

Dissolution of Neptunium Oxide Residues

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January 12, 2009

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Summary:

This report describes the development of a dissolution flowsheet for neptunium (Np) oxide (NpO_2) residues (i.e., various NpO_2 sources, HB-Line glovebox sweepings, and Savannah River National Laboratory (SRNL) thermogravimetric analysis samples). Samples of each type of materials proposed for processing were dissolved in a closed laboratory apparatus and the rate and total quantity of off-gas were measured. Samples of the off-gas were also analyzed. The quantity and type of solids remaining (when visible) were determined after post-dissolution filtration of the solution.

Recommended conditions for dissolution of the NpO_2 residues are:

Solution Matrix and Loading: ~50 g Np/L (750 g Np in 15 L of dissolver solution), using 8 M nitric acid (HNO_3), 0.025 M potassium fluoride (KF) at greater than 100 °C for at least 3 hours.

Off-gas: Analysis of the off-gas indicated nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) as the only identified components. No hydrogen (H_2) was detected. The molar ratio of off-gas produced per mole of Np dissolved ranged from 0.25 to 0.4 moles of gas per mole of Np dissolved. A peak off-gas rate of ~0.1 scfm/kg bulk oxide was observed.

Residual Solids: Pure NpO_2 dissolved with little or no residue with the proposed flowsheet but the NpCo and both sweepings samples left visible solid residue after dissolution. For the NpCo and Part II Sweepings samples the residue amounted to ~1% of the initial material, but for the Part I Sweepings sample, the residue amounted to ~8 % of the initial material. These residues contained primarily aluminum (Al) and silicon (Si) compounds that did not completely dissolve under the flowsheet conditions. The residues from both sweepings samples contained minor amounts of plutonium (Pu) particles. Overall, the undissolved Np and Pu particles in the residues were a very small fraction of the total solids.

Background:

Currently housed in HB-Line inventory is approximately 1.5-2 kg of neptunium oxide (NpO_2) of insufficient purity to ship as product. This material includes 'NpCo' (a term designating combined legacy NpO_2 standards), sweepings material from mechanical line processing and lab sample returns. Additional NpO_2 samples returns from the SRNL are also planned for inclusion in this inventory. HB-Line Phase I is identified as the facility for dissolution of these materials. HB-Line Phase II recently finished production of NpO_2 material and is soon to begin the 'flush and lay-up' process. To transfer this 'off-specification' material to H Canyon with other Phase II processing losses, the material must be dissolved.

'NpCo' material was combined from legacy NpO_2 sources several years ago. According to the Materials Control and Accountability information, the material traces to the early 1980's in the Old HB-Line vault.¹ Procedures completed during packaging indicate visual inspection confirmed each portion is oxide. All indications are that this material is NpO_2 produced in Old HB-Line by an oxalate precipitation process very similar to the process operated in HB-Line Phase II today. Previous characterization found that the 'NpCo' material contained ~6 wt % insoluble sodium, aluminum, and silicon compounds^{2,3,4}. These contaminants are likely from desiccants used in the original sources.

Np sweepings are materials produced in HB-Line Phase II that were retained due to their significant Np content but were not shippable as pure NpO_2 product. The Phase II process produced NpO_2 from calcination at ~635 °C from the product of an oxalate precipitation process. Therefore, the bulk of the sweepings materials are oxides but residue swept from the floor of the glovebox was probably included in the sweepings material. Unused NpO_2 samples and precipitator cleanout residues were also retained as sweepings.

SRNL sample returns are all materials that were produced in HB-Line Phase II during either the Part I or Part II campaigns. Some of this material was heated to higher temperatures during TGA or BET analyses (1000 to 1300 °C) and may exhibit different dissolution behavior as higher temperatures reduce the surface area of the oxide.

The dissolution of NpO_2 by nitric acid is expected to produce NO_x gases due to the oxidation of Np^{4+} to Np^{5+} and Np^{6+} . HB-Line controls the dissolver purge rate to limit flammable gas concentrations during dissolution. No H_2 off-gas would be expected to be produced if the materials are only oxides^{5,6}. The dissolution of NpO_2 has not been a routine activity in HB-Line but flowsheets for the recovery of small quantities of NpO_2 are described in internal site documents^{7,8}.

The NpO_2 considered for dissolution consists of Np Part I Sweepings (accumulated August 2004 through September 2006), Np Part II Sweepings (accumulated January 2008 through November 2008), 'NpCo' and SRNL sample return oxides. It is expected that a total of ~2 kg of Np oxide will be dissolved in HB-Line Phase I with a batch size of ~1 kg of Np. The target Np concentration in the dissolver is ~50 g Np/L^{9,10}. A single dissolution flowsheet for processing all the identified Np oxides in a Phase I dissolver using 2-12 M nitric acid

with up to 0.1 M KF is preferred. The dissolver is assumed to operate at $> 100\text{ }^{\circ}\text{C}$ with a 20 scfm purge rate. HB-Line Engineering requested that the flowsheet dissolve a high percentage of the material (although it is expected that some insoluble silicate compounds may be present). SRNL was also requested to measure the total gas generation rate during the dissolution and the percent residual solids for each class of materials.

Three classes of materials are identified for testing: 1) 'NpCo' (combined legacy Np oxide standards, Vial 898 sample received April 27, 2007), 2) Np Sweepings (Part I Vial 895 received April 27, 2007, and Part II Vial 946 received December 1, 2008, and 3) SRNL sample returns (Vials 838 & 951 received from M. L. Crowder, October 7, 2008, Vial 200 received from B. C. Hill, November 9, 2005). The calcination temperature history of these materials varies and it was anticipated that oxides heated to higher temperatures might have different dissolution characteristics. (Vials 838 and 951 contain TGA materials heated to 1000°C and 1300°C respectively which should be bounding materials for testing.) An additional sample of Part II Np Sweepings (Vial 946) was tested due to HB-Line concerns about the uniformity of the sweepings materials.

HB-Line will use 34 wt % aluminum nitrate solution to complex the fluoride used for dissolution at the ratio of three moles of Al per mole of fluoride. HB-Line requested demonstration that Al solubility downstream of the dissolution step would not be exceeded.

Experimental:

Test Description: Small samples of NpO_2 were dissolved in acid solution in two types of tests. Simple batch dissolution tests were performed to determine appropriate conditions for dissolution of the materials without leaving significant solid residues. Many of these tests were performed in air, but the later tests were performed in argon. The completeness of dissolution was primarily judged based on visual observations for solids after filtration. UV-visible spectroscopic examination of solution samples taken over time also looked for changes in Np concentration and valence state. Post-dissolution filtration of the solution (0.45 μm membrane filter) after cooling was used to determine the quantity of residual solids that remained.

When determination of off-gas volumes and rates was required, the dissolution apparatus was operated as a closed system. This second type of dissolution test was performed with a sample gas bag connected to the closed system. Because NO/NO₂ gases were anticipated to be a significant component of the off-gas, the system was flushed at the beginning of each test with inert argon (Ar) gas. Air, especially oxygen (O₂), was flushed from the apparatus to prevent reaction with NO to form additional NO₂. No liquid sampling of this system was performed until after the gas generation slowed and gas samples (if needed) were pulled for gas chromatography (GC) analysis. Gas volumes were determined in these experiments by collection of the off-gas in the sample bag and measurement of the volume of water displaced as the bag inflated. Gas samples were collected while the system was at temperature.

Previous testing observed the evolution of brown NO₂ fumes during dissolution of NpO_2 . These gases are products from the oxidation of Np^{4+} to Np^{5+} and Np^{6+} . Depending on the chemical conditions during dissolution Np may exist in any or all of these oxidation states.

When composition determination of the gas samples was required, the analysis was performed by the Analytical Development (AD) department on a Hewlett Packard model 5890 gas chromatograph (GC) equipped with a 60/80 Carboxen 1000 column (15 feet X 1/8 inch stainless steel, 2.1 mm ID) and thermal conductivity detector (TCD). Calibration was carried out prior to and after the sample analyses using Scott Gas Mix 218, as well as calibration verification using blank air. Samples were normally analyzed in duplicate for confirmation of results but in some cases only a single determination on duplicate samples was performed. Argon carrier gas was used.

Experimental Setup: The experimental setup for all gas collection testing consists of a 125 mL 4-port boiling flask fitted with a small condenser. Tygon® tubing (0.125 in. ID) connected a Swagelok®

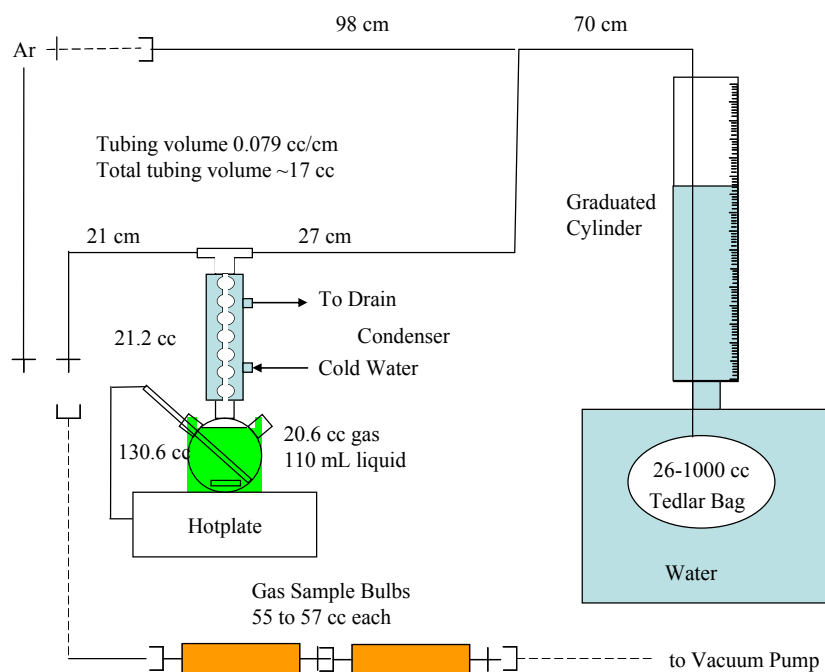
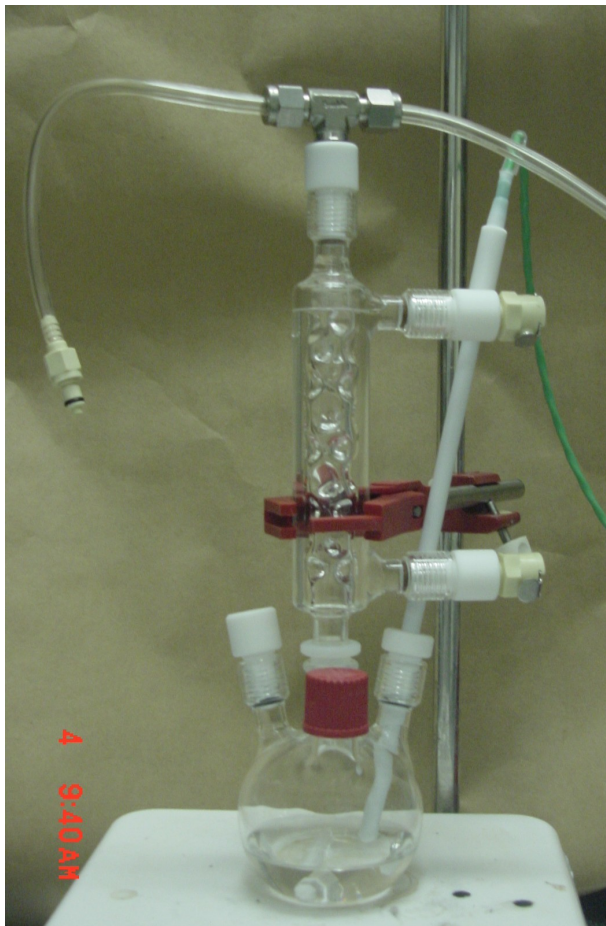


Figure 1. Experimental Setup.

Tedlar® bag allows for a significantly larger quantity of gas than is anticipated in any experiment (with up to 9 g of oxide). This bag will burst at 2 to 2.5 psig providing for a safe-failure mechanism¹¹. The apparatus was repeatedly filled and purged with argon before each experiment. A leak-check step was later incorporated into the procedure as part of the argon purge after the apparatus was assembled and loaded with solution and oxide. Gas sample bulbs were alternatively filled with argon and evacuated with a small vacuum pump capable of evacuating the bulbs to 25-27 in. of Hg. Argon was chosen due to its inertness and the consideration that any air in-leakage would be readily detected by the presence of oxygen or nitrogen. Argon is also the carrier gas for the GC method used in the gas analysis. Gas samples were taken after off-gas generation was complete and with the dissolver system at temperature. A sketch of the experimental setup showing approximate tubing lengths and volumes is shown in Figure 1. Photos of the actual apparatus follow in Figures 2a, 2b, and 2c.

connected a Swagelok® “T” to the 1-L Tedlar® gas bag. The gas bag was submerged in a ~3-L glass kettle with a ~325-mL graduated cylinder installed on top. Two other Tygon® lines allow connection to the argon supply and gas sample bulbs. These lines and the gas sample bulbs are fitted with quick-connect fittings that seal when disconnected so that the system can be kept closed. The 1-L



a)



b)



c)

Figure 2. Equipment: a) Dissolver & Condenser Apparatus, b) Gas Collection and measurement by Water Displacement, c) Gas Sampling Bulbs with NO, N₂O, NO₂ Present.

Experiments that were only directed at investigating dissolution conditions were performed with a relatively small volume of solution in the boiling flask (typically 33 mL). Tests performed with a relatively large volume of vapor space in the boiling flask resulted in a significant volume of expansion gas due to the increased partial pressure of water vapor and displacement of the argon gas as the solution warmed. Experiments directed at gas volume measurement were performed with a relatively large volume of solution in the boiling flask (typically 110 mL). This volume of solution left a relatively small volume of vapor space (~20.6 cc). Tests with 12 M HNO₃ but limited to 100 °C had a smaller heat-up volume effect due to the smaller partial pressures generated.

Calculations/Corrections: Correction of the gas volume for the liquid pressure head, the gas temperature and the volume displaced by the collection tubing in the graduate were required to convert the measured gas volume to Standard Temperature and Pressure (STP; 1 atm, 0 °C). Atmospheric pressure was assumed constant at 1 atm. The pressure correction due to water pressure on the gas bag varied linearly with the amount of gas collected as shown in Table 1 and Figure 3. The gas temperature correction was made based on a meas-

Table 1. Pressure Correction for Gas Collection System.

V	P	P*
cc	in. H ₂ O	
25	4.6	1.1%
42	5.0	1.2%
86	6.0	1.5%
130	7.0	1.7%
174	8.0	2.0%
218	9.0	2.2%
262	10.0	2.5%
306	11.0	2.7%
350	12.0	2.9%

$P=4.0579+V*0.0227$
 $P*=P/12/33.899$

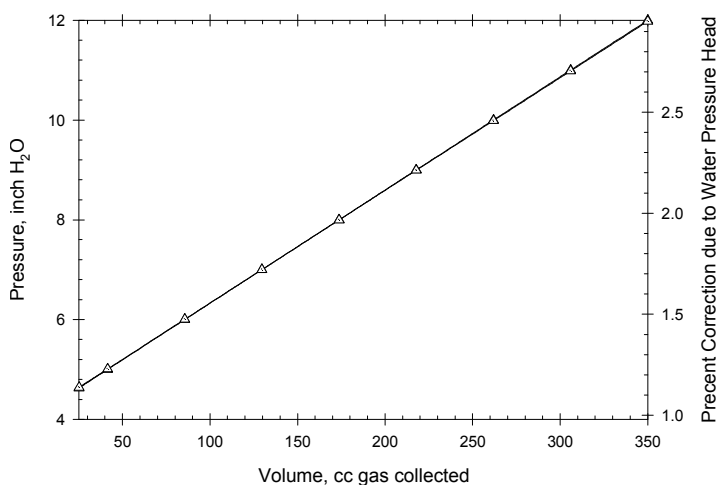


Figure 3. Correction due to Pressure Head.

ured temperature of the laboratory (i.e., the gas bag was placed after the cooling condenser) as a direct measurement of the gas was not readily performed. The laboratory temperature varied from 22 to 25 °C during the performance of this work. The water in the gas displacement apparatus in the glovebox was assumed to closely track the laboratory temperature. The gas volume was measured by the change in the water volume in the graduated cylinder (Figure 2b). A correction of the gas volume for the tubing volume was a constant reduction of 1.825% (based on the ratio of the cross-sectional areas of 0.25 in. OD Tygon® tubing to the 4.7 cm ID graduated cylinder).

Results:

Collection Test with Gas Standard: An experiment was performed to demonstrate the ability to accurately retain, sample and analyze for H₂. In this test 150 cc of a known standard gas mixture was injected into a clean duplicate of the glovebox apparatus using a 50-cc gas syringe. This gas was taken from a partially filled Tedlar® gas bag to ensure that the gas was at atmospheric pressure. The dissolver apparatus contained 110 mL of 8 M HNO₃ and was previously purged with argon to eliminate air. The initial gas volume of the apparatus was estimated based on a combination of measurements and calculations to be 84.9 cc which would dilute the known standard gas (150 cc) with argon to 64% of its original concentration. The hotplate was turned on and the apparatus was heated similar to that done in the dissolution experiments. After 1 hour (including heating time), a pair of argon-flushed and evacuated gas sample bulbs was connected to the apparatus and a pair of duplicate gas samples were collected with the apparatus at temperature. These samples were submitted for gas analysis by GC along with an undiluted sample of the known standard gas. The results are shown in Table 2. CO₂ was not detected although it was present at the 0.64 to 1% level (probably due to CO₂'s longer retention time). H₂ was reported at the expected value within the 20% uncertainty. O₂ was consistently reported at 30 to 50% of the expected value. Although the uncertainties are significant, this test demonstrated the ability of the experimental apparatus, sampling methods and analytical procedures to collect and quantify H₂ and other atmospheric gases.

Table 2. Gas Analysis Test with a Known Standard Gas^a.

		H ₂	O ₂	N ₂	NO	N ₂ O	CO	CO ₂		
H ₂ Std Known	Lot# 607403L	1	1	95	0	0	1	1		
H ₂ Std Analyzed	300255212	1.2	0.31	90	< 0.1	< 0.1	1.3			
		H ₂	O ₂	N ₂	NO	N ₂ O	CO	CO ₂ ^b	Ar ^b	
Diluted H ₂ Std	Calc	0.64	0.64	61.05	0.00	0.00	0.64	0.64	36	
H ₂ calibration #1	300255136	0.77	0.22	62	< 0.1	< 0.1	1			
H ₂ calibration #2	300255137	0.67	0.33	60	< 0.1	< 0.1	0.87			

^aUnits are volume percent.

^bArgon and CO₂ concentrations are calculated by dilution.

Initial Dissolution Tests: Initial experiments were performed to dissolve pure NpO₂ in 12 M HNO₃ based on the prior process reports^{7,8}. Although KF was typically used in the prior flowsheets, it was thought that KF might not be necessary to dissolve NpO₂. However, attempts to dissolve pure NpO₂ samples without KF did not give reproducible results. In several tests without KF in 12 M HNO₃ significant NpO₂ remained after 2 to 5 hours at 100 °C. The solids changed color during this time and turned from darker green to yellow-green (Figure 4). An X-ray diffraction (XRD) analysis of the solids showed them to be NpO₂ but the color and appearance were very different from that of the starting material. After digestion in 12 M HNO₃, solid KF (equivalent to 0.08 to 0.1 M KF) was added to the hot solution and dissolution of the NpO₂ occurred with 5 to 30 s (noted in Table 3 as KF delay). This sort of rapid dissolution behavior was repeatedly observed even though several attempts at dissolution without KF did appear successful. Based on the inconsistent dissolution of NpO₂ without KF, further attempts to avoid KF usage were not pursued. However, lower KF and acid concentrations were attempted with success. Dissolution conditions of 8 M HNO₃ with

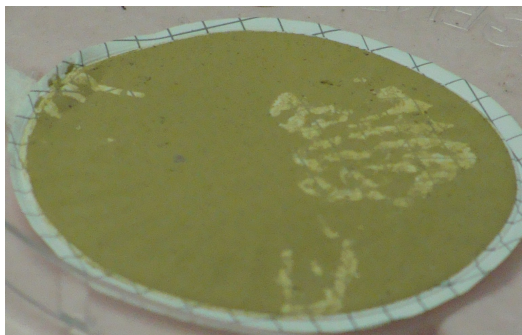


Figure 4. Digested NpO_2 without KF.

0.025 M KF at 100 °C for < 1 hour gave consistent dissolution of pure NpO_2 calcined at 650, 1000, and 1300 °C without any significant evidence of residual solids.

Gas and Valence State Observations: During the initial heating of the dissolver flask, brown NO_2 fumes were not observed until the temperature of the solution reached ~70-90 °C. Above 90 °C, the brown color was very noticeable in the condenser (see Figure 5). Similar gassing behavior was observed when a mixture of Np^{4+} and

Np^{5+} solution (without any valence stabilizers) in 12 M HNO_3 was heated in the apparatus. It was not determined if the NpO_2 was first dissolved and then oxidized to Np^{5+} and Np^{6+} or if oxidation was part of the dissolution behavior. Sampling and measurement of the solution

spectra indicated widely varying mixtures of Np^{4+} , Np^{5+} and Np^{6+} . Depending on the dissolution conditions (e.g. acid concentration and length of heating time), any one of the valence states of Np could dominate the mixture but all three were often present in the same solution. The data require further examination but initial review indicates that longer times at 12 M HNO_3 may favor a high percentage of Np^{6+} . In other tests, dissolution at 8 M HNO_3 resulted in a high percentage of Np^{4+} . When gas samples were not removed from the system for analysis, the re-absorption of the majority of the off-gas was observed as the apparatus cooled to ambient temperature. This gas volume loss is likely due to re-adsorption of the NO/NO_2 gases rather than leakage since the apparatus was tested repeatedly with argon and appeared capable of holding argon under 12 inches of water head pressure for 2.5 days with very little volume loss. A single instance of leakage from the thermocouple fitting was observed but in that case no gas could be collected at all. After that single observed leak issue, a leak check was incorporated into the experimental procedure as part of the apparatus flush with argon.



Figure 5. NpCo Vial 898 Dissolution Test.

Overall Dissolution Tests: Table 3 contains a summary of the dissolution conditions, dissolution time and amount of solid residue for each of the NpO₂ dissolution tests performed. Many of the initial experiments occurred at higher HNO₃ and KF concentration than were found to be necessary. The amount of solids observed and measured will be discussed in more detail in a later section of the report. The Np value is calculated based on the values for Np assay provided for each material by HB-Line¹².

Table 3. Np Dissolution Test Conditions^c.

Date	Test ID	Vial	HNO ₃ M	KF M	Np g/L	KF ^d Delay	NpO ₂ g	Np g	Vol mL	Time min	Solids g	Solids %	^e
09/15/08	200 14MF	200	14.13	3.448	47.5		0.54	0.48	10		0.542	100%	Solids
09/30/08	198 12MF	198	11.62	0.099	18.8		0.52	0.45	24	203	0.012	2.3%	
10/06/08	198 12M	198	11.78	0.000	13.8		0.51	0.44	32	197	0.014	2.8%	
10/07/08	197 12M	197	12.27	0.000	14.2		soln	0.46	32	190	0.007	0.0%	
10/09/08	838 12M	838	11.78	0.070	19.2		0.70	0.61	32	378	0.009	1.3%	
10/10/08 6:45	838 12MF	838	11.78	0.095	14.0		0.51	0.45	32	136	0.001	0.2%	
10/11/08 6:50	838 12M2	838	11.78	0.000	14.4		0.53	0.46	32	300	0.005	1.0%	
10/14/08 9:05	898 2M	838	1.96	0.086	14.9		0.55	0.48	32	323	0.005	0.9%	
10/16/08 9:25	951 12M	951	11.78	0.077	14.6	Y	0.53	0.47	32	240	0.000	0.0%	
10/24/08 8:55	898 12M	898	11.78	0.080	14.6	Y	0.55	0.47	32	325	0.005	0.9%	
10/24/08 9:00	838 2M2	838	1.96	0.087	13.6	Y	0.50	0.44	32	220	0.006	1.2%	
10/28/08 13:26	838 12M3	838	11.78	0.083	14.1		0.51	0.45	32	64	0.004	0.8%	
10/29/08 9:35	838 12M4	838	11.78	0.086	53.2		1.94	1.70	32	58	0.000	0.0%	
10/31/08 9:06	838 12M5	838	11.78	0.087	52.2	Y	1.90	1.67	32	104	0.006	0.0%	Leak
11/4/08 10:08	200 12M1	200	11.78	0.048	51.4	Y	1.88	1.65	32	143	0.009	0.5%	
11/5/08 8:43	200 12M2	200	11.78	0.048	51.5		1.88	1.65	32	47	0.003	0.2%	
11/5/08 13:47	200 12MF3	200	13.74	0.028	52.1		1.90	1.67	32	43	0.000	0.0%	
11/6/08 8:33	200 8MF4	200	8.09	0.025	50.2		1.89	1.66	33	47	0.011	0.6%	
11/6/08 13:03	951 8MF2	951	8.09	0.029	50.2		1.89	1.66	33	59	0.032	1.7%	
11/7/08 8:35	838 8MF6	838	8.09	0.026	51.9		1.95	1.71	33	60	0.000	0.0%	
11/7/08 12:13	200 8MF5	200	8.09	0.028	50.7		1.91	1.67	33	60	0.000	0.0%	
11/12/08 12:45	200 8MF6 ^g	200	8.56	0.023	15.4		1.93	1.69	110	60	0.000	0.0%	
11/18/08 8:37	895 8MF1 ^g	895	8.56	0.023	59.6		8.91	6.56	110	155	1.321	14.8%	Solids
11/19/08 9:50	898 8MF2 ^g	898	8.56	0.024	68.7		9.19	7.56	110	150	0.069	0.8%	Solids
11/21/08 9:10	200 8MF7	200	8.09	0.000	13.3		0.50	0.44	33	222	0.048	9.6%	Solids
12/1/08 10:05	200 8M8	200	8.09	0.027	70.1		2.64	2.31	33	110	0.005	0.2%	
12/2/08 8:55	838 MF7 ^g	838	8.56	0.024	54.8		6.87	6.03	110	127	0.000	0.0%	
12/2/08 13:42	895 8MF2 ^f	895	8.09	0.027	0.0		0.51		33	105	0.000	0.0%	Solids
12/3/08 9:20	895 8MF2 ^f	895	8.09	0.107	0.0		0.51		33	58	0.061	11.9%	Solids
12/3/08 13:13	946 8MF1 ^g	946	8.56	0.098	16.3		2.10	1.79	110	67	0.000	0.0%	
12/4/08 7:52	946 8MF2 ^g	946	8.56	0.024	61.9		7.97	6.81	110	120	0.085	1.1%	Solids

^c Test 200 14MF was performed at 50°C and Test 198 12MF was performed at 95 °C. All other tests were performed at 100 °C.

^d KF Delay refers to the addition of KF to a hot dissolution batch after the initial batch failed to completely dissolve the solids.

^e Solids noted indicates that solids were visible on filter paper after filtration of the solution post-dissolution.

^f Test 895 8MF2 is shown twice. The initial entry indicates the unsuccessful attempt to dissolve the 895 8MF1 residue in fresh dissolver solution. The 2nd entry is the continuation of that dissolution with additional KF added which still left a significant quantity of solids.

^g Gas generation data available for these tests.

Gas Yield and Rates: Time, temperature and gas volume were measured for six dissolution experiments that span the range of the target materials for this campaign (i.e., NpCo source material, 898, HB-Line glovebox sweepings, 895 and 946, and SRNL thermogravimetric analysis samples, 200, 838 and 951). Figures 6 and 7 are plots of the temperature and gas generation results for these six experiments. Note that several tests used significantly less mass of Np (see Table 3) and generated significantly less gas which limits the usefulness of that data. Correction of the data for the volume expansion of the headspace gas during heat-up was not performed due to insufficient volume-temperature data. This correction should be relatively small when the total gas generated is > 200 cc. The lack of this correction is conservative in that it biases the gas generation results high.

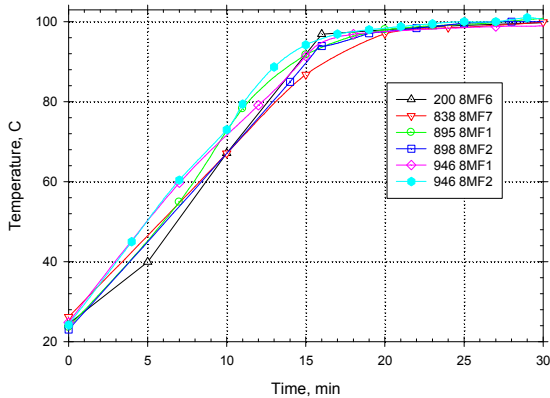


Figure 6. Temperature Profile over Time for 110 mL Dissolution Experiments.

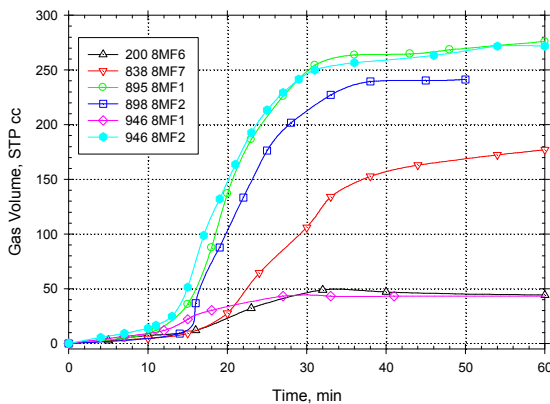


Figure 7. Gas Volume Evolved over Time.

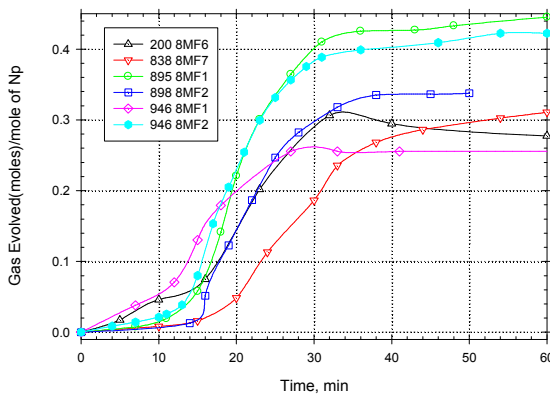


Figure 8. Gas Yield over Time

If all the Np were dissolved and oxidized to Np^{6+} , a maximum of two moles of NO_2 gas could be evolved for each mole of Np. If NO were the only gas product, a maximum 0.67 moles of NO could be evolved. As will be discussed later a mixture of nitrogen oxide gases (including N_2O) was observed in all tests. Figure 8 shows the molar gas yield for the same six dissolution tests. The ultimate yield of gas ranged from 0.25 to 0.42 moles of gas per mole of NpO_2 dissolved.

The off-gas processing concern during dissolution is the potential to produce more gas than the vessel ventilation system is designed to handle. This concern could be either for flammable gas dilution or pressurization of the vessel. This study sought to measure not only the total amount of gas evolved but also the rate at which that gas evolves over time during processing. Figures 9 and 10 are plots of rate data over time for the six dissolution experiments in units of moles per mole of Np and units of scfm per kilogram of bulk oxide. Use of the latter units avoids the composition uncertainty of the residue as it is scaled to the total mass of material charged to the

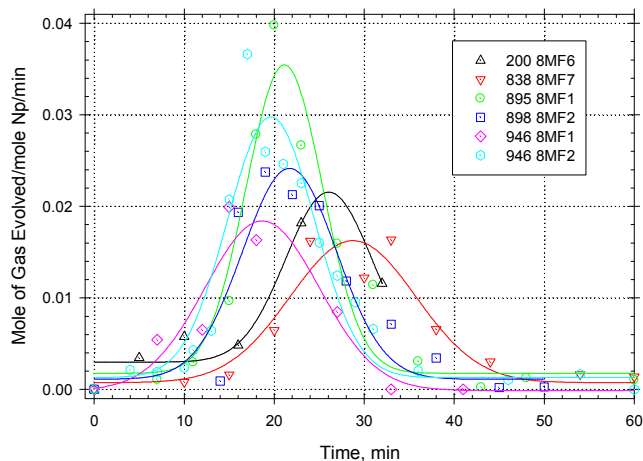


Figure 9. Molar Gas Yield Rate over Time.

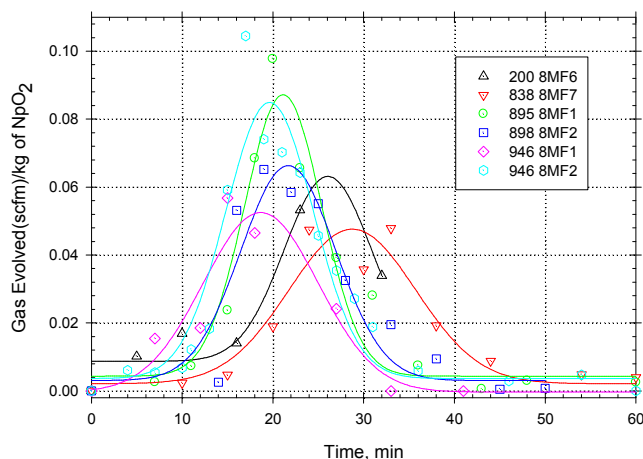


Figure 10. Rate of Gas Evolution per kg of Bulk Oxide over Time.

dissolver. Smooth curves were not readily fit through the data but a 4-parameter Gaussian Peak fit using SigmaPlot 10.0 software produced the curves shown.

Peak off-gas rates of ~ 0.104 scfm/kg of bulk Np material (0.036 moles/mole of NpO_2/min) were observed. This off-gas rate compares favorably with a 20 scfm purge rate for the HB-Line dissolver. The generation values based on moles of Np dissolved are expected to increase by $\sim 10\%$ when corrected with a measured Np assay value for the actual samples tested.

Tables 7 through 12 in the appendix contain the gas evolution data for Figures 6 through 10.

Gas Analyses: Gas compositional analysis was initially not part of the scope of this work but was incorporated as the work proceeded due to the amount of gas produced. Sampling was performed as described in the gas collection test section and analyzed per the standard GC

method. This method was recognized to be limited in that it does not attempt to quantify NO_2 which is a significant component of the off-gas from these dissolution experiments. Based on the calculated internal volume of the apparatus of 84.9 cc, an argon concentration

Table 4. Gas Analysis Results for Dissolution of NpO_2 Samples^a.

	LIMS ID	H ₂	O ₂	N ₂	NO	N ₂ O	CO	NO ₂
Vial #898 NpCo Gas#1	3-255203	<0.13	<0.13	<0.13	64	14.1	<0.13	21
Vial #898 NpCo Gas#2	3-255204	<0.13	<0.13	<0.13	71	7.8	<0.13	21
Vial #895 Part I Sweepings Gas#1	3-255205	<0.13	<0.13	<0.13	50	3.0	<0.13	46
Vial #895 Part I Sweepings Gas#2	3-255206	<0.13	<0.13	<0.13	73	1.6	<0.13	25
Vial #946 Part II Sweepings Gas#1	3-255746	<0.13	<0.13	<0.13	28	2.6	<0.13	69
Vial #946 Part II Sweepings Gas#2	3-255747	<0.13	<0.13	<0.13	30	5.9	<0.13	63
Vial #838 1000 °C NpO ₂ Gas#1	3-255744	<0.14	<0.14	<0.14	35	7.2	<0.14	57
Vial #838 1000 °C NpO ₂ Gas#2	3-255745	<0.14	<0.14	<0.14	66	3.2	<0.14	30

^aUnits are volume percent on an Ar-free basis.

was calculated for each experiment and a NO₂ concentration was estimated assuming that argon and NO₂ were the only un-quantified gases present. Gas samples were analyzed from dissolution experiments using the following materials: NpCo source oxide, 1000 °C Calcined TGA NpO₂, and Np sweeping samples from the Part I and Part II campaigns. In each case duplicate gas samples were taken simultaneously. In the Part I Sweepings experiment (Vial 895), the gas samples were taken after 141 min, but for the other three materials, gas samples were taken at ~1 hour. As shown in Table 4, none of these experiments showed any indication that hydrogen was produced during dissolution of any of these NpO₂ samples. There was also no indication that the integrity of the sample was affected by any in-leakage of air. The duplicate samples did not show good agreement on the nitrogen oxides. The NO result appears to vary widely between duplicate samples. With the variation between duplicate samples, it is difficult to determine if there is any significance between differences in the NO yield between the different material types. Note that the results as shown in Table 4 are corrected to an Ar-free basis to reflect the composition of the gas evolved. (For the laboratory apparatus, the argon dilution amounted to 20-26% of the total off-gas collected.)

Residual Solids: Table 3 contains results of the amount of solids found on air-dried filter papers from the filtration of the dissolver solution at the end of each test. In six experiments some visible solids were observed. Three of those experiments involved the solids found in the Part I Sweepings material. (Two out of those three were additional attempts to completely dissolve the silica residue from the first experiment.) The material from Part I Sweepings dissolution (895 8MF1) was dried overnight and contained ~15% of the initial mass of material used. However, after sampling for SEM and XRD analyses (usually < 0.1 g bulk) and air drying for two weeks, the remaining sample had lost significant weight (1.321g dropped to 0.513g or only 5.7% of the original mass charged). The residue from the Part I Sweeping dissolution had a significant thickness (compared to that from the other experiments) and apparently took much longer to dry than other samples. Rather than the 15 wt % initially measured, it was likely no more than ~8 wt % residual solids (including estimated mass of samples). The dried residue from this initial test (895 8MF1) was later used as feed material for a separate dissolution test with fresh solution (895 8MF2). After 105 min of heating without visible progress, the solution was allowed to cool overnight, the KF concentration was increased to 0.1 M and the solution was again heated for another 58 min. Although the amount of solids did decrease during this treatment, the final solution remained nearly colorless indicating that an insignificant amount of Np leached from the solids. This lack of solution color is consistent with the SEM observations that the residual solids from Part I Sweepings dissolution did not contain significant Np solids.

The only other experiment where significant solids were observed was a dissolution attempt

Table 5. XRD and SEM Characterization of Np Dissolution Residues.

895 Np Sweepings I: mostly Si, lesser amounts of Fe-Cr-Ni, Pu; some small Np particles Non-crystalline Si not identified by XRD
898 NpCo: largest particles are Al-Si round beads; lesser amounts of Pu, Np, and Sn XRD indicated Boehmite (AlOOH)
946 Np Sweepings II: mostly Si, lesser amounts of Fe-Cr-Ni, few large Pu particles, some small Np particles XRD identified Quartz, talc, NpO ₂ with a large non-crystalline signal as in 895 sample

without KF to prepare a solid sample of the yellow green residue to confirm the X-ray pattern of the solids. With 0.025 M KF present, only the Part I Sweepings sample left significantly more than 1 wt % solid residue after heating for 1 to 2.5 hours. The Part I Sweepings sample was initially heated for 2.6 hours and although there was significant residue, that residue proved to be mostly composed of silica, stainless steel and other non-actinide compounds (Table 5). Further heating of that residue for 3 additional hours with fresh solution and additional fluoride reduced the residue mass but did not appear to leach significant Np from the residue. Because a significant fraction of the Np materials to be processed are from the sweepings category, a dissolution time of no less than 3 hours is recommended for plant processing. Additional time beyond 3 hours should reduce the amount of total residues left from the sweepings, but the NpO_2 is expected to dissolve during the initial 1 to 2.5 hours at temperature.



Figure 11. Solids from Vial 895 (Sweepings I) Dissolution.

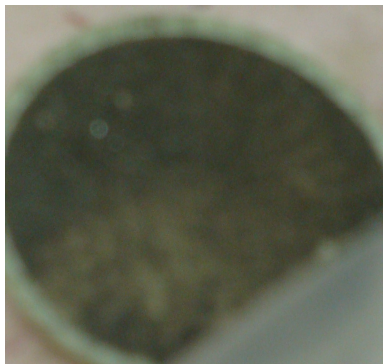


Figure 12. Solids from Vial 946 8MF2 (Sweepings II) Dissolution.

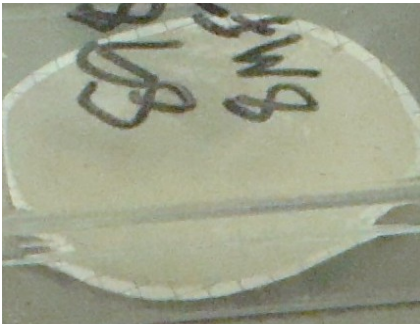


Figure 13. Solids from Vial 898 (NpCo) Dissolution.

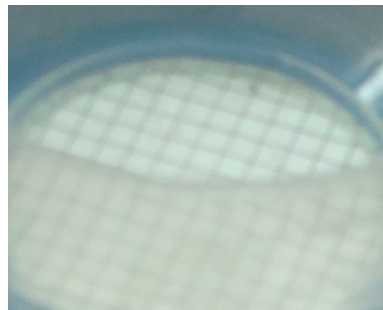


Figure 14. Solids from Vial 200 (650°C NpO_2) Dissolution.



Figure 15. Solids from Vial 838 (1000°C TGA NpO_2) Dissolution.

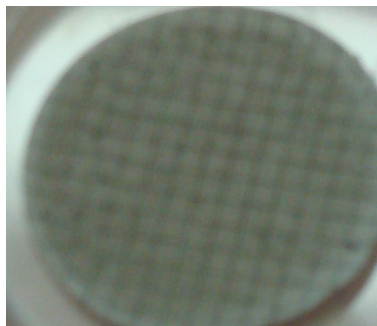


Figure 16. Solids from Vial 946 8MF1 Dissolution

Photos of the Part I and II Sweepings residues after dissolution and filtration are included as Figures 11 and 12. Although the photo is blurred, it can be seen that the Part II Sweepings resulted in appreciably less residual solids after dissolution. The NpCo material resulted in less residual solids than the Part II Sweepings. None of the other materials tested generated significant residue. Comparable photos of NpCo, 1000 °C TGA, 650 °C NpO_2 , and the initial Part II Sweepings residues (946 8MF1) are included as Figures 13, 14, 15, and 16. Table 5 provides a description of the dissolution residues as identified by XRD/SEM analyses.

Aluminum Nitrate Solubility: The initial flowsheet proposed for dissolution of these materials was 12 M HNO₃ and 0.1 to 0.3 M KF based on prior internal reports^{7,8}. At those levels of nitrate and fluoride, the complexation of fluoride at a 3:1 molar ratio would be expected to exceed the solubility of aluminum nitrate unless significant dilution of the nitrate was performed. Aluminum nitrate solubility in 12 M HNO₃ is reported at ~0.12 M at 20 °C whereas at 8 M HNO₃, the solubility is reported at ~0.67 M at 20 °C¹³. Dissolution in 12 M HNO₃ requires attention to the amount of dilution performed prior to the addition of aluminum nitrate solution (usually in the form of 34 wt % aluminum nitrate). When dissolution is performed in 8 M HNO₃ with < 0.1 M KF, aluminum nitrate solubility should not be a concern.

Table 6. Aluminum Nitrate Solubility Test.

	Np, g/L	HNO ₃ , M	KF, M
895 8MF2 w ANN	0.0	7.13	0.095
946 8MF2 w ANN	61.5	8.32	0.023
946 8MF1 w ANN	14.2	7.66	0.087
895 8MF1 w ANN	68.4	8.32	0.023
898 8MF2 w ANN	66.8	8.32	0.023

Tests were performed on the five final dissolver samples listed in Table 6 to confirm that these solutions show the expected solubility behavior. In each case a minimum of 3 moles of aluminum nitrate (34 wt % solution in water) were added per mole of fluoride in the solution. The concentrations shown in Table 6 reflect the dilution from the water from the use of a 34 wt % aluminum nitrate reagent.

No solids were observed to form in any of the five dissolver solution samples within two weeks of adjustment with 34 wt % aluminum nitrate.

Recommendations:

- 1) Dissolve NpO₂ materials in an 8 M HNO₃/0.025 M KF solution at 100 °C for no less than 3 hours. Np loading of 50 to 70 g Np/L was demonstrated but silica and other non-Np impurities did not completely dissolve in the time allotted. A loading of 50 g Np/L is recommended (equivalent to 750 g Np dissolved into 15 L of acid solution) as this loading should be sufficient to process the projected inventories in a reasonable number of batches.
- 2) Be prepared for concentrations of harder-to-dissolve impurities (i.e., silica, iron-nickel-chromium, and boehmite) in the range of 1 to 8 wt % of the bulk material charged. Longer dissolution cycles and higher levels of fluoride will tend to reduce the amount of residual solids produced but are not expected to eliminate them entirely.
- 3) Be prepared for an off-gas rate as great as to 0.11 scfm/kg of bulk material. The off-gas will be composed of NO, NO₂ and N₂O. No H₂ off-gas is expected. Since HB-Line operates with an air purge, the NO produced will be rapidly oxidized to NO₂ which will reduce the actual off-gas rate observed in the field.

Conclusions:

A dissolution flowsheet for processing various NpO₂ materials has been developed and demonstrated by SRNL with samples of the materials from HB-Line. This flowsheet should allow for the disposition of these types of materials in HB-Line with only limited amounts of non-Np solid residues remaining. The off-gas from this process will be composed of NO, NO₂ and N₂O gases but no H₂ was observed in the laboratory.

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Appendix

Table 7. Gas Results for Pure NpO₂ Material.

200 8MF6, NpO ₂ 650 °C, 1.927g oxide, 22 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	32	24.5	0.0	0.000		
5	35	39.9	2.8	0.017	0.003	0.010
10	40	67.1	7.4	0.046	0.006	0.017
16	45	96.9	12.0	0.075	0.005	0.014
23	67	98.8	32.3	0.202	0.018	0.053
32	85	100	48.9	0.306	0.012	0.034
40	83	100	47.1	0.295		
60	80	100	44.3	0.277		
80	50	79.4	16.6	0.104	Apparatus cooled	

V* is the gas volume collected corrected to standard conditions.

Table 8. Gas Results for Pure NpO₂ Material.

838 8MF7, NpO ₂ 1000 °C, 6.871g oxide, 23.7 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	50	26.2	0.0	0.000		
10	55	67.1	4.6	0.008	0.001	0.002
15	60	86.8	9.2	0.016	0.002	0.005
20	80	97	27.6	0.048	0.006	0.019
24	120	98.5	64.5	0.113	0.016	0.047
30	165	99.9	106.2	0.186	0.012	0.036
33	195	100	134.1	0.235	0.016	0.048
38	215	100	152.7	0.268	0.007	0.019
44	226	99.9	163.0	0.286	0.003	0.009
54	236	100	172.4	0.303	0.002	0.005
60	241	100	177.1	0.311	0.001	0.004
62	170	100	110.8	Gas Samples Pulled		
163	168	100	109.0			
167	168	100	109.0			

Table 9. Gas Results for NpCo Source Material.

898 8MF2, NpCo, 9.193g oxide, 23 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	40	23	0.0	0.000		
14	50	85	9.2	0.012	0.001	0.003
16	80	93.9	36.8	0.050	0.019	0.053
19	135	97.1	87.7	0.119	0.023	0.065
22	184	98.4	133.3	0.181	0.021	0.058
25	230	99.6	176.4	0.239	0.019	0.055
28	257	100	201.7	0.274	0.011	0.032
33	284	100	227.1	0.308	0.007	0.020
38	297	100	239.4	0.325	0.003	0.009
45	298	99.7	240.4	0.326	0.000	0.001
50	299	100	241.3	0.327	0.000	0.001
58	293	100	235.6			
64	200	100	148.3	Gas Samples Pulled		
145	94	100	49.8			

Table 10. Gas Results for Np Sweepings Material.

895 8MF1, Sweepings, 8.908g oxide, 23.4 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	42	23.6	0.0	0.000		
7	47	54.9	4.6	0.008	0.001	0.003
11	55	78.3	11.9	0.021	0.003	0.007
15	81	91.7	35.9	0.063	0.010	0.024
18	137	96.4	87.6	0.153	0.030	0.068
20	190	98	136.9	0.239	0.043	0.098
23	243	99	186.5	0.326	0.029	0.066
27	285	99.8	225.9	0.395	0.017	0.039
31	315	101	254.2	0.444	0.012	0.028
36	325	100	263.7	0.461	0.003	0.008
43	326	99.5	264.7	0.462	0.000	0.001
48	330	99.9	268.4	0.469	0.001	0.003
60	338	100	276.0	0.482	0.001	0.003
141	257	100	199.6	Gas Samples Pulled		
155	256	100	198.7			
262	114	33	66.3			
280	115	30.5	67.2			

Table 11. Gas Results for Np Sweepings Material.

946 8MF1, Sweepings 2, 2.095g oxide, 23.7 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	43	24.8	0.0	0.000		
7	50	59.7	6.4	0.037	0.005	0.015
12	56	79.1	11.9	0.070	0.006	0.019
15	67	91.4	22.0	0.128	0.020	0.057
18	76	96.9	30.3	0.177	0.016	0.047
27	90	98.8	43.2	0.252	0.008	0.024
33	90	99	43.2	0.252	0.000	0.000
41	90	99	43.2	0.252	0.000	0.000
67	90	99	43.2	0.252	0.000	0.000

Table 12. Gas Results for Np Sweepings Material.

946 8MF2, Sweepings 2, 7.971g oxide, 23.8 °C						
Time,	V,	T,	V*,	Gas Yield,	Gas Rate,	
min	cc	°C	cc	mol gas/ mol Np	mol gas mol Np/min	scfm/ kg oxide
0	38	24.2	0.0	0.000		
4	44	45	5.5	0.008	0.002	0.006
7	48	60.4	9.2	0.014	0.002	0.005
10	53	73	13.7	0.021	0.002	0.007
11	56	79.4	16.5	0.025	0.004	0.012
13	65	88.7	24.8	0.038	0.006	0.018
15	94	94.2	51.4	0.079	0.020	0.059
17	145	96.9	98.6	0.151	0.036	0.104
19	181	98	132.0	0.202	0.026	0.074
21	215	98.8	163.7	0.251	0.024	0.070
23	246	99.5	192.7	0.295	0.022	0.064
25	268	100	213.3	0.327	0.016	0.046
27	285	100	229.3	0.351	0.012	0.035
29	298	101	241.5	0.370	0.009	0.027
31	307	100	250.0	0.383	0.006	0.019
36	314	99.8	256.6	0.393	0.002	0.006
46	321	99.8	263.2	0.403	0.001	0.003
54	330	100	271.7	0.416	0.002	0.005
60	330	100	271.7	0.416	0.000	0.000
61	258	100	203.9	Gas Samples Pulled		
113	258	100	203.9			
160	258	100	203.9			