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THE SUITABILITY OF SODIUM PEROXIDE FUSION FOR PRODUCTION-SCALE PLUTONIUM PROCESSING OPERATIONS

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ABSTRACT

Sodium peroxide (Na_2O_2) fusion is a method that offers significant benefits to the processing of high-fired plutonium oxide (PuO_2) materials. Those benefits include reduction in dissolution cycle time, decrease in residual solids, and reduction of the potential for generation of a flammable gas mixture during dissolution. Implementation of Na_2O_2 fusion may also increase the PuO_2 throughput in the HB-Line dissolving lines. To fuse a material, Na_2O_2 is mixed with the feed material in a crucible and heated to 600-700 °C. For low-fired and high-fired PuO_2, Na_2O_2 reacts with PuO_2 to form a compound that readily dissolves in ambient-temperature nitric acid without the use of potassium fluoride.

The Savannah River National Laboratory (SRNL) demonstrated the feasibility of Na_2O_2 fusion and subsequent dissolution for the processing of high-fired PuO_2 materials in HB-Line. Testing evaluated critical dissolution characteristics and defined preliminary process parameters. Based on experimental measurements, a dissolution cycle can be complete in less than one hour, compared to the current processing time of 6-10 hours for solution heating and dissolution. Final Pu concentrations of 30-35 g/L were produced without the formation of precipitates in the final solution.

INTRODUCTION

The HB-Line Facility has a long-term mission to dissolve fissile materials and disposition them. Many of these materials contain high-fired PuO_2, which requires strong oxidizing agents for dissolution. The Na_2O_2 fusion process is a technology that could provide substantial benefits to the processing of high-fired plutonium oxide materials in HB-Line. Those benefits include reduction in dissolution cycle time, decrease in overall residual solids (especially plutonium-bearing residues), and reduction of the potential for generation of a flammable gas mixture during dissolution. The technique is an established method for dissolving analytical samples [1]. The technique has been previously evaluated by researchers at SRNL [2,3] and Pacific Northwest National Laboratory [4], but never implemented on a productions scale.

To fuse a sample, Na_2O_2 is mixed with sample in a crucible at ~3:1 Na_2O_2-to-sample weight ratio. The crucible is heated to 600-700 °C where Na_2O_2 reacts with the sample to form a compound that readily dissolves in nitric acid (HNO_3) at ambient temperature without the use of potassium fluoride (KF). Due to facility conditions, the target final Equivalent Pu-239 concentration leaving the dissolver should be between 21 and 35 g/L.

The primary goal is to demonstrate an improved process cycle time relative to the current process cycle time. While the Na_2O_2 fusion process requires heating a mixture of the PuO_2 material with Na_2O_2 at 600-700 °C for 30-60 min, this operation can occur in parallel with the dissolution operation. It is anticipated that dissolution to 21-35 g/L Pu will occur in about one hour, compared to 6-11 hours for the baseline process.

EXPERIMENTAL PROCEDURE

Over 100 separate fusion plus dissolution tests with Pu-bearing materials have been completed. Consequently, all of the data are not tabulated in this paper. Only those tests specifically discussed in the paper are listed, but all of the data (listed and unlisted sample data) are included in statistical calculations.

Fusion with Sodium Peroxide

Fusion of samples was performed in the following manner. First, the crucible was weighed on a calibrated balance. For most tests, 5-mL zirconium (Zr) crucibles were used. For some tests, however, a 55-mL Zr or 115-mL alumina (Al_2O_3) crucible was used. In a separate weighing dish, the appropriate amount of Na_2O_2 (Fisher Scientific, 96% pure, +140 mesh) was added. The material to be fused was added to the weighing dish. Specific test data are listed in Table I for small-scale experiments and Table II for pilot-scale experiments. The materials in the weighing dish were mixed with a spatula and added to the crucible. For larger-scale tests (Tests 41-45), a layer of Na_2O_2 cover salt was added prior to placing the crucible in the furnace. The crucible was placed into a standard muffle furnace and heated to 700 ^{o}C. Heating to temperature required 20-30 min. The crucible was typically held at temperature for 45-75 min. The furnace was turned off and allowed to cool. The sample preparation steps are depicted in Figure 1.

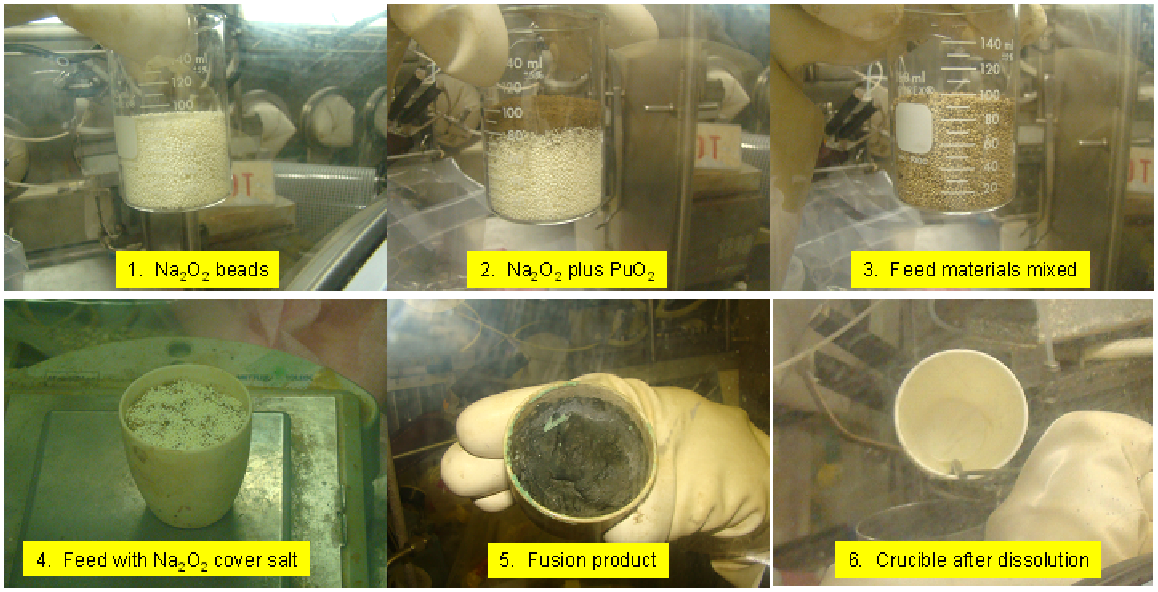

Fig. 1. Preparation and dissolution of sodium peroxide fusion product (Test #44)

The preparation of materials for fusion is not labor-intensive. The steps involved in combining the pre-weighed feed materials, mixing, transferring to the materials to the crucible, adding the cover salt, and placing the crucible in the furnace were timed at 10 min. The pictures in Figure 1 show that the mixing between the Na_2O_2 and PuO_2 was fairly uniform. Very few fines from the bottom of the beaker were noted at the top of the crucible when the contents were transferred from the beaker to the crucible.

Table I. Sample Preparation and Dissolution Data for Small-Scale Samples

Test #	Sample Mass (g)	Na_2O_2 Mass (g)	HNO_3 Conc (M)	HNO_3 Volume (mL)	Temp Start (°C)	Temp Max (°C)	Dissolve Time (s)	Gas Volume (mL)	Residue (g)
1	0.735	3.627	7	150	39.3	46.6	---	---	0.076
2	0.620	2.505	8	70	22.7	52.3	---	---	0.420
3	4.653	16.387	12	180	---	---	---	---	0.653
4	1.030	3.086	8	80	23.5	48.8	31	240	0.038
5	1.077	2.999	7	80	33.7	58.1	33	280	0.054
6	0.992	3.012	7	80	34.3	58.8	39	260	0.157
7	0.903	2.703	7	80	34.6	54.6	30	380	0.062
8	0.742	2.197	8	150	32.8	42.0	---	---	0.015
9	1.780	6.120	8	120	---	---	---	---	0.021
10	2.914	9.762	8	150	---	---	---	---	0.034
11	0.620	1.879	8	150	34.8	43.3	---	---	0.229
12	3.504	11.996	12	245	---	---	---	---	0.029
13	4.152	11.166	8	125	---	---	---	---	0.109
14	6.346	21.920	8	225	28.0	94.5	---	---	0.305
15	2.177	3.361	8	100	---	---	---	---	0.235
16	0.972	2.916	6.0	140	20.8	35.4	35	210	0.041
17	0.972	2.916	5.5	136	35.1	49.8	28	330	
18	0.972	2.916	5.0	132	48.8	62.3	30	360	
19	0.972	2.916	4.5	128	59.5	71.1	39	340	
20	0.972	2.916	4.0	124	66.7	77.4	37	360	
21	0.972	2.916	3.2	120	72.6	83.1	41	280	
22	0.972	2.916	4.0	140	21.2	35.2	82	190	0.119
23	0.972	2.916	3.5	136	34.6	47.8	49	270	
24	0.972	2.916	3.0	132	20.6	34.8	60	160	
25	0.972	2.916	2.2	128	34.7	48.7	60	340	
26	0.972	2.916	1.8	124	20.3	34.8	420	220	
27	0.972	2.916	1.5	120	34.8	48.1	140	520	
28	0.905	2.700	6.0	125	21.6	35.6	36	90	0.069
29	0.905	2.700	5.4	125	32.1	45.4	30	120	
30	0.905	2.700	4.9	125	43.8	54.6	36	190	
31	0.905	2.700	4.3	125	52.6	62.6	32	210	
32	1.218	3.011	6.0	150	23.2	38.0	26	170	0.044
33	1.008	3.001	4.1	134	38.0	53.0	33	500	0.099
34	1.206	3.009	6.0	85	21.2	44.2	38	300	0.100
35	1.200	2.998	4.3	81	34.7	56.1	33	400	
36	1.198	3.005	3.3	77	41.8	62.7	35	280	
37	0.998	3.002	6.0	95	22.1	42.0	60	250	0.107
38	0.999	3.003	4.2	91	25.2	55.1	47	400	
39	1.002	3.000	3.5	87	40.4	61.1	41	310	
40	0.941	2.856	2.5	83	41.8	63.2	51	310	

Table II. Sample Preparation and Dissolution Data for Pilot-Scale Samples

Test #	Sample Mass (g)	Na_2O_2 Mass (g)	HNO_3 Conc (M)	HNO_3 Volume (mL)	Temp Start (°C)	Temp Max (°C)	Dissolve Time (s)	Residue (g)
41	13.16	45.54	9	750	23.0	76.6	105	0.308
42	26.37	89.96	6.3	1250	23.5	78.1	105	
43	36.76	116.8	6	1500	18.8	80.6	74	0.722
44	47.82	152.3	8	2250	18.8	74.8	87	1.039
45	45.51	187.1	9	1550	28.1	98.7	165	---

Dissolution of Fused Product

During the proof-in-principles stage of the program, samples were dissolved in a 250-mL stainless-steel beaker with a thermocouple immersed in solution. For later studies, most samples were dissolved in an apparatus designed to measure temperature and gas generation volumes. The dissolution vessel consisted of a 250-mL Nalgene^{TM} bottle with a glass thermowell passing through the side wall to the bottom of the vessel. A hot-glue gun was used to seal the thermowell to the bottle. A Type-K thermocouple was inserted into the thermowell and attached to a thermocouple reader. The cap of the bottle had a hole drilled through it and a stainless-steel bulkhead fitting passed through the hole. Viton^{TM} o-rings created a gas-tight seal on either side of the hole. A 7.5-cm length of Viton^{TM} tubing, nominal 0.25 inch outside diameter, passed from the bulkhead fitting to a 1-liter Tedlar^{TM} gas sample bag.

Prior to the dissolution, HNO_3 was placed in the dissolver vessel. The thermocouple reader was turned on and the thermocouple reading allowed to equilibrate; the starting temperature was recorded. With the dissolver cap off, the fused product and its crucible were added to the dissolver vessel. The dissolver cap was immediately put on the vessel and sealed, a timer initiated, and the valve in the Tedlar^{TM} bag opened.

Timing continued until the dissolution was visibly complete (bubbling ceased). The dissolution time and maximum temperature were recorded. Within 2-5 minutes of dissolution being complete, the Tedlar^{TM} bag was sealed and the gas volume in the bag measured using water displacement. For several of the tests, gas samples were submitted for analysis using gas chromatography (GC). After dissolution, residues were filtered through 47-mm diameter 5-μm filter papers (mixed cellulose esters). The filter papers were dried in air and weighed. Several of the residues were analyzed using scanning electron microscopy (SEM).

Larger-scale samples (Tests 41-45) were dissolved in an 8-liter Nalgene^{TM} bottle with the top removed. The dissolver solution was added to the bottle and a Type K thermocouple attached to a thermocouple reader was inserted into the dissolver solution prior to the addition of the fused product.

RESULTS AND DISCUSSION

Many aspects of the Na_2O_2 fusion process were studied to demonstrate its effectiveness and to define process conditions for deployment. The studied parameters have been divided into two groups, dissolution characteristics and process parameters. Dissolution characteristics included several parameters of which dissolution rate, gas generation, and residue characterization are presented here. The definition of process parameters also entailed numerous parameters. This paper discusses identifying the dissolver acid concentration for achieving Pu concentration targets, optimizing the Na_2O_2-to-sample ratio, and performing pilot-scale tests.

Dissolution Rate

During the dissolution tests discussed here, the crucible did not dissolve significantly. Therefore, dissolution occurs only at the top surface. Accurate determination of an actual dissolution rate is not possible due to the short dissolution times observed, non-uniformity of the material surface, and the rapidly changing solution temperature during dissolution. Although an accurate dissolution rate cannot be obtained, the more-important issue relates to the dissolution times that can be expected during full-scale operations.

The data in Table I convey that the dissolution rates for Na_2O_2 fusion product are measured in seconds instead of hours. The larger-scale tests in conjunction with Tests 16-21 provide the data to make a good approximation of overall production dissolution cycle times. The approximation is based on 1) the thickness of fusion product dissolved in a specific time and 2) the effect of sequential dissolutions on dissolution rate.

In Test 41, the fusion product depth was 24 mm (product density ~2.4 g/mL) and the sample dissolved in 105 s, or 0.23 mm/s. For Test 42, the fusion product depth was 38 mm (product density ~2.3 g/mL) and the sample dissolved in 115 s, or 0.33 mm/s. The linear dissolution rate for Test 44 was 0.46 mm/s. For the small samples of Tests 16-21, the product depth was nominally 13 mm and the samples dissolved in 28-41 s, or 0.32-0.46 mm/s.

Tests 16-21 show the impact of sequential dissolution in the same acid volume. Tests 16-21 simulated the series of dissolutions envisioned in HB-Line to achieve a final Pu concentration of 30-35 g/L. The dissolution times for Tests 16-21 were 35 s, 28 s, 30 s, 39 s, 37 s, and 41 s, respectively. There appears to be a gradual increase in dissolution rate at the start when the solution temperature increases, but then a decrease in dissolution rate as the acid concentration decreases. Overall, the dissolution times are relatively consistent.

Applied to the dissolution of Pu-bearing materials at a production-scale, the overall dissolution times can be estimated. Assuming a feed material weight of ~125 g and a Na_2O_2-to-sample weight ratio of 3.0, the charge would contain 375 g of Na_2O_2 for a net sample weight of 500. Assuming a fused bulk density of 2.3 g/ cm^3 (measured from the product of Test 42), the net sample volume would be 217 cm^3. For crucibles of 2.5-in diameter (the charge port has a 3-in diameter), the sample volume would translate into a sample height of 69 mm. For an average dissolution rate of 0.33 mm/s, the samples would dissolve in 209 s. Based on the above data and assumptions, each Na_2O_2 fusion product charge is estimated to dissolve in 3-5 min. Assuming sequential addition of 3-6 charges, dissolution will be complete in less than one hour. The dissolver does not need to be heated prior to the first dissolver charge, nor does it need to be cooled between individual charges.

Statistical analyses of the dissolution time data evaluated the impact of HNO_3 from 2.5-8.0 M, initial dissolver solution temperature, and beaded versus ground Na_2O_2. The analyses showed that dissolution time was not a function of HNO_3 concentration or initial dissolver solution temperature. Absent any data, the minimum recommended dissolution temperature is 20 °C. The use of ground Na_2O_2 yielded slightly lower dissolution times when compared to beaded Na_2O_2, but at a 95% confidence level the dissolution times are the same.

Gas Generation

A reaction for the formation of an Na_2O_2-PuO_2 fusion product has been proposed [5].

$$PuO_2 + 2\,Na_2O_2 \rightarrow Na_4PuO_5 + \tfrac{1}{2}\,O_2 \qquad \text{(Eq. 1)}$$

In the reaction of Eq. 1, Pu(IV) reacts to form Pu(VI), which readily dissolves in HNO_3. The reaction implies that the release of oxygen gas (O_2) occurs during the fusion reaction. Gas measurements made during the dissolution of fusion products have shown that O_2 is released during dissolution. Test data are listed in Table III. . For these tests, the head space of the reaction vessel was not purged prior to the dissolution reaction. Therefore, 125-160 cm^3 of air space is present in the apparatus when the sample is added and the cover sealed. Consequently, nitrogen (N_2) and O_2 from air are expected in samples and are diluted by gas generated during dissolution.

The data in Table III indicate that O_2 is released during dissolution and dilutes the N_2 concentration. In all tests, the gas released during dissolution was colorless. The calculated O_2 value in the table assumes that only O_2 was released during dissolution. In the first four tests, the measured O_2 value was higher than the calculated value, which indicates that the gas released during dissolution is not well-mixed with the gas in the head space. It also supports the finding that the gas released is primarily O_2. No measurable quantities (<0.2 vol %) of hydrogen gas (H_2) were detected.

Table III. Gas Generation from the Dissolution of Fusion Product

Test #	3013 DE Material	Head Space (mL)	Gas Volume (mL)	H_2 [b] (vol %)	N_2 [b] (vol %)	O_2 [b] (vol %)	Calc O_2 (vol %)
28	B258	125	90	<0.2	40	60	53
29	B251	125	120	<0.2	24	75	59
30	B226	125	190	<0.2	24	74	68
31	B216	125	210	<0.2	21	78	70
33	B244 [a]	116	500	<0.1	23	75	85
38	B196 [a]	159	400	<0.1	40	44	77

a Material pretreated by vacuum salt distillation
b Analytical uncertainty = 10%

The generation of O_2 during dissolution does not mean that O_2 is released only during dissolution. Testing using thermogravimetric analysis with mass spectroscopy (TGA-MS) has shown that during the fusion of PuO_2 with Na_2O_2 at 700 °C, gas with Mass 32 is released between 200 and 400 °C and then again above 600 °C. No other mass numbers were detected. No H_2 gas is released as part of the dissolution of fusion product. Approximately 250-300 mL of gas is released per gram of sample dissolved at a Na_2O_2-to-sample ratio of 2.5-3.5. The average value for all tests is 286 mL per gram of sample with a root mean square error of 108%.

Residue Measurements

The generation of residues during the dissolution of Pu-bearing materials is expected. The primary goal for dissolution of materials in HB-Line is to limit Pu in the residues, preferably to below 2% of the initial Pu content. The secondary goal is to reduce overall residues to less than 10% of the initial bulk weight.

Testing has shown that dissolution of fused materials yields residues that are low in Pu concentration. Those residues have been analyzed using SEM. Because SEM is not a quantitative method, the data from the analyses is broken into qualitative categories. Based on peak heights from the SEM analyses, the elements detected are nominally listed as major (>20 wt %), minor (~2-20 wt %) or trace (<2 wt %) and in order of decreasing peak height. Table IV contains data on the materials before dissolution and Table V presents the post-dissolution residue data. Zirconium in the samples comes from crucibles which are slightly oxidized by Na_2O_2; some of the Zr oxide dissolves in HNO_3.

Several important points can be drawn from Table IV. First, there is excellent dissolution of Pu from the samples and Pu is never more than a minor component of the residue. Tantalum (Ta) is consistently a major or minor component which indicates that it is resistant to dissolution. Other components found among the major and minor components (Na, Mg, and Ni) are likely the result of either incomplete mixing of the Na_2O_2 with the sample or incomplete rinsing of the dissolved sample after filtration. The trace components are included in the table for completeness, but little issue should be made from their presence other than Pu is frequently present in the residues at only trace levels.

Table IV. Comparison of Feed Material Compositions for Peroxide Fusion and Dissolution from X-ray Diffraction Analyses (Listed in Order of Decreasing Concentration)

Test	% Pu in Feed	Major Components	Minor Components
1	71.2	PuO_2	SiO_2
2	34.2	PuO_2, WO_3, $WNiO_4$	Fe_2O_3, SiO_2, $Ca_2Ta_2O_7$, $NiCr_2O_4$
3	52.3	PuO_2, MgO	$NiCr_2O_4$, SiO_2, NiO, Fe_2O_3, ThO_2
4	87.7	PuO_2	NiO, $NiCr_2O_4$
5	76.6	PuO_2	NiO, $NiCr_2O_4$, Fe_2O_3
6	70.6	PuO_2, $Ta_{0.5}W_{0.5}O_{2.75}$	$NiCr_2O_4$, NiO
7	72.3	PuO_2	NaCl, KCl
32	63.4	PuO_2	$NiCr_2O_4$, NiO, $CaUO_4$, Na_2WO_4-$2H_2O$
40	70.2	PuO_2	NaCl, KCl, MgO

Table V. Comparison of Residue Compositions from Peroxide Fusion and Dissolution (Listed in Order of Decreasing Concentration) from Scanning Electron Microscopy

Test	% Pu in Feed	Wt % Residue	Major Components	Minor Components	Trace Components
1	71.2	10.3	Ta	Pu	Fe, Cr, Al, V
2	34.2	67.7	Ta, W	Zr, Na	Pu, Fe
3	52.3	14.0	Na, Si	Zr	Pu, Fe, Cr, Ni
4	87.7	3.7	Zr	Na, Pu	Fe, Ni
5	76.6	5.0	Zr	Ta, Pu, Ni	Fe
6	70.6	15.8	Ta, Na	none	Pu
7	72.3	6.9	Zr	Pu, Ta	Fe, Ni, Mg
32	63.4	3.6	Zr, Mg, Ni	none	Pu, Fe, Ta
40	70.2	11.4	Zr	Na, Pu	Fe, Ni, Ta

In addition to producing residues that are low in Pu concentration, the process also reduced the quantities of residues compared to flowsheet dissolution. Table VI compares the residue obtained from flowsheet testing with those quantities obtained with dissolution of fused materials. Figure 2 shows a residue comparison of the residues from Tests 9 and 10.

Table VI. Comparison of Residues for Baseline Flowsheet Testing and Peroxide Fusion Plus Dissolution

Test	% Pu in Feed	12 M HNO_3 – 0.2 M KF	Na_2O_2 Fusion + 4-8 M HNO_3
8	71.2	12.5 wt %	2.0 wt %
9	78.6	11.7 wt %	1.2 wt %
10	59.6	22.5 wt %	1.1 wt %
11	34.2	53.7 wt %	36.9 wt %
12	70.0	2.5 wt %	0.8 wt %
13	52.3	25.1 wt %	2.7 wt %
14	53.3	7.6 wt %	4.8 wt %
15	34.2	77.4 wt %	11.1 wt %

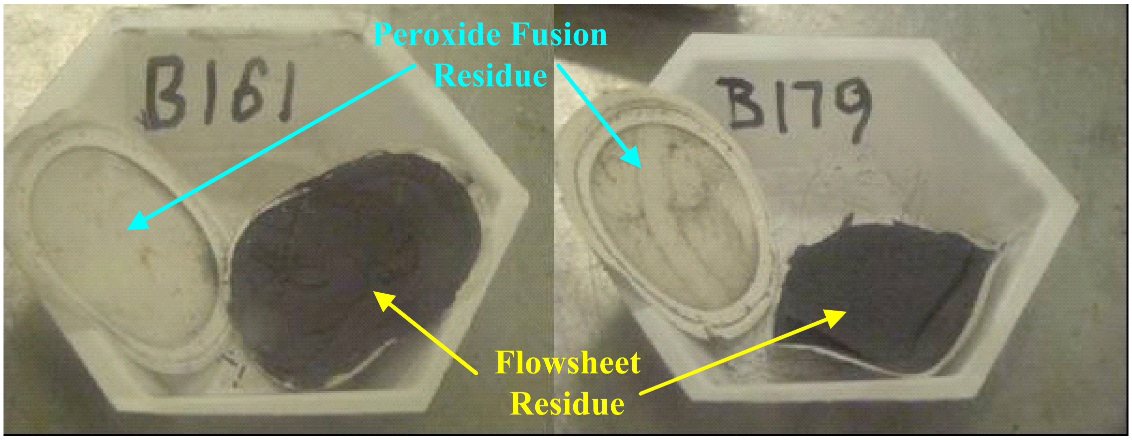

Fig. 2. Comparison of residues from peroxide fusion and dissolution with baseline flowsheet dissolution for Test 9 (left) and Test 10 (right)

Dissolver Acid Concentration

The dissolver acid concentration impacts the process in several ways. First, the dissolver acid concentration must be high enough so as not to be depleted during the dissolution cycle. Second, the dissolver acid concentration should be low enough so as not to exceed the solubility of sodium nitrate ($NaNO_3$) when the Na_2O_2 dissolves in HNO_3 [6]. Last, the acid concentration must provide for dissolution of Na_2O_2 fusion product to a final Pu concentration of 21-35 g/L without excessive fissile material in the residues.

A series of experiments were performed in which between three (i.e., Tests 34-36) and six (i.e., Tests 16-21) tests with sequential charging of fused materials were completed. The tests dissolved fused materials to the targeted (30-35 g/L) Pu concentrations, measured the acid concentrations, filtered for residues, and observed for at least 21 days for the formation of $NaNO_3$ precipitate. The test data are listed in Table VII. In the four sequential dissolutions, final Pu concentrations of 30-35 g/L were produced without the formation of precipitates in the final solution. In one of the test sets (Tests 16-21), a precipitate was observed after 13 days of storage. The precipitate had the visual appearance of $NaNO_3$, but the quantity was too small to sample.

Based on the data from Tests 22-27, the use of 4 M HNO_3 produces a final HNO_3 concentration that risks being sufficiently low to lead to Pu polymerization. There were no precipitates in Tests 23-25, but their presence in Tests 17-19 indicates that the use of an HNO_3 concentration greater than 6 M HNO_3 may yield higher quantities of $NaNO_3$ precipitate and possibly $NaNO_3$ precipitate in the final solution. Although undesirable, the formation of $NaNO_3$ is a minor issue that can be overcome by diluting the dissolver solution with low-molar HNO_3 after dissolution is complete. The use of 5-6 M HNO_3 as the dissolver solution appears optimal for the conditions tested.

Table VII. Changes in HNO_3, Pu, and Na Concentrations during Dissolution

Test #	Initial HNO_3 Conc. (M)	Final HNO_3 Conc. (M)	Final Pu Conc. (g/L)	Final Na Conc. (M)	Test #	Initial HNO_3 Conc. (M)	Final HNO_3 Conc. (M)	Final Pu Conc. (g/L)	Final Na Conc. (M)
16	6.0	5.5	4.7	0.5	22	4.0	3.5	4.7	0.5
17	5.5	5.0	9.5	1.0*	23	3.5	3.0	9.5	1.0
18	5.0	4.5	14.4	1.5*	24	3.0	2.2	14.4	1.5
19	4.5	4.0	19.5	2.1*	25	2.2	1.8	19.5	2.1
20	4.0	3.2	24.7	2.6	26	1.8	1.5	24.7	2.6
21	3.2	2.8	30.1	3.2	27	1.5	0.75	30.1	3.2
16-21 Residue = 0.041 g (0.7 wt %)					22-27 Residue = 0.041 g (2.0 wt %)				
34	6.0	4.3	11.1	0.90	37	5.0	4.2	8.3	0.8
35	4.3	3.3	22.8	1.8	38	4.2	3.5	16.9	1.7
36	3.3	2.2	35.0	2.8	39	3.5	2.5	26.0	2.5
34-36 Residue = 0.100 g (2.8 wt %)					40	2.5	1.6	35.0	3.4
					37-40 Residue = 0.107 g (2.7 wt %)				
* Trace post-precipitate after solution cooled, but not enough to weigh or sample									

Na_2O_2-to-Sample Weight Ratio

Proof-in-principle testing focused primarily on a Na_2O_2-to-sample weight ratio of 3.0-5.0. Initial parametric studies altered the focus to a ratio of 2.5-4.0. However, when the data showed no discernible difference between the quantities of residues observed at ratios of 2.5-4.0, subsequent testing explored the ratios of 2.5 and 3.0. It is important to remember that many of the later tests were performed sequentially so that the initial acid concentration for dissolution decreases. A variability chart of residue quantity as a function of Na_2O_2-to-sample ratio is shown in Figure 3. Variability in the residue quantity increases at Na_2O_2-to-sample ratios below 3.5.

Based on the data, the use of a Na_2O_2-to-sample weight ratio of 2.5 is feasible. However, its use may occasionally lead to unacceptable quantities of post-dissolution residues. Furthermore, the use of the lower ratio will place more emphasis on the technique used to mix the Na_2O_2 with the sample.

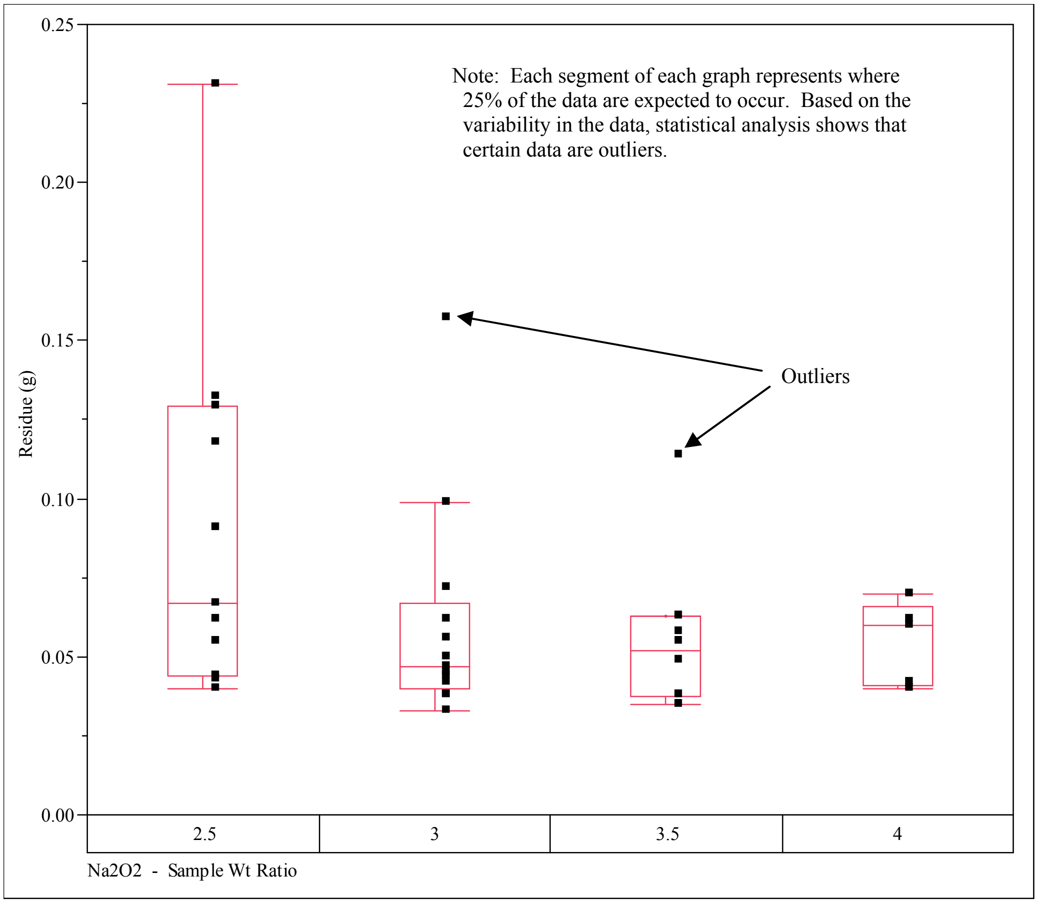

Fig. 3. Variability chart of residue quantity as a function of Na_2O_2-to-sample ratio

Pilot-Scale Testing

Five tests have been successfully completed with larger sample sizes (Tests 41-45). The expected HB-Line dissolver charges are expected to contain 100-150 g of feed material. Therefore, experiments are complete at samples sizes that are one-half to one-third the projected sample size in HB-Line. In pilot-scale tests, the Na_2O_2-to-sample weight ratio was ~3.0-3.5.

During dissolution, the contents began reacting with the ambient-temperature acid within seconds. Vigorous bubbling was observed and steam was released during the dissolution reaction. All five tests showed complete dissolution in less than 3 min (Table II). The temperature of the dissolver solution rose quickly – a temperature profile from Test 44 is shown in Figure 4, which dissolved to a final Pu concentration of ~16 g/L. The changes in temperature for all five pilot-scale tests are shown in Table II. Test 45 dissolved to a Pu concentration of ~24 g/L with a single charge, which is 2-3 times greater than what is recommended for a single charge in the current HB-Line dissolver. Post-dissolution residues for the larger-scale tests ranged from 0.7 to 2.2 wt %.

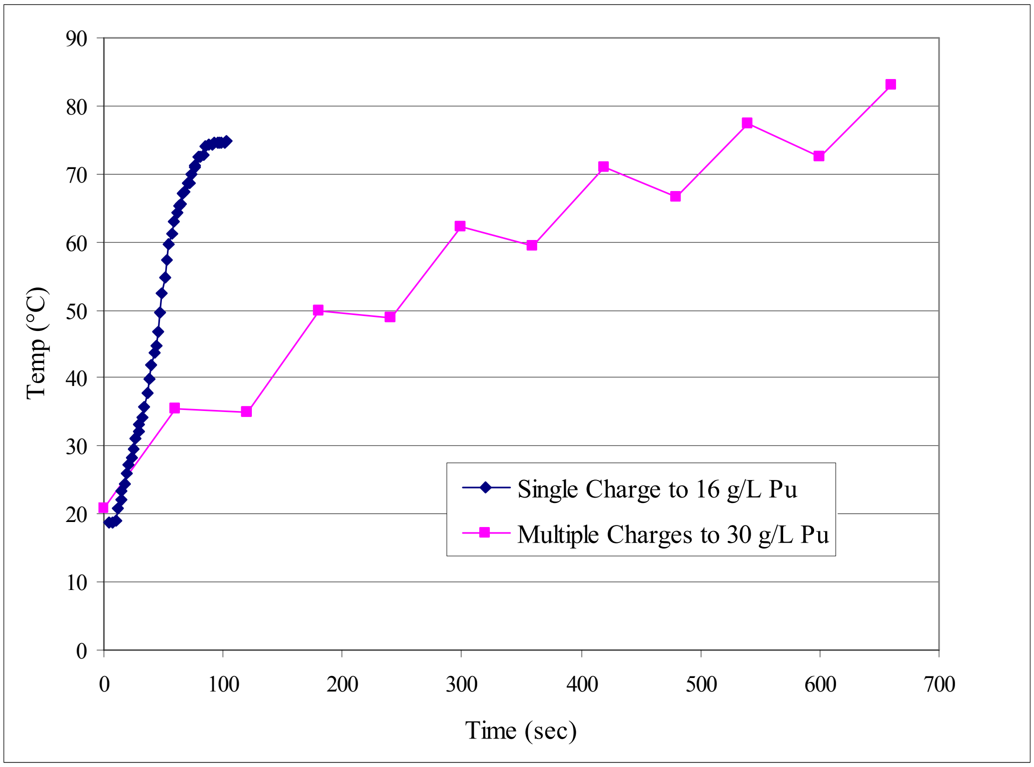

Fig. 4. Temperature profiles for dissolution of fusion product for single addition of a pilot-scale sample (Test 44) and sequential addition of small-scale samples (Tests 16-21).

CONCLUSIONS

SRNL demonstrated the feasibility and suitability of Na_2O_2 fusion and dissolution for the processing of Pu-bearing materials in HB-Line. Many aspects of the Na_2O_2 fusion process were studied to demonstrate its effectiveness and to define process conditions. Over 100 Pu-bearing samples containing 52-88% fissile material were successfully fused and dissolved (i.e., low Pu content in the residue).

Five tests with pilot-scale quantities of Na_2O_2 and Pu-bearing material were performed. Fusion product was made with up to 48 g of Pu-bearing material, which is one-third to one-half the scale recommended for implementation in HB-Line. During dissolution, a 45-g sample was dissolved as a single charge to a final Pu concentration in solution of 24 g/L. This concentration from a single charge is 2-3 times greater than what is recommended for a single charge to the existing HB-Line dissolvers. Each pilot-scale sample dissolved in HNO_3 in less than three minutes. Post-dissolution residues ranged from 0.7 to 2.2 wt %. The results from the pilot-scale tests were consistent with those observed during small-scale testing. Approximations based on available data and equipment configuration help predict that the dissolution cycle can be complete in less than one hour without a heating cycle.

Some amount of residue is expected after Na_2O_2 fusion and dissolution. Peroxide fusion and dissolution reduced the quantities of residues when compared to the baseline dissolution flowsheet, sometimes by a factor of 5-10. The residues are low in Pu concentration. Initial testing focused primarily on a Na_2O_2-to-sample weight ratio of 3.0-5.0. The data showed minimal discernible difference between the quantities of residues observed at the different ratios.

Subsequent testing compared the ratios of 2.5 and 3.0 and found that there are small differences in residue formation.

During the dissolution of fusion product, O_2 is released. Neither H_2 nor any other gas was directly measured. On average, approximately 250-300 mL of gas is released per gram of Pu-bearing samples dissolved at a Na_2O_2-to-sample ratio of 2.5-3.5.

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