup and the gas generation rate associated with this phase of the reaction is discussed in Section 3.5. This phase of the reaction consumed at least 403 grams of aluminum, based on the reaction that gives the lowest heat generation rate per mole of aluminum dissolved. This reaction is shown in Equation 1. This reaction also gives the highest gas generation rate per mole of aluminum dissolved.

In Section 3.5, the analysis was terminated after the temperature reached 107.65 °C, per Appendix B. The reaction continued at temperatures above this for an additional 10.66 minutes before falling to 107.45 °C. It is reasonable to assume the reaction was occurring at the rate for the interval from about 100 °C to 107.65 °C. The temperature does not rise much during this time because boiling is occurring, and the condenser is returning subcooled water to the dissolver. The latent heat of vaporization far exceeds the sensible heat required to increase the temperature of nitric acid-water mixtures. The heat input is then 2.68E+02 Kcal/minute for 10.66 minutes, for a total of 2.86E+03 Kcal. Using the conservative reaction heat associated with Equation 1, this requires (2.86E+03/7.28) ~ 390 grams. The projected amount of aluminum in the charge, assuming MC02-201A also has 52% aluminum, is 757 grams. The heats assumed to be liberated consume $403 + 390 \sim 793$ grams of aluminum.

The extra heat may be liberated by uranium. Uranium generates 1.51 Kcal/gram when dissolved. MC02-181A had 6.1% U, or ~ 73 grams Uranium. This would only account for the amount of heat generated by $(1.51/7.28)73 \sim 15$ grams of aluminum. This demonstrates that the gas generation rates have been conservatively calculated, since the

reactions chosen require more aluminum and uranium than is in the material charged to generate those rates. Therefore, the gas generation rates shown in Table 2 are conservative with respect to the amount of aluminum and uranium in the material charged.

The 7.2 cfm of gas shown in Table 2 would not be sufficient to overcome the 20 cfm that was available for purge. In addition, this peak gas generation rate still falls within the uncertainty allowed by the JCO. The 30 cfm was actually measured during the HB-Line flow test as described in Reference 13. Therefore, more than 20 cfm was still available for purge. This analysis discounts the increased flow provided by the scrubbers as described in Section 3.3.

3.5 Analysis of Hydrogen Concentration During Event

HB-Line is required to control hydrogen to 25% of the Lower Flammability Limit. HB-Line is required to maintain hydrogen concentration in all vessel vapor spaces to below 1% by volume. This analysis evaluates if there was a sufficient purge to keep hydrogen at or below 1% concentration during the rapid reaction rate period of the first Desicooler charge. This analysis shows hydrogen concentration was maintained less than 1%. The analysis follows.

From the Mixed Scrap Charge Plan, Run 131-01 consisted of material from two cans:

-MC02-181A:	1188.7 grams
-MC02-201A:	267.8 grams

A laboratory analysis was performed on Can MC02-181A and is documented in LIMS 200241588. An aliquot of the sample was dissolved in nitric acid in the laboratory, and was held for 30 minutes at room temperature prior to heatup. The sample was then heated to boiling. Every 10 minutes, the amount of gas collected was logged on lab data sheets. If 5 ml of gas sample was available, a sample was drawn to analyze the hydrogen content.

The concentration of hydrogen in the gases measured increased as the reaction progressed in the lab. The nitric acid concentration will diminish from reactions of the nitric acid with aluminum to produce aluminum nitrate $[Al(NO_3)_3]$ and nitrogen oxides. The data from the 10-minute period with maximum hydrogen production was selected for evaluation. The data is:

-Total gas generated: 5 ml in 10-minute period -Hydrogen concentration in gas: 3.28% -Weight of sample analyzed: 0.7548 grams

The amount of gas generated must be multiplied by a scaleup factor to account for hydrogen generation in the dissolver. This scaleup factor is $(1188.7/0.7548) \sim 1575$.

Therefore, the gas generated in the dissolver scales to $(1575*5ml/10 \text{ minutes}) \sim 788 \text{ ml/minute}$. The gas volume is measured at lab conditions of 25 °C (298 °K) and one atmosphere.

The rapid reaction rate in the dissolver was not expected. To account for a higher reaction rate, the scaled-up gas production rate was multiplied by a factor of 10. Based on engineering judgement, this factor is expected to suitably bound the situation. The total gas production rate conservatively assigned to the dissolver, for this evaluation, is thus (788*10) = 7,880 ml/minute.

The measured hydrogen concentration was 3.28%. To account for any differences between the actual acid used in HB-Line and in the laboratory, the concentration of hydrogen measured in the laboratory is conservatively doubled to account for this potential effect. Based on engineering judgement, applying this factor suitably bounds the differences in acid concentration. Therefore, the maximum rate of hydrogen generation assigned from conservative use of laboratory data is (7,880*0.0328*2) ~ 517 ml/minute.

Bounding values were calculated for Can MC02-201A, by statistically projecting the analyzed results from 15 analyzed cans from that statistical population. This is documented in N-CLC-H-00509, Rev. 0. The hydrogen concentration from the 10-minute interval that contained the maximum hydrogen concentration from each run was entered into a statistical database, and projections were made for bounding hydrogen generation rates in dissolver charges including mixed scrap cans that had not been analyzed. The total gas generation rate in ml/minute from the maximum gas generation rate in any 10-minute interval, regardless of hydrogen concentration, was also projected. These projections were made for a 95% confidence level. An unanalyzed population of 20 dissolver batches was conservatively chosen for establishing controls; the actual number of dissolver batches containing unanalyzed cans is seven, including the charge already made. The projected bounding values, at the 95% confidence level, are listed below. Values from Appendix F of N-CLC-H-00509 have been divided by 2000 to back out the scaleup factor used in the projection.

Parameter	Projected value, 20	Projected value, 7
	dissolver batches	dissolver batches
Hydrogen concentration,	33.314	23.058
volume %		
Hydrogen generation rate,	2.284	1.394
ml/minute/gram of material		
dissolved		

 Table 3: Projected Hydrogen Generation Parameters for MC02-201A

The projected hydrogen generation rate is (2.284) (267.8) ~ 612 ml/minute hydrogen from Can MC02-201A. This number has considerable conservatism, as follows:

- Maximum total gas generation rate, regardless of hydrogen concentration associated with the gas, is chosen.
- 95% confidence level chosen for projection
- Projection based on 20 dissolver charges containing unanalyzed cans, rather than seven charges planned.

Additionally, the rate of generation was assumed to double, and the concentration of hydrogen in the gas was also assumed to double, for evaluation of the second can. This gives an effective hydrogen concentration for evaluation of ~66%. This is almost double the concentration of any can analyzed in the entire Desicooler characterization program. This accounts for potential differences in the reaction rate in the dissolver as compared to the laboratory apparatus. The total hydrogen generation rate from material from Can MC02-201A is thus $(2*2*612) \sim 2448$ ml/minute.

The total hydrogen generation rate is the sum of the contribution from each can charged, or 517 + 2448 ml/minute, or 2965 ml/minute. This is evaluated at laboratory conditions of one atmosphere and 25 °C. The purge flow was measured at one atmosphere and 72 °F (22.2 °C). Correcting the gas generation rate to bring it to the purge conditions, the gas generation rate is ((295.2/298)*2965) ~ 2937 ml/minute. This is converted to cubic feet per minute, by dividing by 28,316 ml/cubic feet. The resulting hydrogen generation rate is 0.104 cubic feet/minute.

The credited dilution flow is 20 cubic feet/minute. The hydrogen concentration, neglecting dilution by other chemically-generated gases, is $(0.104/20) \sim 0.0052$ volume fraction, or 0.52%. Even with bounding conservative assumptions, the hydrogen concentration remained well below 1% during this event.

Per the conservative assumptions discussed above, scrap from MC02-181A generates hydrogen at a rate of 0.435 cc/minute/gram scrap dissolved, and scrap from MC02-201A generates hydrogen at a rate of 2.284 cc/minute/gram of scrap dissolved. The weighted average of the generation rate for scrap dissolved when the two cans are mixed is given below:

[(0.435)(1188.7)+(2.284)(267.8)]/[1188.7+267.8] = 0.775 cc/minute/gram scrap dissolved

From Table 2, the heat generation at the peak reaction rate is the sum of the heat generated to raise the temperature plus the heat generated to replace ambient losses. This is $(2.85E+02+2.33E+02) \sim 5.18E+02$ Kcal/minute. The rate of aluminum dissolution that produces this amount of heat is $((5.18E+02/7.28) \sim 71.2$ grams of aluminum per minute. The aluminum is assumed to be about 52% of the total for both cans, so $(71.2/0.52) \sim 137$ grams of scrap are assumed to be dissolved per minute. This will produce $(137*0.775) \sim 106.2$ cc of hydrogen per minute.

It is conservatively assumed the volume increases 5% due to bubble retention during the maximum gas generation rate (Reference 6). It is also assumed that a "mound" of liquid and gas underneath the charge chute occupies about 1.5 liters of the gas space volume. This reduces the dissolver gas space to about 11 liters volume. If liquid is expelled during "burps," the vapor space increases.

From gas flow rates, the duration of a "burp" is expected to be five seconds or less. The hydrogen concentration is evaluated for a very conservative "burp" duration of 25 seconds, five times the expected value.

In 25 seconds, 44.2 cc of hydrogen is expelled into 11,000 cc of vapor space. The hydrogen concentration in the vapor space, with 20 cfm purge flow, is very low. If there is no purge flow for 25 seconds, the 44.2 cc of hydrogen is added to the 11,000 cc vapor space, resulting in a concentration of $(44.2/11,000) \sim 4.0E-03$ or 0.40 % hydrogen. This neglects potential temperature differences between the hydrogen and the vapor space but these would not cause the hydrogen concentration to exceed 1%. Therefore, even with a very conservative flow interruption time, and conservatively neglecting the dilution by other chemically-generated gases, the hydrogen concentration stays well below 1% during the event.

The purge flow rate is 20 CFM at one atmosphere and 72 °F. Conservatively assuming the vapor space is at the same conditions, a 14-liter vapor space will be replaced seven times in about 11 seconds. This will dilute any hydrogen in the vapor space by a factor of about 1000, or to a negligible concentration. Therefore, an 11-second duration between burps is sufficient to reduce any accumulated hydrogen to negligible concentrations.

This conservative analysis shows that the hydrogen concentration in the dissolver was maintained at or below 1% by volume during the event. In addition, it is recognized that the LFL is reduced with increasing temperature. At ambient conditions, the LFL for hydrogen in air is 4 volume %. This value is reduced as temperature is increased.

In this case, the large purge rate serves to limit the temperature rise in the dissolver vapor space, minimizing the decrease in the LFL. The analysis presented above shows that a maximum concentration of 0.52 volume percent hydrogen could have occurred in the dissolver. The minimum LFL that would be protected during the event would be four times the maximum hydrogen concentration (since HB-Line is required to control to 25% of LFL and 1/0.25 = 4). This results in a minimum LFL of 2.08 volume percent.

The LFL would have to be reduced to 2.08 volume percent for HB-Line to have violated the 25% of LFL requirement. The magnitude of this shift is not possible given the temperatures associated with Phase I operations. Therefore, no violation of the 25% of LFL requirement occurred during the event.

In the event of a loss of purge, HB-Line would still have maintained hydrogen below 25% of the LFL. The mechanism by which purge flow would have been lost in this event would require a gas flow rate that was larger than was calculated in Section 3.3. The total flow rate of gasses would have to be greater than the 7 cfm of gasses calculated in Section 3.3. The hydrogen production rate from the first charge would remain unchanged because the increased gas generation rate would have produced nitrogen oxides. Section 3.5 calculates that 0.104 cfm of hydrogen conservatively represents the hydrogen generated from the combination of cans MC02-181A and MC02-201A. This would result in a hydrogen concentration in the generated gasses of (0.104/7) 1.5 volume percent. Since much more nitrogen oxides gas would have been produced, the concentration of hydrogen would be less than 25% of the LFL as required by the HB-Line Safety Basis.

3.6 Description of Potential Mechanism That Discharges Liquid/Gas Through the Charge Chute

One mechanism was proposed that could explain an eruction of a liquid/vapor mixture through the charge chute. Such a mechanism has the potential to block the charge chute for brief periods of time. The analysis has shown that even during brief losses of purge, HB-Line maintained hydrogen concentration below 1% by volume. The following provides a description of how such a mechanism may have occurred in HB-Line, describe the potential behavior of the eruction, and propose how such this mechanism may be prevented in the future.

Reference 2 shows the dissolver dimensions. The dissolver contained about 16 liters of 12M nitric acid. The liquid height in the dissolver was about 9 inches, and the liquid height was about 7 inches below the top of the dissolver at ambient conditions. The charge chute is 3-inch schedule 40 pipe and the vessel vent system connection is 2-inch schedule 40 pipe.

Up to 7 cfm of non-condensable gas can be produced at peak reaction conditions. Per the previous analyses on heat losses, the maximum reaction rate occurs when the reaction first reaches the highest temperatures. If this postulated mechanism were correct, it would be more likely to occur at times of peak gas generation rates, rather than during the heatup.

A two-phase flow expert was consulted (Reference 6). The opinion was that entrainment of the gas generated in the bulk liquid was unlikely if the reaction were occurring throughout the bulk of the liquid. A volume increase of about 5% was stated to be bounding, based on judgment. However, the expert felt there was a potential mechanism for carrying a liquid-air mixture up the charge chute. If the mixer did not rapidly disperse the scrap when poured in, and most of the scrap settled to the side of the dissolver under the charge chute, enough gas could be generated locally to cause a vertical "mound" of gas-water mixture above the bulk liquid level. The gas velocity could be sufficient to

carry some material from the top of the liquid-gas "mound" into the charge chute and expel this mixture from the charge chute. The upflow of liquid below the charge chute from the agitator in the dissolver enhances the chances of forming a "mound." This could temporarily block the charge chute when the gas-liquid mixture "burped" from the top of the charge chute. This process can repeat as often as long sufficient gas is released. Gas and liquid would rapidly separate once the mixture cleared the top of the charge chute. Hot yellowish-colored nitrogen dioxide (NO₂) fumes would rise into the glovebox from the separated mixture.

This mechanism would block the charge chute while the column of liquid-gas mixture was being expelled. The charge chute clears once the liquid-gas column is expelled. The flow rate of gas to suspend the gas-liquid column is about one foot/second or greater, and the charge chute is about 1.5 feet in length, so gas would travel the length of the column in about 1.5 seconds. The liquid velocity in the mixture would travel slower, but the time of blockage would probably be less than five seconds.

This mechanism could explain the presence of colored gas in the glovebox during heatup and the presence of liquid around the dissolver charge chute after the event was over. This mechanism does not explain the response of the pressure instrumentation that shows long periods of positive pressure in the dissolver. This is discussed in Section 3.2 of this report.

Per Reference 6, this phenomenon can be avoided by charging smaller portions of aluminum. The gas generation rate would be smaller since there is less aluminum to react with the acid and create gas bubbles.

4.0 Analysis of the Appropriateness of LCO 3.3.2A Condition B with Exothermic Reactions

The HB-Line Safety Basis requires control of hydrogen to 1% by volume. The analysis presented has shown that HB-Line did not exceed this limit. The LCO control requires that the heater block be turned off and material stop being added to the dissolver when an upset in purge occurs. Given the highly exothermic nature of the reaction without additional heat input has called into question the adequacy of this response. The following analysis will show that the action required by the LCO is appropriate and prove that the Safety Basis controls protect against the hydrogen hazard.

The Safety Basis controls in place for H2 generation are two fold. The first is TSR Administrative Control 6.4.17.4A and the other is the JCO actions (3.3.2.A) that require turning off the heater block if air purge is lost to the dissolver. Each will be discussed.

Administrative control 6.4.17.4A is in place to limit the amount of material to ensure the facility does not exceed H_2 concentration of 25% of the LFL during dissolution in normal operations. Administrative Control 6.4.17.4 states "Controls shall be in place to prevent dissolution of Mixed Scrap material whose hydrogen generation rate could challenge the

capability of the dissolver hydrogen dilution and removal controls to perform their safety functions." It further states "Before Mixed Scrap material can be processed, engineering shall evaluate its hydrogen capability." The engineering evaluation shall specify limits on the amount of material that can be charged in a dissolver batch. The information for developing H₂ calculations is derived from analytical lab analysis and statistical analysis of the material being charged. The Administrative Control further states that "The processing of any Mixed Scrap material whose hydrogen generation rate (radiolytic and chemical) could challenge the capability of the Scrap Recovery Glovebox Exhaust System and dissolver vacuum instrumentation to maintain a hydrogen concentration less than or equal to 25% LFL in the dissolver vapor space, or whose chemical hydrogen rate could cause the hydrogen concentration in the dissolver vapor space to exceed the LFL if the Scrap Recovery Glovebox Exhaust System and/or dissolver vacuum instrumentation became inoperable and compensatory controls were not established, shall not be permitted." This requirement applies to all factors (radiolytic and chemical) that could cause hydrogen generation, including the heat of reaction and its contribution to the hydrogen gas evolved.

The IMMEDIATE ACTION to turn the heater block off associated with LCO 3.3.2.A, is concerned with slowing down the chemically generated hydrogen into the dissolver vapor space if the heater is on. Once heatup of the process begins, using the heater, a calculated amount of H_2 will be produced based on the above calculations (in the Administrative Control). Therefore, the total amount of H_2 is calculated prior to each charge. If the total H_2 generation is limited by charge size then the action to turn off the heater block is proper for conditions affecting the air purge.

5.0 Safety Basis Requirements Applicable to Event

All Safety Basis requirements applicable to this event are listed below. This includes controls from the: SAR, JCO for Alternate Hydrogen Control, TSR, and Double Contingency Analysis (DCA) controls. HB-Line Safety Basis compliance is discussed below each control.

SAR (WSRC-SA-2001-00009, Rev. 0)

Commitment: Rejected material will be processed after adequate controls have been developed and implemented.

Compliance: The JCO for Alternate Hydrogen Control (Reference 12) was written, approved, and implemented to meet the SAR commitment

Commitment: Materials will be evaluated for CEDE compliance.

Compliance: Each hydrogen calculation contains a section addressing the CEDE of the material that is authorized for processing. None of the Desicooler material contains a CEDE higher than stated in the SAR.

JCO for Alternate Hydrogen Control (WSRC-RP-2002-000615, Rev. 0)

LCO 3.1.2A: The LCO contains requirements of the Glove Box Exhaust System for processing of high hydrogen generating material. This LCO replaces LCO 3.1.2 of the HB-Line TSR. The requirements of the LCO are as follows:

- 1. Each HB-Line Glovebox Exhaust System shall be OPERABLE (1 fan in service, 1 OPERABLE fan in standby)
- 2. Each glovebox low vacuum alarm shall be OPERABLE with a setpoint that ensures the alarm actuates if the vacuum in the respective glovebox is less than 0.3 inches Water Gage (WG) relative to maintenance areas

Compliance: The glovebox exhaust system was OPERABLE as defined by the LCO and vacuum alarm setpoints are set to ensure 0.3 inches water gage vacuum is maintained. No glovebox low vacuum alarms were received during the event. All Surveillance Requirements associated with the LCO were current at the time of the event.

LCO 3.3.2A: The LCO contains the requirements of the Air Purge for Dissolvers (RD-13 and RD-14). This LCO replaces LCO 3.3.2 of the HB-Line TSR. The requirements of the LCO are as follows:

- 1. Each charge chute cover shall be removed and made inaccessible
- 2. The charge chute on each dissolver is free of obstructions
- 3. Three (3) H-Canyon Exhaust Fans are Operating
- 4. The Building Backup Power System is OPERABLE

Compliance:

- 1. The charge chute cover was removed from the charge chute and bound by wire to a fixed object away from the charge chute. This ensured that the charge chute cover was removed and inaccessible.
- 2. The charge chute cover must remain unobstructed to ensure that adequate purge flow is available for hydrogen dilution to maintain the hydrogen concentration to below 25% of the LFL. Based on the evaluation of this event, the ability of the system to supply sufficient purge for hydrogen dilution was not compromised. Periodic "burping" of the dissolver would not have compromised the ability of the system to supply purge to maintain 25% of the LFL.
- 3. Three H-Canyon Exhaust Fans were Operating during the event.
- 4. The Building Backup Power System was operable during the event

All Surveillance Requirements associated with the LCO were current at the time of the event.

AC 6.4.17.4A: This Administrative Control (AC) replaces AC 6.4.17.4 of the HB-Line TSR. This AC requires an engineering evaluation to ensure that the hydrogen concentration can be maintained less than or equal to 25% of LFL with a flow rate through the dissolver charge chute of 20 cfm during normal operations. It shall ensure that the hydrogen concentration can be maintained at less than LFL with a flow rate of 6.6 cfm through the dissolver charge chute during abnormal operations (inoperable Scrap Recovery Glovebox Exhaust System).

Compliance: An engineering evaluation as described above was performed for all material charged to the dissolver during this event. This evaluation was based on a laboratory analysis of the hydrogen generation properties of the Desicooler material. The hydrogen calculation also serves as the vehicle for complying with a SAR commitment to analyze the CEDE of the material and supplements the administrative control for preventing an uncontrolled reaction. The requirements of these controls are listed separately in the sections related to the SAR and TSR. The hydrogen controls outlined in the evaluation were not violated during the event.

Design Feature A.1.3A Process Vessels

The design feature replaces Design Feature A.1.3 of the HB-Line TSR. The only change made was to remove the credit taken for a hole in the dissolver charge chute cover. Under TSR purge controls, this hole provides the path for purge air through the dissolvers. Under the JCO purge controls, the charge chute cover is removed so the hole becomes the entire charge chute. The requirements to assure that the hole retains its function are covered in LCO 3.3.2A. The charge chute cover is prevented from being restored by LCO 3.3.2A. Since entry into LCO 3.3.2A was not required, the design feature was intact during the event.

TSR (WSRC-TS-97-7, Rev. 13)

LCO 3.4.1: This LCO contains the requirements for the Backup Power System. The requirement is as follows:

The Building Backup Power System shall be OPERABLE

Compliance: The Building Backup Power System was OPERABLE during the event. All Surveillance Requirements associated with the LCO were current at the time of the event and did not impact the event.

AC 6.4.17.1: This AC requires that process controls to prevent an uncontrolled reaction in a Phase I dissolver. Controls shall be in place to prevent the processing of quantities of metals incompatible with nitric acid dissolution that could cause an uncontrolled reaction.

Compliance: An uncontrolled reaction is controlled primarily by engineering evaluation. The evaluation for hydrogen required by AC 6.4.14.4A also analyzes the reactivity potential of the material to be processed. In addition, all material is passed through a #10 mesh screen prior to charging in a Phase I dissolver.

Design Feature A.1.6 Vessel Vent System Piping

The VVS piping serves as an SS component to prevent the hydrogen deflagration. The system piping provides a vent path to the H-Canyon Exhaust Ventilation System for sweeping hydrogen from the vessels.

During the event, no deflagration or detonation occurred. No other accident or event occurred which could prevent the VVS piping from serving the function of providing a vent path to the H-Canyon Exhaust Ventilation System.

Design Feature A.1.13 Scrap Recovery Glovebox Exhaust System Ductwork

The Scrap Recovery Glovebox Exhaust System ductwork serves as a SS component to prevent hydrogen deflagration. The ductwork provides a continuous flow path for purge air to be drawn through the process vessels to the H-Canyon Exhaust Ventilation System.

During the event, no deflagration or detonation occurred. No other accident or event occurred which could prevent the Scrap Recovery Glovebox Exhaust System Ductwork from serving the function of providing a vent path to the H-Canyon Exhaust Ventilation System.

Double Contingency Analysis (N-NCS-H-00120, Rev. 7)

There are no credible criticality scenarios for the Scrap Recovery dissolvers.

The CSL for full water reflected, dry plutonium oxide is 9 kg of Pu-239. HB-Line procedurally limits dissolver runs to less than 1.5 kg Pu-239 equivalent. HB-Line screens all material prior to charging to ensure that no fissile metal is charged to the dissolver. The dissolver charge was less than 1.5 kg Pu-239 equivalent. Since these requirements were met, no violation of DCA controls occurred during the event.

Other Scrap Recovery Controls

Scrap Recovery controls also include requirements on the handling of material, movement of the dissolved material to the Product Hold Tanks (PHT's), and the transferring of dissolved material to H-Canyon for further disposition. Among these controls are LCO 3.3.1 for Process Air compressors, LCO 3.3.3 for Process Air Purge in PHT's and filtrate tank, and LCO 3.5.2 for Nuclear Safety Interlocks on the PHT's. Scrap Recovery also contains additional criticality controls. None of these additional controls are applicable to the dissolvers.

HB-Line also has facility requirements. LCO's for the sand filter, ventilation interlocks, tornado dampers, fire detection system and NIM coverage all appear in the HB-Line TSR. None of these controls applied directly to the event and are not further explained in this report.

All controls applicable to the event have been identified above along with an explanation of how HB-Line maintained compliance through the event. Since compliance with all requirements was maintained, no Safety Basis violation occurred.

6.0 ISMS Review

The technical analysis presented in Section 3.0, 4.0, and 5.0 concludes that no Safety Basis violations occurred and that no PISA exists for this event. The technical analysis verifies that hydrogen generation did not exceed 1% of LFL in the dissolver vapor space nor were dissolver purge requirements violated.

Applying the principles of the ISMS, it is recognized that WSRC failed to implement adequate process controls to limit the rate of exothermic reaction in RD-13. The rate of the aluminum reaction was not adequately forecasted. Lab characterization results indicated the material had significant amounts of aluminum, which should have resulted in more restrictive operating controls to limit the rate of material addition to the dissolver to account for aluminum generated exothermic reactions. The laboratory analysis adds acid to scrap versus the scrap to acid addition in HB-Line. The addition of acid to scrap in the lab disperses the scrap at the bottom of the laboratory dissolver. This emulates the effects of the HB-Line agitator.

Future charges of scrap will be more thoroughly controlled to ensure the rate of addition is not going to produce exothermic reactions beyond expected values. For the remaining desicooler material the rate of addition will be controlled to ensure total heat generated from the scrap will not exceed a predetermined total temperature rise in the liquid. The implementation for the new restrictions is going to be controlled through technical engineering evaluations consistent with current administrative TSR/JCO controls and facility procedures.

7.0 Analysis of Adequacy of the Safety Basis

During the Desicooler event, the Safety Basis succeeded in controlling the hazards. The controls ensured that the hydrogen concentration in the dissolver vapor space did not exceed 25% of the LFL as shown above. The Safety Basis Hazard Analysis considered hazards of this type in Reference 11 (Event Number SR-14) and determined them to be Hazard Category III and not require controls in the Safety Basis. Based on this, the HB-Line Safety Basis is deemed adequate to prevent the hazards associated with this event.

8.0 Conclusions

Analysis of the Desicooler event with respect to Safety Basis requirements has shown that no Safety Basis violation occurred during the Desicooler event. Applying the principles of the ISMS, it is recognized that WSRC failed to implement adequate process controls to limit the rate of exothermic reaction in RD-13. This is not a Safety Basis issue and will be addressed through the ISMS process.

The conservative analysis of the available information shows that the hydrogen concentration during the event did not exceed 25% of the LFL. The purge rate of 20 CFM was maintained except for possible brief periods where liquid-gas mixture was possibly being expelled through the charge chute. Even during these brief periods, the hydrogen concentration did not exceed 25% of the LFL. All other Safety Basis controls were maintained and no Safety Basis violation occurred. The Safety Basis successfully controlled hydrogen to below 25% of LFL. The Safety Basis controls successfully prevented an uncontrolled chemical reaction and this type of event was analyzed in the Hazards Analysis. Based on these results, a PISA does not exist and the Safety Basis protects the worker, the facility and the public.

9.0 References

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- 12. WSRC-RP-2002-00615, Rev. 0, Justification for Continued Operations: Alternate Hydrogen Control for Phase I Scrap Recovery Processing (U), March, 2003.
- 13. WSRC-TR-2003-00029, Rev. 0, *HB-Line Dissolver Dilution Flows and Dissolution Capability with Dissolver Charge Chute Cover Off* (U), January 15, 2003.

Appendix A: Narrative Time Line of Desicooler First Charge Event

0449 hrs. Charge started for RD 13. Assume a one minute charge time. Temp = 28.53C at beginning of the charge.

0450 hrs. Charge complete. (Logs and procedures match completion time). Temp = 31.51 C at the end of the charge. Agitator is on during charge.

0454:30 hrs. Initial rise in vacuum pressure as indicated by RD 13 instrumentation.

0456 hrs. High level alarm received in the Phase 1 CCR.. Temp is 68.82C. 0500-0502 hrs. Gas in GB line reported two at two different times by operators (0500 hrs and 0502 hrs). Two different log books accounts record varying times of eyewitness accounts of gas in the glove box. Temp is 100 C (0500 hrs) and 110 C (0502 hrs). Gas lasted ~ 5 minutes per eyewitness accounts.

0505:50 hrs. Max temp = 111 C.

0509:30 hrs. Dissolver temperature starts to drop off from 111 C. Duration of boiling plateau (max temperature) = 3 minutes 40 seconds.

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Appendix B: Temperature Profile for First Desicooler Charge



RD-13 Temperature (5-29-03 Time Adjusted back 67 Min 30 Sec)

Appendix C: Aluminum Dissolving Effects of Chemical Variables on Dissolving and Gas Evolution Rates, Ray McJunkin,

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From: Ray McJunkin, 772-F

RTA 544-S: Aluminum Dissolving-Effects of Chemical Variables on Dissolving and Gas Evolution Rates

Initiation of work on this RTA was indicated in last month's report. The work has been continued and all of the data collected to date is presented in this report.

A generous amount of literature on Al and U-Al alloy dissolutions using Hg^{++} catalyzed HNO3 reactions has been received as the result of a literature search by Erma Kauer, TIS Library. Most of the information is concerned with continuous dissolver processes and offers no aid with respect to the problem of liquid ejection in the batch type operation. However, notice is paid to the initial vigorous, reaction that occurs and has been prominent in the tests conducted here; and, if controlled might eliminate liquid ejection.

RTA 544-S requests analysis of evolved gases at various stages of the dissolving process using different dissolving conditions. Compositions of the gases evolved from Al-HNO3 reactions is well documented in the literature and, I think, is not a necessary analysis in this study. One appraisal of the various reactions and the gases evolved is given by J. T. Long(1). He states that "Aluminum and nitric acid can react in several different proportions, forming the reaction products given by Eqs. 4.6 to 4.10".

$AL + 6HNO_3 \longrightarrow AL(NO_3)_3 + 3NO_2 + 3H_2O$	(4.6)
$AL + 4HNO\overline{3} \longrightarrow AL(NO\overline{3})\overline{3} + NO\overline{4} 2H_2O\overline{1}$	(4.7)
8AL + 30HNO3 \rightarrow 8 AL(NO3)3 + 3N20 + 15H20	(4,10)
$10AL + 36HNO_3 \rightarrow 10AL(NO_3)_3 + 3N_2 + 18H_2O_1$	(4.20)
$2AL + 6HNO_3 \rightarrow 2AL(NO_3)_3 + 3H_2$	(4.10)

Where 6, 4, 3.75, 3.6, and 3 moles of acid are consumed, respectively, per mole of aluminum. All these reactions occur to some extent, evidence of all the gaseous products being found in the dissolver off-gas. However, as the concentration of the reacting acid decreases, the dissolution shifts toward the reactions that consume the least acid, i.e. from the top of the list (Eq. 4.6) to the bottom (Eq. 4.10). Hydrogen evolution is very low at concentrations above 1 or 2 M nitric acid but becomes appreciable (as much as 23 percent of the off-gas) in acid deficient systems."

The first series of tests was intended to show gas flow and dissolving rate characteristics at various acid and mercury catalyst concentrations. The quantity of aluminum, volume of dissolver solution, and concentrations of dissolver (except 10M HNO₃) led to an acid deficient system - a condition not acceptable for our plant process dissolver. The test data are shown in Table 1. The gas flow numbers reflect the relative violence of the initial reaction. Redish-brown gases dominated the evolved gases during the first 3 to 6 minutes after initial reaction. They were gradually replaced by colorless gases at acidities less than 7M but remained throughout the dissolution for higher acidities. A globule of metallic

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mercury was present in the final solution in all cases except for 10M HNO₃. The low mercury concentration (1.7×10^{-6}) resulted in a very vigorous, pulsating type reaction that dissolved the aluminum at a slow rate, only 50% was dissolved in a period of 50 minutes. Figure 1 is a plot of the gas flow from the reaction (as indicated on a rotometer) vs. dissolver time for (1) 5M HNO3, 10^{-4M} Hg, and 5.5 g of AL raised from a cold start to boiling during a 10 minute interval, and (2) for addition of Hg⁺⁺ to AL-HNO3 at the boiling point. The vigor of the initial reaction is reduced to some extent when proceeding from a cold start.

Test data for the reaction of 1.1 gram samples with about 9 and with about 15 square centimeters of surface area, and 5.5 gram samples with about 28 square Centimeters of surface area are shown in Table 2 for comparison of surface area effect, the effect of mercury additions at boiling vs. cold starts with mercury present in the dissolver, and acid deficient conditions (5.5 gram Al specimens) vs. acid conditions.

Aluminum nitrate is regarded as an inhibitor of the Hg++ catalyzed nitric acid reaction with aluminum. Tests were made to determine if $Al(NO_3)$ at concentration of 0.25M and 0.1M in the dissolver solution would reduce the vigor of the initial reaction. The test data are presented in Table 3. As expected, the dissolution rate is lowered and the vigor of the initial reaction is significantly reduced.

Dissolution tests were conducted using three different uranium-aluminum alloy compositions and varied combinations of HNO₃-Hg⁺⁺ concentrations. The data are presented in Table 4. The tests proceeded from a cold start to boiling in 10 minutes. 100 M volumes of HNO₃ Hg⁺⁺ dissolver solution were used. The alloy specimen ranged from 1.3 to 1.7 grams in weight and 4 to 6 sq. cm. in surface area. There were no initial vigorous reactions such as those observed with aluminum metal. Gas evolution was less in all cases than the mildest case for 1100 aluminum.

It appears that at least 3 dissolving systems are capable of reducing the initial violent reaction between aluminum and HNO3 with Hg++ catalyst below the level experienced for Hg++ addition to aluminum in boiling nitric acid which is the plant procedure.

- Starting cold with Hg⁺⁺ present in the HNO3.
 Starting cold with Hg⁺⁺ + about 0.1M Al(NO3)3 in the HNO3.
 Starting cold with Hg⁺⁺ in ~ 3M HNO3, then increasing the HNO3 concentration after initial reaction.

J. M. McKibben and J. E. Koonce, WT-ST will be consulted before additional work is performed on RTA 544-S

(1) J. T. Long, "Spent Fuel Dissolution", Engineering for Nuclear Fuel Reprocessing.

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Appendix C:	Aluminum Dissolving Effects of Chemical	Variables on Dissolving and
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5 M HN03 5 M HN03 6 M HN03 7 M HN03 6 M HN03 6 M HN03 10 M HN0	NO3 6.9×10^{-4} M Hg ++ NO3 1.1×10^{-3} M Hg ++ NO3 2.3×10^{-4} M Hg ++ NO3 1.1×10^{-3} M Hg ++ NO3 1.1×10^{-3} M Hg ++ NO3 1.1×10^{-3} M Hg ++ NO3 1.1×10^{-4} M Hg ++ NO3 1.1×10^{-4} M Hg ++ NO3 1.1×10^{-5} M Hg ++	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
5 M HNO3 5 M HNO3 5 M HNO3 5.5 M HNO3 5.5 M HNO3 5.5 M HNO3 5.5 M HNO3 6 M HNO3 7 M HNO3 7 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 1.1 6 M HNO3 1.2 10 M HNO3 1.3 10 M HNO3 1.1 10 M HNO3 1.3 1.1 10 M HNO3 1.1 10 M HNO3 1.3 1.1 10 M HNO3 1.3 1.1 1.1 1.1 1.1 1.1 1.1 1.	$\begin{array}{c} 1.1 \times 10^{-3} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-3} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-3} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 2.3 \times 10^{-4} \text{ M H}_8^{++} \\ \text{NO}_3 & 1.1 \times 10^{-3} \text{ M H}_8^{++} \\ \text{NO}_3 & 1.1 \times 10^{-3} \text{ M H}_8^{++} \\ \text{NO}_3 & 1.7 \times 10^{-6} \text{ M H}_8^{++} \\ \text{MO}_3 & 1.7 \times 10^{-6} \text{ M H}_8^{++} \\$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	00000000000000000000000000000000000000
5 M HNO3 5.5 M HNO3 5.5 M HNO3 5.5 M HNO3 5.5 M HNO3 5.5 M HNO3 6 M HNO3 7 M HNO3 7 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 1.1 6 M HNO3 1.1 10 M HNO3 1.2 10 M HNO3 1.1 10 M HNO3 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.	NO3 2.3 x 10-3 M Hg ++ NO3 2.3 x 10-4 M Hg ++ NO3 3.3 X 10-4 M Hg ++	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	00000000000000000000000000000000000000
5.5 M HNO3 2.3 5.5 M HNO3 2.3 6 M HNO3 2.3 6 M HNO3 2.3 6 M HNO3 2.3 6.5 M HNO3 2.3 7 M HNO3 2.3 10 M HNO3 1.1 10 M HNO3 1.1 10 M HNO3 1.7 6 M HNO3 1.7 </td <td>$\begin{array}{c} 4.6 \times 10^{-5} \text{ M Hg} \\ \text{NO3} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1003 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1003 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1.0 \\ 3.3 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.0 \\ 3.3 \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-6}$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>00000000000000000000000000000000000000</td>	$\begin{array}{c} 4.6 \times 10^{-5} \text{ M Hg} \\ \text{NO3} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1003 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1003 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1.0 \\ 3.3 \\ 2.3 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.0 \\ 3.3 \\ 1.1 \times 10^{-5} \text{ M Hg} \\ 1.1 \times 10^{-6} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	00000000000000000000000000000000000000
J.J. M. HNO3 J.J. M. HNO3 J.	NO3 2.3 × 10-3 M Hg ++ NO3 2.3 × 10-4 M Hg ++ NO3 2.3 × 10-3 M Hg ++ NO3 2.3 × 10-4 M Hg ++ NO3 2.3 × 10-5 M Hg ++ NO3 2.5 × 10-5 M Hg ++	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
6 M HNO3 2.3 6 M HNO3 2.3 6.5 M HNO3 2.3 7 M HNO3 2.3 7 M HNO3 2.3 7 M HNO3 2.3 7 M HNO3 2.3 10 M HNO3 1.1 10 M HNO3 1.1 10 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 1.1 6.9 10 M HNO3 1.1 10 M H	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
6 M HNO3 6.5 M HNO3 7 M HNO3 7 M HNO3 7 M HNO3 7 M HNO3 7 M HNO3 10 M HNO3 1.1 6 M HNO3 1.1 10 M HNO3 1.2 10 M HNO3 1.1 10 M HNO3 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1100 ALUMINUM (~ 28 GM ² 8	
6.5 M HNO3 7 M HNO3 7 M HNO3 7 M HNO3 7 M HNO3 10 M HNO3 1.1 6 M HNO3 1.1 10 M HNO3 1.2 10 M HNO3 1.1 10 M HNO3 1.1 1.1 10 M HNO3 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
 A HNO3 A HNO	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1100 ALUMINUM (~ 28 GM ² 8	000000000
7 M HNO3 6.9 7 M HNO3 1.1 7 M HNO3 1.1 7 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 1.1 6 M HNO3 1.1 10 M HN	$\begin{array}{c} & & & & & & & & & & & & & & & & & & &$	1100 ALUMINUM (~ 28 GM ² s	
7 M HNO3 7 M HNO3 10 M HNO3 1.1 10 M HNO3 1.7 10 M H 1.7 10 M H 1.7	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19 9 20 30 32 10 10 ALUMINUM (~ 28 CM ² s	0000000 77 23 77 23
7 M HNO3 7 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 10 M HNO3 1.1 6 M HNO3 1.1 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker soids ejected liquid f flow is shown as	NO3 2.3 x 10 ⁻³ M Hg ⁺⁺ NO3 4.6 x 10 ⁻³ M Hg ⁺⁺ NO3 6.9 x 10 ⁻⁴ M Hg ⁺⁺ NO3 6.9 x 10 ⁻⁴ M Hg ⁺⁺ NO3 1.1 x 10 ⁻⁴ M Hg ⁺⁺ NO3 1.7 x 10 ⁻⁶ M Hg ⁺⁺	9 20 30 . ≫ 20 32 . ∞ 20 ≫ 20 	000000
7 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 1.1 6 M HNO3 1.7 TABLE 1. DISSOLUTION DATA 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker soids ejected liquid f flow is shown as	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
10 M HNO3 2.3 10 M HNO3 2.3 10 M HNO3 1.1 6 M HNO3 1.7 TABLE 1. DISSOLUTION DATA 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker soids ejected liquid f flow is shown as	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32 20 100 ALUMINUM (~ 28 CM ² S	
10 M HN03 1.1 6 M HN03 1.7 TABLE 1. DISSOLUTION DATA 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker acids ejected liquid f flow is shown as	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	>>20 20 1100 ALUMINUM (~ 28 CM ² S	
6 M HNOJ 1.7 TABLE 1. DISSOLUTION DATA 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker acids ejected liquid f flow is shown as	NO3 1.7 x 10 ⁻⁶ M Hg ⁺⁺	20 1100 Aluminum (~ 28 cm² s	0
TABLE 1. DISSOLUTION DATA 100 MILLILITERS The dissolver so boiling in 10 mi time under the d in weaker acids ejected liquid f flow is shown as	SOLUTION DATA FOR 5.5 GRAMS OF 1	1100 ALUMINUM (\sim 28 cm ² s	
The dissolver so boiling in 10 mi time under the d in weaker acids ejected liquid f flow is shown as	MILLILIERS OF NIERIC ACLD DISC	SOLVER SOLUTION	URFACE AREA) IN
in weater acids ejected liquid f flow is shown as	dissolver solution and aluminum	n specimen were heated fro of reaction varied widely	m a cold start to with respect to
** 	weaker acids and as late as boil acted liquid from the boiling fla aw is shown as greater than 200.	ling in 10M acid. The vig 1sk in those cases where t	or of the reaction he maximum gas
*			
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I uge e o			
TABLE	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		WT. Q
2 DISSOLUTION DAT/ OF ALUMINUM, DIF BOILING ACID The 5.5 gram alu point in the rea for 5M HNO3, 3 f provide a system	28 28 28 28 28 28 28 28 28 28 28 28 28	00005 15	SAMPLE SURFACE, CM ²
FOR COMPARISON OF GAS FLOW AND DISSOLVING RATES FERENT ACIDITIES, AND COLD START UING MIXED ACID minum samples in 100 ml dissolver solutions give retion to completion. For each mole of aluminum or 6M HNO3 is provided. 3.8 moles of HNO3/mole of that is not acid deficient.	6M HNO3 2.3 × 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 3M HNO3 2.3 × 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 3M HNO3 Made 1.7 × 10 ⁻⁴ M Hg ⁺⁺ At Boiling 5M HNO3 Made 1.7 × 10 ⁻⁴ M Hg ⁺⁺ At Boiling 5M HNO3 2.3 × 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 6M HNO3 2.3 × 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 6M HNO3 Made 1.7 × 10 ⁻⁴ M Hg ⁺⁺ At Boiling	5M HNO3 2.3 \times 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 5M HNO3 Made 1.7 \times 10 ⁻⁴ M Hg ⁺⁺ At Boiling 5M HNO3 Made 1.7 \times 10 ⁻⁴ M Hg ⁺⁺ At Boiling 5M HNO3 2.3 \times 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 3M HNO3 2.3 \times 10 ⁻⁴ M Hg ⁺⁺ From Cold Start 3M HNO3 Made 1.1 \times 10 ⁻⁴ M Hg ⁺⁺ At Boiling 6M HNO3 Made 1.1 \times 10 ⁻⁴ M Hg ⁺⁺ At Boiling	TEST CONDITIONS, 100 ML SOLUTIONS
AT DIFFERENT WEI + Hg ⁺⁺ ADDITI an acid deficien .5 moles of acid f aluminum is rea	4 1/2 45 24 22 24 22 24 1/2	8 6 1/4 9 3/4 6 3/4 10 1/4 12 7 1/2	DISSOLVING TIME, MIN.
GHTS AND SURF ON OF Hg ⁺⁺ TO t reaction fr for 3M HNO ₃ , quired to	90 100 170 100 9 200 200	70 120 70 70 40	MAXIMUM GAS FLOW
ACE AREAS	9 7 4 4 F ∞ ∞ 7	10 10 10 10 10 10 10 10 10 10 10 10 10 1	DISSOLVING RAT MG/MIN/CM ²

Appendix C: Aluminum Dissolving Effects of Chemical Variables on Dissolving and Gas Evolution Rates, Ray McJunkin, Page 5 of 7

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Appendix C:	Aluminum Dissolving Effects of Chemical Variables on Dissolving and
	Gas Evolution Rates, Ray McJunkin,

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Appendix C:	Aluminum Dissolving Effects of Chemical Variables on Dissolving and
	Gas Evolution Rates, Ray McJunkin,

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•	TABLE 4 DISSOL In case of not	EXTRUDED GRADE	CAST URANIUM ALUMINUM ALLOY 9.5% U 13.2% U 25% U
· · · · ·	JTION DATA FOR DIFFE s where the dissolut being catalyzed by t	7	5.5 M HNO3 2.3 x 10-4 M Hg++ 1.2 0.3 5
	RENT COMPOSITIONS OF tion was less than 3 the Hg++. H2 bubble	. 10	5.5 M HN03 2.3 x 10-3 M Hg++ 6 3 10
	URANIUM-ALUMINUM A mg/min/cm ² , the re s were large and li	I	SM HNO3 1 × 10-2 M Hg++ 2.5 8
	LLOY AND FOR COMPAR action had the visu ttle or no foaming	22	DISSOLVING RATE, 7M HNO3 2.3 x 10-3 M Hg++ 6 4
	ISON, 1100 ALUMINUM al appearance has observed.	VIOLENT REACTION EJECTED LIQUID	Mg/MIN./Cm ² 10M HNO3 1.1 × 10-3 M Hg++ 2 0.9

Compound	Heat of		Heat of	Units on	Reference #
-	Formation,		Formation,	Heat of	
	Kcal/mole			Formation	
A12O3	-399.09	8			3
Al(NO3)3	-275.87	9	-1155	kJ/mole	7
Al(NO3)3:6H2O	-680.69	10			3
Al(NO3)3:9H2O	-897.59	11			3
Ca(NO3)2	-228.29	13			3
Ca(NO3)2:2H2O	-367.95	14			3
Ca(NO3)2:3H2O	-439.05	15			3
Ca(NO3)2:4H2O	-509.43	16			3
HNO3	-41.35	18			3
HNO3:H2O	-112.91	19			3
HNO3:3H2O	-252.15	20			3
H2O	-68.3	22			3
NO	21.6	24			3
NO2	7.96	25			3
N2O	19.49	26	81.6	kJ/mol	7
UO2(NO3)2	-319.11	31	-1472	btu/lb	8
UO2(NO3)2:6H2O	-756.8	32			3
UO3	-291.6	33			3
U3O8	-845.1	34			3

Appendix D: Thermodynamic Values and Reactions for Aluminum and Uranium Dissolution in Nitric Acid, Page 1 of 4

Appendix D: Thermodynamic Values and Reactions for Aluminum and Uranium Dissolution in Nitric Acid, Page 2 of 4

Reaction 1:					
Delta Hf =	-208.787	Kcal/mole Al =		-7.73	Kcal/gm Al
Reaction 2:					
Delta Hf =	-225.467	Kcal/mole Al =		-8.35	Kcal/gm Al
Reaction 3:	8Al + 30H	NO3 = 8Al(NO)	D3)3 + 1	3N2O + 15	H2O
Delta Hf =	-1932.47	Kcal/8 moles A	1=	-8.95	Kcal/gm Al
Reaction 4:	10Al + 36l	HNO3 = 10Al(1)	NO3)3 -	+ 3N2 + 18	H20
Delta Hf =	-2499.47	Kcal/10 moles	Al=	-9.26	Kcal/gm Al
Reaction 5:	2Al + 6HN	JO3 = 2Al(NO3)	3)3 + 3H	-12	
Delta Hf =	-303.634	Kcal/2 moles A	1=	-5.62	Kcal/gm Al
Reaction 6:	A12O3 + 61	HNO3 = 2Al(N)	O3)3 +	3H2O	
Delta Hf =	-109.444	Kcal/2 moles A	1=	-2.03	Kcal/gm Al

Appendix D: Thermodynamic Values and Reactions for Aluminum and Uranium Dissolution in Nitric Acid, Page 3 of 4

Reaction 1: $Al + 6HNO3 + 3H2O = Al(NO3)3:6H2O + 3NO2$												
delta Hf =	-203.81	kcal/mole A	Al =	-7.28	kcal/gram Al							
Reaction 2:	Reaction 2: $Al + 4HNO3 + 4H2O = Al(NO3)3:6H2O + NO$											
Delta Hf =	-220.49	kcal/mole A	<u>1</u> =	-7.87	kcal/gram Al							
Reaction 3:	8A1 + 30H	NO3 + 33	H2O = 8Al(NO3)3:6H2	2O + 3N2O							
Delta Hf =	-1931.63	kcal/8 mole	Al =	-8.62	kcal/gram Al							
Reaction 4:	10Al + 36	HNO3 + 42	2H2O = 10	Al(NO3)3:6	H2O +3N2							
Delta Hf =	-2449.7	Kcal/10 mc	al Al =	-8.75	Kcal/gram Al							
Reaction 5:	2Al + 6HN	103 + 12H2	2O = 2Al(N)	O3)3:6H2C) + 3H2							
Delta Hf =	-293.68	Kcal/2 mole	es Al=	-5.24	kcal/gram Al							
Reaction 6:	A12O3 + 6	HNO3 + 9	H20 = 2Al(NO3)3:6H2	20							
Delta Hf =	-99.49	Kcal/2 mole	e Al=	-1.84	Kcal/gm Al							
Reaaction 7	7: $Al + 6HN$	103:H2O =	Al(NO3)3:	6H20 + 3N	O2 + 3H20							
Delta Hf =	-184.25	Kcal/mole /	Al =	-6.82	Kcal/gm Al							

Appendix D: Thermodynamic Values and Reactions for Aluminum and Uranium Dissolution in Nitric Acid, Page 4 of 4

Reaction 1:	U + 5.5HN	IO3 = UO20	(NO3)2 + 2	.25NO2 +	1.25NO + 2	2.75 H20		
delta Hf =	-234.596	Kcal/mole U	U					
Adjust for f	ormation of	different U p	product					
Reaction 2:	U+5.5HN	NO3 + 6H20	0 = UO2(N	O3)2:6H2C	+2.25NO	2 + 1.25*N	O + 2.75 H	20
Delta Hf =	-262.49	Kcal/mole U	U					
Reaction 3:	U + 4HNC	D3 + 4H2O	= UO2(NC	03)2:6H2O	+ 2NO			
Delta Hf =	-275	Kcal/mole U =		-1.17	Kcal/gm U			
Stoller says	the reaction	n generates 2	2713 BTU/lt	o (Reaction	2). Get com	version toge	ther.	
One $lb = 43$	54 grams, 1	cal = 3.968	E-03 BTU,					
2713	BTU/lb (1 1	b/454 gram	s)(1 cal/3.9	68E-03BTU	J) =	1505.99	cal/gm	
Convert to	Kcal =	1.51	Kcal/gm					

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Appendix E: Pressure Sensor Output During Event



RD-13 Pressure (5-29-03 Time Adjusted back 67 Min 30 Sec)

Time

Appendix F: Heat Loss Equations and Results

The following equations were used to determine the heat loss expected from the dissolver to the environment:

$$Q = h \cdot A \cdot \Delta T$$

$$Q = rate \ of \ heat \ loss\left(\frac{J}{s}\right)$$

$$h = heat \ transfer \ coefficient\left(\frac{W}{m^2 \cdot K}\right)$$

 ΔT = temperature difference between ambient and max (K)

$$\rho = \frac{m}{V} = \frac{P \cdot M}{R \cdot T}$$

$$\rho = density of air\left(\frac{grams}{L}\right)$$

$$m = mass of air (grams)$$

$$P = pressure of air (atm)$$

$$R = gas \ constant \ 0.08206\left(\frac{L \cdot atm}{mol \cdot K}\right)$$

$$T = temperature \ of \ air (K)$$

$$\beta = \frac{-1}{\rho} \cdot \left[\frac{\rho_{\infty} - \rho}{T_{\infty} - T} \right]$$

 $\beta = Coefficient of Volumetric Thermal Expansion\left(\frac{1}{K}\right)$ $\rho_{\infty} = density of air at distance\left(\frac{grams}{L}\right)$ $\rho = density of air at temperature\left(\frac{grams}{L}\right)$ $T_{\infty} = temperature of air at distance (K)$ T = temperature of air at temperature (K)

Appendix F: Heat Loss Equations and Results

 $Gr_{L} = \frac{g \cdot \beta \cdot (T_{s} - T_{\infty}) \cdot L^{3}}{v^{2}}$ $Gr_{L} = Grashof Number (dimensionless)$ $\beta = Coefficient of Volumetric Thermal Expansion \left(\frac{1}{K}\right)$ $g = gravitational constant \left(\frac{m}{s^{2}}\right)$ L = height (m) $v = viscosity \left(\frac{m^{2}}{s}\right)$ $T_{\infty} = temperature of air at distance (K)$ $T_{s} = temperature of air at surface (K)$ $Re_{L} = \frac{u_{\infty} \cdot L}{v}$ $Re_{L} = Reynolds Number (dimensionless)$ L = height (m)

$$v = viscosity\left(\frac{m^2}{s}\right)$$

 $Ra_{L} = Gr_{L} \cdot Pr$ $Ra_{L} = Rayleigh Number (dimensionless)$ Pr = Prandtl Number (dimensionless) $Gr_{L} = Grashof Number (dimensionless)$

For Free Convection

$$\overline{N}u_{L} = \left\{ 0.825 + \frac{0.387 \cdot Ra_{L}^{1/6}}{\left[1 + (0.492/Pr)^{9/19} \right]^{8/27}} \right\}^{2}$$

$$\overline{N}u_{L} = Average \ Nusselt \ Number \ (dimensionless)$$

$$Ra_{L} = Rayleigh \ Number \ (dimensionless)$$

$$Pr = Prandtl \ Number \ (dimensionless)$$

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Appendix F: Heat Loss Equations and Results

For Forced Convection $\overline{N}u_L = 0.664 \cdot Re_L^2 \cdot Pr^{1/3}$

 $\overline{N}u_L = Average Nusselt Number (dimensionless)$

 $Re_L = Reynolds Number (dimensionless)$

Pr = Prandtl Number (dimensionless)

			-mole												
		Meters/sec2	grams/gram	ters											
		9.8	29	square me		Gms Al/	minute			3.9	3.5	3.0	2.6	1.7	
VCE	degK	gravity =		1.235	q	Heat Xfer,	Kcal/	minute		28.67	25.45	22.21	18.95	12.32	
S REFEREN	298	celeration of g	air =	area =	meters/secon	Heat Xfer	Coefficient,	Watts/M2-	degK	1.91E+01	1.92E+01	1.93E+01	1.95E+01	1.99E+01	
SFPE A	degC =	meters, ac	weight of a	eat transfer	10	Nusselt	Number			307.31	316.25	326.01	336.72	361.69	
IE, USING			, molecular	in degK, h	ulk air =	Prandtl	Number			6.98E-01	6.99E-01	7.00E-01	7.02E-01	7.05E-01	
SFER RAT	25	0.4985	mole-degK)	temperature	w rate of bu	Reynolds	Number			2.72E+05	2.88E+05	3.06E+05	3.26E+05	3.75E+05	
AT TRAN			liter-atm/(g	divided by	calories, flo	Grashoff	Number			1.03E+09	1.02E+09	9.97E+08	9.57E+08	8.06E+08	
TION HE	g cabinet =	lver =	0.08206	353.40	0.2389	Beta,	1/degK			3.36E-03	3.36E-03	3.36E-03	3.36E-03	3.36E-03	
CONVEC	ature in win	ight of dissc	instant =	air =		Dissolver	Temp.,	degK		383	373	363	353	333	
FORCED	Air temper	Vertical he	Gas law co	Density of a	One Joule :	Dissolver	Temp.,	degC		110	100	06	80	60	

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Appendix G: Instrument Report Data



Figure 1 RD-13/RD-14 Pressure (5-29-03 Time Adjusted back 67 Min 30 Sec)

This chart shows the effects of the event on both RD-13 and RD-14 as seen by the pressure instrumentation.

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Appendix G: Instrument Report Data



This chart shows the effects of the RD-14 charge chute being obstructed and the corresponding change in RD-13 as seen by the pressure instrumentation