WSRC-TR-2004-00342

Dissolution of Plutonium Metal Using a HAN Process

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June 2004

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Summary

Thermal stability tests were conducted with a nitric acid (HNO_3) / hydroxylammonium nitrate (HAN) / potassium fluoride (KF) solution. The solution has great potential for use in plutonium dissolution because of the small quantity of hydrogen and other offgases produced. Tests were carried out in a Reactive Systems Screening Tool (RSST). The RSST is a calorimeter equipped with temperature and pressure probes as well as a heater that can heat a liquid sample at a programmed rate. In most cases, the calorimeter was pressurized with nitrogen to reduce evaporation of the liquid sample during heating.

For the proposed solution, 2 M HNO_3/0.6 M HAN/0.1 M KF, an autocatalytic reaction occurred between 113 and 131ºC with 300 psig or 50 psig nitrogen inside the RSST vapor space. At ambient pressure, the solution boiled at about 110ºC. After extensive boiling, the concentrations of HNO_3 and HAN increased and the autocatalytic reaction occurred. Tests were also conducted with 1000 ppm Fe present in the HNO_3/HAN/KF solution. The range of the autocatalytic reaction initiation temperature was reduced to 105-120.5ºC. With iron at ambient pressure, boiling still occurred above 100ºC prior to the autocatalytic reaction, which occurred at 108-109ºC. These results demonstrated the stability of the proposed HAN flowsheet, for which the planned dissolving temperature is 50-60ºC.

Additional tests were carried out with more concentrated solutions to further characterize the autocatalytic reaction initiation temperature. Increasing the nitric acid concentration to 3M decreased the reaction initiation temperature to 102-103ºC. Increasing the HAN concentration increased the temperature rise of the reaction from 10-30ºC to >40ºC. Increasing both reactants – to 3M nitric acid and 0.9M HAN – yielded a reaction initiation temperature of 91ºC (with or without iron), the lowest observed in this study.

This study was the first part of a larger flowsheet development / demonstration program for the plutonium metal dissolving process. The results of the study may be useful for similar flowsheets.

Background

Much of the excess plutonium from reduction in the nuclear weapons stockpile is still in the form of pits. Before this material can be dispositioned in a mixed oxide fuel, the pits must be disassembled and impurities potentially harmful to the fuel removed. Dissolution of the Pu metal following pit disassembly facilitates the required purification. Pu metal dissolutions have been performed in SRS facilities using both sulfamic acid and nitric acid/fluoride flowsheets. Since that time, the maximum allowable concentration of hydrogen in offgas from the dissolution process has been reduced to 1 volume percent to meet NFPA requirements. The concentration of hydrogen in the offgas from both demonstrated flowsheets will exceed this value unless large volumes of air are used for dilution. In response to this problem, the feasibility of using a nitric acid (HNO_3) / hydroxylammonium nitrate (HAN) / fluoride flowsheet was demonstrated by D.G. Karraker[1]. This flowsheet generated 10-15% of the gas evolved from the sulfamic acid process and a very small quantity of hydrogen; however, the small scale of the experiments did not allow for precise quantification of the hydrogen produced. Other advantages of the HNO_3 / HAN / KF flowsheet are that dissolving residues are not pyrophoric and dissolving rates higher than a sulfamic acid flowsheet are readily attainable.

Historically, HAN has been used as a reductant in the PUREX and other plutonium processing operations. The reaction is given as

$$2NH_3OH^+ + 4Pu^{+4} \rightarrow 4Pu^{+3} + N_2O + H_2O + 6H^+$$

Incidents at Hanford, the Savannah River Site, and elsewhere[2] have focused attention on the safe use of hydroxylamine (HAN) and its compounds. Early work on the oxidation of HAN by HNO_3 demonstrated that "reaction is only observed at sufficiently high nitric acid concentrations; at 25 C the cut-off is about 2.5M HNO_3."[3] After an induction period, the reaction is rapid and autocatalytic, producing heat very quickly. The reactions involved are

$$4NH_3OH^+ + 2HNO_3 \rightarrow 3N_2O + 3H_2O + 4H^+$$
$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_2O + H^+$$
$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$

In the first task of the Pu metal dissolving program, the thermal stability of the 2M HNO_3 / 0.6M HAN / 0.1M KF solution proposed for the process was demonstrated.

Experimental

All tests were conducted in a Reactive Systems Screening Tool (RSST) from Fauske and Associates, Inc. The RSST is a nearly adiabatic calorimeter equipped to heat samples at a programmed rate and to record sample temperature and pressure at specified intervals. With the RSST, a sealed 350-mL Parr bomb houses an uncovered sample in a small, thin round-bottomed flask. The flask is surrounded by a small resistance heater and insulation before being loaded into the calorimeter. A thermocouple is placed in contact with the sample solution. For most tests in this study, the RSST vessel was pressurized with nitrogen gas to minimize vaporization of reactive components. Samples were nominally 11 g (10 mL) and a small magnetic stir bar was used. The experimental set-up is shown in Figure 1. In this study, the programmed heating rate was 1ºC/min and temperature and pressure were typically recorded every 1ºC.

Figure 1. Reactive Systems Screening Tool (RSST) during Testing.

Test solutions were made from reagent grade nitric acid, a commercial grade 1.8M HAN stock solution, and distilled water. Potassium fluoride was added as anhydrous, but iron was added in the form of ferric nitrate nonahydrate: $Fe(NO_3)_3 \bullet 9H_2O$. Solution batches were 75 mL, providing enough material for about 6 RSST tests per batch.

Results

Typical temperature versus time plots for the dissolver solution used in this study are shown in Figure 2. Notice that for the typical solution pressurized at 300 psig with nitrogen, the temperature of the solution increases at the programmed rate until the reaction occurs almost instantaneously. In contrast, the typical solution at ambient pressure reaches a temperature plateau where vaporization begins and the solution is concentrated. The reaction occurs almost instantaneously, but the magnitude is lower. For the more concentrated solution, the reaction begins at a lower temperature, as expected.

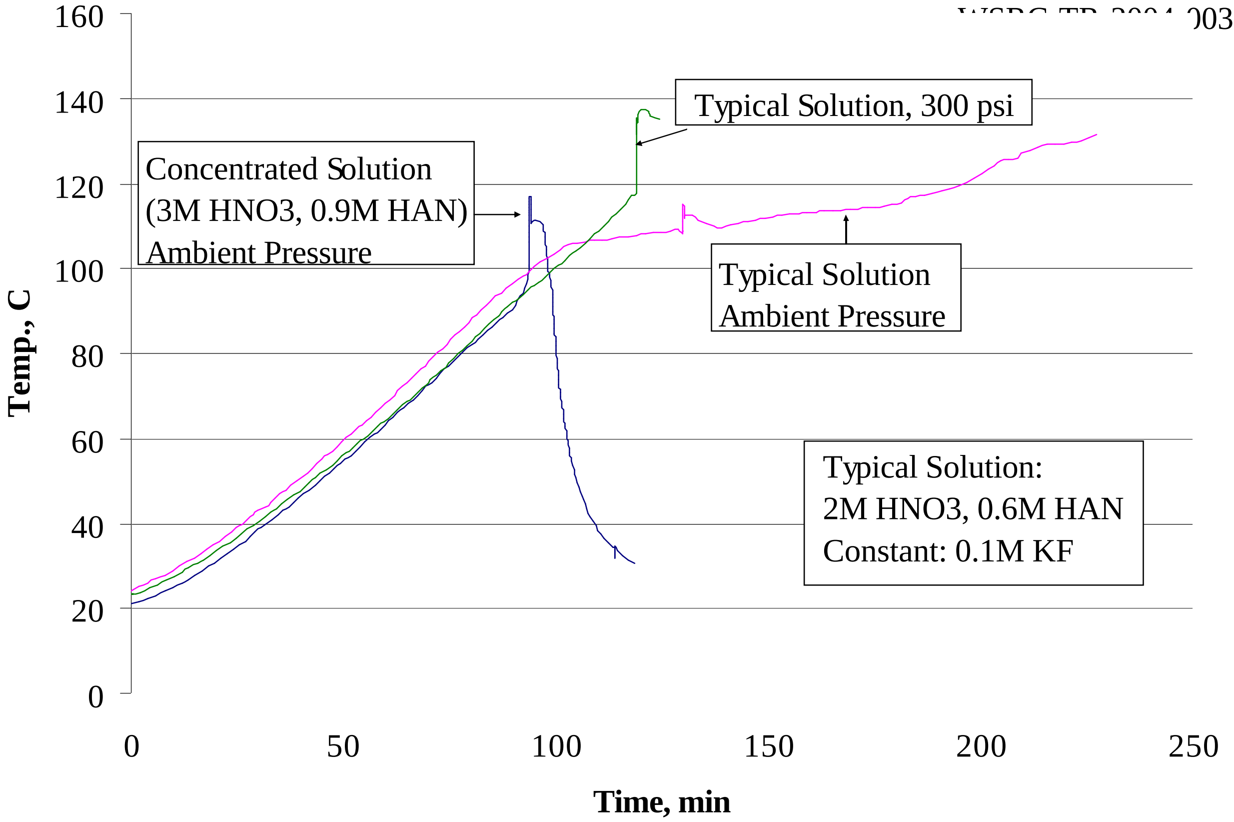

Figure 2. Characteristic reaction curves for dissolver solutions at different conditions.

Reaction characteristics for various solutions are provided in Tables 1-3. For the proposed dissolver solution, 2M HNO_3/ 0.6M HAN / 0.1M KF, an autocatalytic reaction occurs between 113 and 131ºC inside the RSST with either 300 psig or 50 psig nitrogen in the vapor space. Decreasing the RSST pressure from 300 to 50 psig did not seem to affect reaction temperature. However, when the RSST was operated at ambient pressure, the HNO_3/HAN/KF solution boiled at about 110ºC. After extensive boiling, the concentrations of HNO_3 and HAN increased and an autocatalytic reaction occurred. These results bode well for the proposed HAN flowsheet, for which the planned temperature is 50-60ºC.

When the concentration of the nitric acid in the dissolver solution was increased, the autocatalytic reaction temperature decreased, as expected. A reference point in the literature[2] gives an autocatalytic reaction temperature of 90ºC for 3.0M HNO_3 and 0.5M HAN. The reaction temperatures observed in this study are about 10ºC higher for 3.0M HNO_3 / 0.6M HAN / 0.1M KF solutions. A reaction temperature of 91ºC was observed with 3M HNO_3/ 0.9M HAN / 0.1M KF, with and without 1000 ppm of iron. For 2-3 M HNO_3, increasing the HAN concentration from 0.6 to 0.9M increased the observed temperature rise of the reaction from nominally 10-30ºC to >40ºC for pressurized reactions.

Table 1. Reaction Characteristics of Dissolver Solutions Pressurized with Nitrogen

HNO_3	HAN	Po	Trxn	ΔT	ΔP	Δt	Comments
M	M	psig	ºC	ºC	psi	sec	
1.99	0.6	300	125	26	9.7	0.55	
2	0.6	300	131	23	14	0.88	Stirrer off until 124ºC
2	0.6	50	113	23	14	1.15	Stirrer off
2.02	0.6	300	128	23	7	0.6	
2	0.6	300	122	26	9	0.99	
2.03	0.6	300	114	27	6	1.15	
2	0.6	300	119	27	8	1.65	
2	0.6	300	118	27	8.5	0.94	0.2M Fluoride*
3	0.6	300	103	29	5.7	0.71	
3	0.6	300	102	27	5.5	0.6	
2	0.9	300	123	40	22	0.71	
2	0.9	300	110	42	19	0.94	
2.5	0.75	300	118	33	13	0.72	
2.5	0.9	300	102	40	18	0.93	
3	0.9	300	91	44	12	0.93	

*All other solutions in Tables 1-3 contained 0.1M KF.

Table 2. Reaction Characteristics of Dissolver Solutions initially at Ambient Pressure

HNO_3	HAN	Iron	Trxn	ΔT	ΔP	Δt	Comments
M	M	ppm	ºC	ºC	psi	sec	
2	0.6	0	109-110	8	11	2.03	Rxn. after boiling
2	0.6	1000	108-109	7	10	1.98	Rxn. after boiling
3	0.6	0	101	15	14	2.3	
3	0.9	0	101	16	14	2.14	
3	0.9	1000	105	12	15	1.59	

For the HNO_3/HAN/KF solution with iron, as shown in Table 3, the reaction initiation temperature ranged from 105 to 120.5 C, which is about 10ºC lower than the range for the same solution in the absence of iron. At ambient pressure with iron, the typical dissolver solution behaves the same as without iron – a period of vaporization followed by a reaction at 108-109ºC. Thus, the presence of iron does not preclude use of the proposed HAN flowsheet, for which the planned temperature is 50-60ºC.

Table 3. Reaction Characteristics of Dissolver Solutions with 1000 ppm Iron.

HNO$_3$	HAN	Po	Trxn	ΔT	ΔP	Δt	Comments
M	M	psig	°C	°C	psi	sec	
2	0.6	300	105	25	6.4	1.54	
2	0.6	300	112	23.5	4.7	1.04	
2	0.6	50	121	17	16	0.82	
2	0.6	50	118	18	15	0.99	
2	0.6	30	112	17	13	1.37	
2	0.6	30			16	0.99	
2	0.6	0	108-109	7	10	1.98	Rxn. after boiling
3	0.6	300	98	25	4.8	0.60	
3	0.9	300	91	39 42	2.7 9	1.94 6.98	
3	0.9	0	105	12	15	1.59	Aged solution[†]

[†] HAN/HNO3/KF solution made 46 days before test. Iron added 44 days before test.

The RSST calculates the heating rate, dT/dt, throughout a run. This can be called the self-heating rate, since the programmed heating rate is known. Figure 3 shows an example of heating rate versus time for samples with a 1°C/min programmed rate. Individual runs were selected as representative, but do not show the range of reaction initiation temperatures observed in this study. In Figure 3, the "Typical" and "Concentrated" terms refer to the same concentrations as in Figure 2.

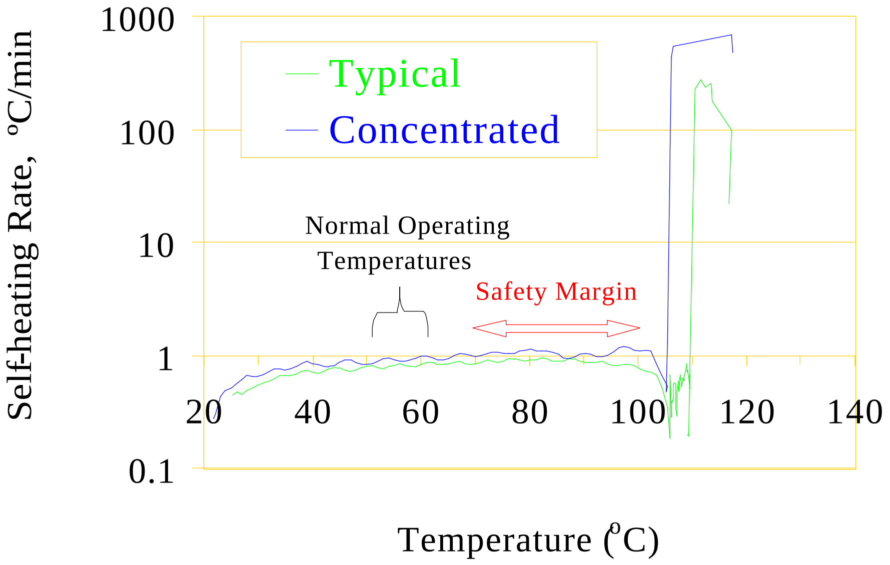

Figure 3. Comparison of upset conditions to normal operating temperatures.

Conclusions

The results of this study lead to the following conclusions.

1. Increasing the nitric acid concentration decreased the runaway reaction initiation temperature.
2. Increasing the HAN concentration increased reaction intensity.
3. Ambient pressure experiments demonstrated excessive boiling was required to achieve runaway reaction with typical flowsheet conditions.
4. Increasing fluoride to 0.2M had no effect on reaction initiation temperature.
5. The presence of iron (1000 ppm) reduced the reaction initiation temperature 5-10ºC.
6. A significant safety margin exists between normal operating conditions for the 2M HNO_3 / 0.6M HAN / 0.1M KF flowsheet and upset conditions which lead to a runaway reaction.

Acknowledgements

The authors thank the Strategic R&D Program at Savannah River Site for funding to perform this work and the Mixed Oxide Fuel Fabrication Project for funding to complete this report. We also thank Bill Crooks for technical assistance in using the RSST.

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[1] D.G. Karraker, Delta-Plutonium Processing – A HAN Process (U), WSRC-TR-90-251, Westinghouse Savannah River Co., Aiken, SC (June 1990).

[2] D.G. Harlow, R.E. Felt, S. Agnew, G.S. Barney, J.M. McKibben, R. Garber, M. Lewis, Technical Report on Hydroxylamine Nitrate, DOE/EH-0555, U.S. Dept. of Energy, Feb. 1998.

[3] Pembridge, J.R., and G. Stedman, "Kinetics, Mechanisms, and Stoichiometry of the Oxidation of Hydroxylamine in Nitric Acid," Chemical Society Journal, Dalton, 1657, 1979.