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Dissolution of Neptunium Oxide in Unirradiated Mark 53 Targets

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Summary

The disposition of 9 unirradiated Mark 53 targets will require dissolution in H-Canyon to allow recovery of neptunium-237 from a neptunium oxide (NpO_2)/aluminum metal cermet used for plutonium-238 production. In past processing campaigns, irradiated targets were dissolved using a concentrated nitric acid (>8M) flowsheet with the addition of fluoride and mercury to catalyze the dissolution. When the unirradiated targets are processed, it would be advantageous to dissolve the material using a much lower nitric acid concentration without the use of fluoride. The modified flowsheet would facilitate blending the material with solutions generated from the dissolution of Savannah River Site reactor fuel without significantly affecting throughput during purification. The nitric acid concentration in the feed to the 1^{st} cycle of solvent extraction is typically 1-2M. The elimination of fluoride from the dissolution flowsheet would alleviate corrosion concerns associated with fluoride during downstream processing operations.

To assess the dissolution behavior of the neptunium in the Mark 53 targets, a series of experiments was performed in which NpO_2 powder was dissolved in 0.8-4M nitric acid. Neptunium oxide powder was used in the dissolution tests since samples of the Mark 53 cermet were not available. The powder was calcined at the highest temperature possible in the Mark 53 fabrication process to ensure the refractory nature of the cermet was simulated. Aluminum was not dissolved with the powder since its presence did not appear to affect the dissolution rate in previous studies with an irradiated NpO_2/aluminum metal slug.

During the dissolution studies, pure NpO_2 powder dissolved in 2M nitric acid in 8-10 h at reflux conditions. In one experiment, an impure NpO_2 powder dissolved in 5-7 h. The increase in the dissolution rate was attributed to a higher surface area of the impure oxide compared to the pure oxide. The use of 0.8 or 4M nitric acid during dissolution tests had little impact on the dissolution rate of the pure oxide. These results suggest that a mass transfer limitation controls the rate of dissolution. In all of the experiments complete dissolution was obtained; no residues were seen following filtration of the dissolving solutions. Based on these results, the nitric acid concentration during the dissolution of the

unirradiated Mark 53 targets should not fall below 0.8M to ensure that the NpO_2 dissolves in a 8-10 h time frame. A mercury catalyst is required to aid the dissolution of the aluminum metal in the target cladding and core. The use of fluoride is not required.

Introduction

Nine unirradiated Mark 53 targets currently stored at the K-Reactor must be dissolved to allow recovery of the neptunium content. The Mark 53 targets are an aluminum clad, neptunium oxide (NpO_2)/aluminum metal cermet used for the production of plutonium-238. The targets will be dissolved in H-Canyon and blended with solutions generated from routine fuel dissolutions for purification by solvent extraction.[1] The increased neptunium concentration should not have a significant effect on the neptunium decontamination factor achieved by the 1st cycle of solvent extraction; however, the neptunium content of the uranium product (1CU) will likely increase in proportion to the increase in the neptunium feed concentration. The recovered neptunium will be combined with the existing inventory of neptunium solution currently stored in H-Canyon. The combined inventory will undergo subsequent purification and conversion to an oxide for shipment to the Oak Ridge National Laboratory where plutonium-238 will be manufactured using the High Flux Isotope Reactor.

In the past, irradiated Mark 53 targets were dissolved using a concentrated nitric acid (>8M) dissolution flowsheet using fluoride and mercury catalysts to aid in the dissolution.[2] Fluoride was used to ensure complete dissolution of the plutonium and neptunium oxides in the target core. Mercury was required to speed the dissolution of the aluminum cladding. The neptunium and plutonium-238 were then purified using an anion exchange process. When the unirradiated Mark 53 targets are processed, it would be advantageous to dissolve the material using a dissolution flowsheet much closer to that used for Savannah River Site (SRS) reactor fuel. SRS reactor fuel is dissolved using a much lower nitric acid concentration (3-4M) with only a mercury catalyst to aid aluminum dissolution. Following dissolution, the nitric acid concentration is typically 1-2M which is required in the feed to the 1st cycle of solvent extraction used for uranium purification. The use of a lower nitric acid concentration during Mark 53 dissolution would facilitate blending the unirradiated material with these solutions and purification through 1st cycle without significantly affecting throughput. The elimination of fluoride would also alleviate corrosion concerns in downstream processing equipment. A slower dissolution time (2-3X) would be an acceptable trade-off for lowering the final acid concentration and eliminating the fluoride.

To determine if the NpO_2 in the core of the Mark 53 targets could be dissolved using a flowsheet similar to the one used for SRS reactor fuel, dissolution studies were required using samples of a material which exhibited dissolution behavior similar to the NpO_2/aluminum cermet. Since samples of the cermet were not available, dissolution experiments were performed using NpO_2 powder. Aluminum was not dissolved during the dissolution experiments. Burney et al. [2] reported that the presence of aluminum in the solution did not appear to affect the rate of dissolution to an appreciable extent when an irradiated

NpO_2/aluminum metal slug was dissolved. The time required to dissolve the aluminum cladding compared to the cermet is not a concern. For a 6M nitric acid/0.02M mercuric nitrate dissolving solution, the estimated time to penetrate the 0.04-in thick cladding was <10 min.[1] The refractory nature of the NpO_2/aluminum cermet was simulated by calcining the NpO_2 at the highest temperature the material could experience during the Mark 53 target fabrication process. The final nitric acid concentration achieved during target dissolution was assumed to be nominally 2M; however, experiments were performed at 4 and 0.8 M to measure the effects of increasing and decreasing the acid concentration on the dissolution rate. The experimental procedures used to perform the dissolution experiments and an evaluation of the data are given in the following sections.

Experimental

Preparation of Neptunium Oxide Powder

Since samples of the NpO_2/aluminum metal cermet used to fabricate the Mark 53 targets were not available, NpO_2 powder was used to simulate the behavior of the material in a series of dissolution experiments. Neptunium oxide powder was obtained from two sources. An impure oxide was recovered from a nondestructive assay (NDA) standard. The standard contained approximately 1 g of NpO_2 powder immobilized in a small plastic vial by an epoxy-like material. The NpO_2 was recovered by scraping out the vial with a spatula and calcining to remove organic material. Pure NpO_2 powder was prepared by initially purifying a neptunium nitrate solution by anion exchange. The neptunium was then precipitated as neptunium (IV) oxalate ($Np(C_2O_4)_2$) and calcined to the oxide.

The fabrication of the Mark 53 target assemblies involved the extrusion of a billet containing a NpO_2/aluminum cermet which had undergone a hot pressing operation to form a metallurgical bond between the cermet and the aluminum cladding. Therefore, the NpO_2 powder used in the dissolution tests was calcined at the maximum temperature possible in the fabrication process to simulate the refractory nature of the Mark 53 material. The temperature during hot pressing was not allowed to exceed 640°C due to the melting of a neptunium aluminum alloy ($NpAl_4$) and aluminum at 649°C by eutectic reaction.[3] The precipitated $Np(C_2O_4)_2$ and impure NpO_2 recovered from the NDA standard were both calcined at 640°C.

Dissolution Experiments

The preferred strategy for dispositioning the Mark 53 material is to charge the 9 unirradiated targets to the 6.1D dissolver in H-Canyon. The 6.1D dissolver has a working volume of nominally 7500 L. The total neptunium content in the 9 targets is 14,300 g (see Table 1).

Table 1. Neptunium Content of Mark 53 Targets

Target Designation	Number	Length (ft)	$\frac{\text{Np Mass}}{\text{Unit Length}}$ (g/ft)	Neptunium Mass (g)
Mark 53A	4	10	120	4800
Mark 53B	5	10	190	9500
Total	9			14300

The dissolution of the 9 targets in the 6.1D dissolver will result in a neptunium concentration of nominally 2 g/L in the dissolving solution. This concentration was used as the target in 5 dissolution experiments using the impure and pure NpO_2 powder. Approximately the same final neptunium concentration was generated in the experiments by dissolving nominally 1 g of neptunium (as oxide) in 500 mL of solution. The impure NpO_2 powder recovered from the NDA standard was used in Experiment 1; pure NpO_2 powder prepared for the dissolution studies was used in Experiments 2, 3, 4, and 5. The dissolution experiments were performed in a 1 L, three-neck flask. A heating mantle equipped with a magnetic stirrer was used to heat and agitate the dissolving solution. The experiments were performed at reflux conditions by boiling the dissolver solution and condensing the offgas vapors using an air-cooled condenser. The temperature of the dissolving solution was monitored using a partial immersion thermometer.

Samples of the dissolver solution were removed from the vessel at 1 h intervals. About 2-3 min before sampling, the magnetic stirrer was turned-off to allow suspended NpO_2 particles to settle. An approximate 2 mL sample of solution was removed from the dissolver using a disposable plastic syringe. A 6-in piece of Teflon™ tubing was threaded onto the end of the syringe to reach the solution level. Once the solution aliquot was removed, a 1 mL sample was expelled through an 0.45 μ m filter disk into a sample vial which had been previously marked at a volume of 1 mL. Excess solution in the syringe was returned to the dissolution flask. The neptunium concentrations were determined by a gamma scan. The initial and final nitric acid concentrations of the dissolving solutions were analyzed by titration.

If the dissolution was not complete at the end of the work day, the heating mantle was turned-off following the removal of the last sample. The air flow through the condenser was maintained for approximately 30 min to condense any solution evaporated during dissolver cooling. When the

dissolving experiment resumed on the following day, a sample of the solution was removed before heating began using the procedure outlined above. Samples were then removed at 1 h intervals in the same manner as the previous day.

Results and Discussion

The neptunium analysis for the samples removed from the dissolver during each dissolution experiment are presented in Appendix A. Before the concentrations can be correlated with the dissolution time, they must be corrected for the change in volume which occurred as a result of sample removal and evaporation losses through the condenser. A small correction must also be made for the dissolved neptunium removed in samples prior to completing the experiment. The procedure used to correct the concentrations and the calculated values are presented in Appendix B.

The corrected neptunium concentrations for each of the dissolution experiments are plotted as a function of sample time on Figure 1. From the figure, it is clear that the impure NpO_2 powder dissolved at a much higher rate than the pure NpO_2 prepared for the experiments. Complete dissolution of the impure material was obtained in only 5-7 h compared to the 8-10 h required for complete dissolution of the pure NpO_2. The more rapid dissolution of the impure oxide was attributed to a higher surface area compared to the pure material. The increased surface area is likely due to conditions used to precipitate and calcine the material during preparation of the NDA standard.

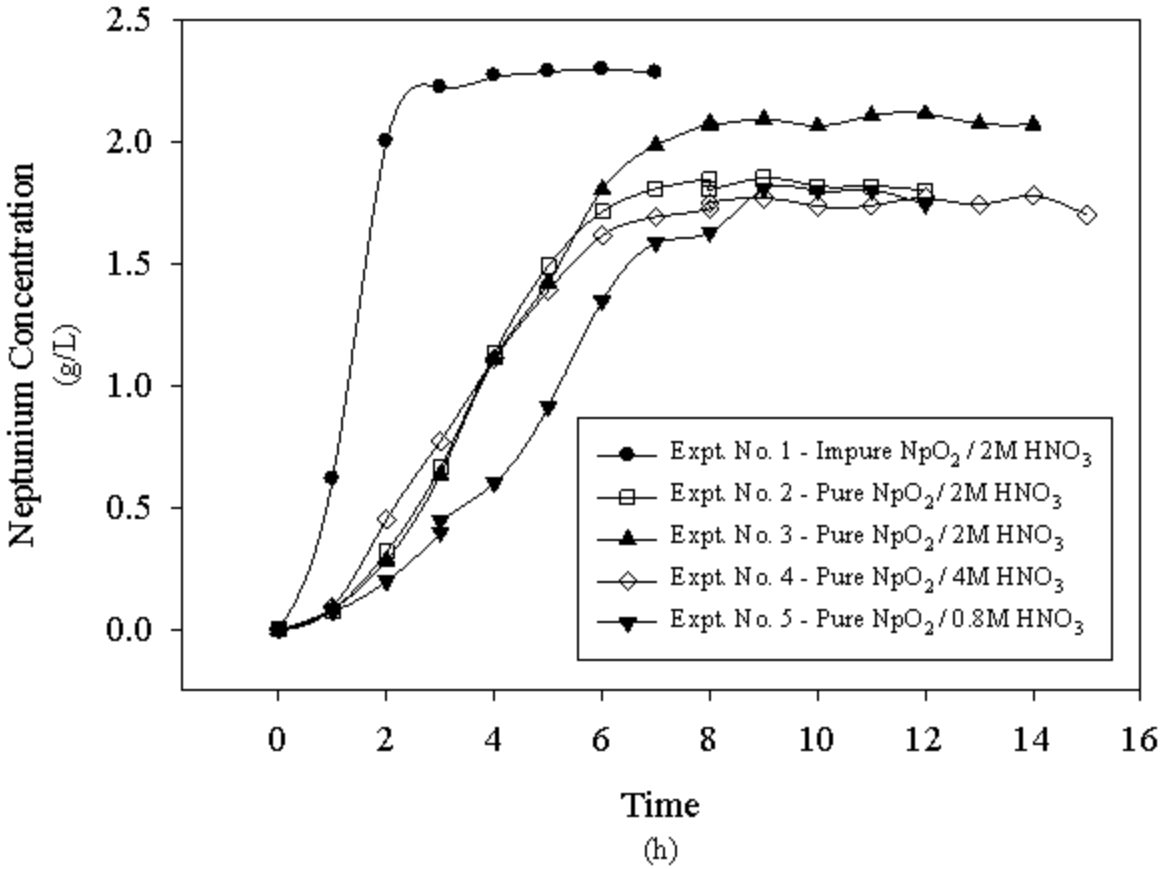

Figure 1. Neptunium Oxide Dissolution

Experiments 4 and 5 were performed to measure the effects of increasing and decreasing the nitric acid concentration on the dissolution rate. The actual initial and final concentrations for the 5 dissolving solutions are summarized in Table 2.

Table 2. Nitric Acid Concentration of NpO_2 Dissolving Solutions

Expt. No.	$HNO_{3initial}$	HNO_{3final}
	(M)	(M)

1	1.78	1.85
2	1.80	1.93
3	1.88	1.93
4	3.65	3.79
5	0.74	0.74

The nitric acid concentration of the dissolving solution generally became more concentrated due to evaporation losses. Depletion of the acid was minimal due to the small amount of NpO_2 dissolved. Surprisingly, increasing or decreasing the nitric acid concentration in the dissolving solution had little effect on the dissolution rate of the pure NpO_2 (see Figure 1). This result suggests that a mass transfer limitation controls the rate of dissolution. For the NpO_2 to dissolve, nitric acid must diffuse to the surface of the particle, reaction must occur, and the resulting aqueous neptunium nitrate species must diffuse back to the bulk solution. Since changes in the nitric acid concentration had essentially no effect on the dissolution rate, diffusion of the reaction products is likely the rate-controlling step. Otherwise, a change in the nitric acid concentration would have changed the rate of diffusion of nitric acid to the surface of the particle and increased the dissolution rate.

Because the experiments were performed at reflux conditions, the temperature of the dissolutions performed during Experiments 4 and 5 would be expected to be slightly different based on the use of higher and lower concentrations of nitric acid. The measured boiling point of the 2M dissolving solution used during Experiments 1, 2, and 3 was 104-105°C. The 4M dissolving solution used during Experiment 4 boiled at approximately 106°C and the 0.8M solution used during Experiment 5 boiled at approximately 103°C; therefore, any small changes in the dissolution rate due to a temperature effect would not be observable given the variability exhibited by the measured neptunium concentrations.

Conclusions

A series of NpO_2 dissolution experiments was performed to assess the ease of dissolution of the NpO_2/aluminum cermet in unirradiated Mark 53 targets. The refractory nature of the cermet was simulated by calcining NpO_2 powder at the highest possible temperature used during the target fabrication process. During the dissolution studies, pure NpO_2 powder was initially dissolved in 2M nitric acid in 8-10 h at reflux conditions. In one experiment, an impure NpO_2 powder dissolved in only 5-7 h. The more rapid dissolution of the impure oxide was attributed to a higher surface area compared

to the pure material. The use of 0.8 or 4M nitric acid during dissolution tests with pure NpO_2 had little impact on the dissolution rate. These results suggest that a mass transfer limitation controls the rate of dissolution. In all of the experiments complete dissolution of the NpO_2 was obtained. No residues were collected following filtration of the dissolving solutions.

Recommendations

The NpO_2 dissolution studies can be used as the basis for recommendations concerning the dissolution flowsheet for the unirradiated Mark 53 targets. Based on the experimental work, the use of at least 0.8M nitric acid is required to dissolve the NpO_2 in the target core within 8-10 h. For the dissolution of the unirradiated targets, the initial nitric acid concentration must be adjusted upward to account for the dissolution of aluminum metal in the cladding and core. A mercury catalyst is required to aid the aluminum dissolution. The use of fluoride to catalyze the dissolution of the NpO_2 is not required. Other dissolution parameters (i.e. temperature, volume of solution, time, etc.) should be maintained consistent with the flowsheet used to dissolve the Mark 22 reactor fuel.

References

1. M. L. Hyder, W. C. Perkins, M. C. Thompson, G. A. Burney, E. R. Russell, H. P. Holcomb, and L. F. Landon, *Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant*, Report No. DP-1500, E. I. du Pont de Nemours & Company, Aiken, SC (April 1979).
2. G. A. Burney and C. A. Prohaska, *Recovery of ^{237}Np and ^{238}Pu from Irradiated Neptunium Oxide*, Report No. DP-417, E. I. du Pont de Nemours & Company, Aiken, SC (November 1959).
3. H. G. Marsh, *Evaluation of NpO_2-Al Slug No. 15*, Report No. DPST-61-261, E. I. du Pont de Nemours & Company, Aiken, SC (April 28, 1961).

Appendix A Analytical Results from Dissolution Experiments

The neptunium analysis for the samples removed from the dissolver during each dissolution experiment are given in Table A.1.

Table A.1. Neptunium Analysis for Dissolver Samples

Dissolution Time	Expt. No. 1 Neptunium Concentration	Expt. No. 2 Neptunium Concentration	Expt. No. 3 Neptunium Concentration	Expt. No. 4 Neptunium Concentration	Expt. No. 5 Neptunium Concentration
	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)

1	0.62	0.08	0.09	0.09	0.07
2	2.05	0.32	0.29	0.46	0.20
3	2.30	0.68	0.65	0.79	0.41
3					0.46
4	2.37	1.16	1.14	1.14	0.63
5	2.42	1.54	1.46	1.43	0.97
6	2.46	1.78	1.87	1.68	1.45
7	2.47	1.89	2.07	1.77	1.73
8		1.94	2.17	1.81	1.80
8		1.90	2.16	1.84	
9		1.96	2.20	1.87	2.03
10		1.94	2.18	1.84	2.05
11		1.95	2.24	1.86	2.08
12		1.94	2.26	1.90	2.04
13			2.23	1.88	
14			2.23	1.93	
15				1.86	

The dissolution of the NpO_2 powder used in experiments 2, 3, 4, and 5 required more time than was available in a single workday; therefore, the dissolutions were suspended and resumed on the following day. For this reason, two concentration measurements are given at 8 h for Experiments 2, 3, and 4 and at 3 h for Experiment 5. The first value is the measured concentration at the end of the first day dissolution.

The second value is the measured concentration in a sample removed from the dissolver on the following day before resumption of heating.

Appendix B Correction of Neptunium Concentrations for Changes in Volume

The neptunium concentration for each of the samples must be corrected for small changes in volume which occurred due to sample removal and evaporation losses through the condenser. A small correction must also be made for the dissolved neptunium removed in samples prior to completing the experiment. The sample volume was held constant at 1 mL during all experiments. The evaporation rate was estimated from the initial and final dissolving solution volumes and the number of samples removed. The calculations are summarized in Table B.1.

Table B.1. Evaporation Rate During NpO_2 Dissolution Experiments

Expt. No.	Initial Soln. Volume (mL)	Final Soln. Volume (mL)	Total Sample Volume (mL)	Evaporated Volume (mL)	Evaporation Rate (mL/hr)
1	500	456	7	37	5.3
2	500	453	13	34	2.8
3	500	452	15	33	2.4
4	500	445	16	39	2.6
5	500	426	13	61	5.1

The calculations in Table B.1 assume the evaporation rate was constant during each dissolving experiment and that no other losses of solution occurred. The estimated volumes of solution in the dissolver prior to the removal of each sample are given in Table B.2.

The corrected neptunium concentrations can now be calculated by adjusting for the change in volume and accounting for the small amount of material removed from the dissolving solution in each sample.

The generalized expression used to calculate the corrected concentration at sample time t ($C_{t\text{corrected}}$) is given as Equation B.1,

$$C_{t\text{-corrected}} = \frac{C_t V_t + V_s \sum_{i=1}^{t-1} C_i}{V_0} \quad \text{(B.1)}$$

where C_t and C_i are the measured concentrations at specific samples times (see Table A.1) and V_t, V_0, and V_s are the estimated volume at time t (see Table B.2), the initial volume (500 mL), and the sample volume (1 mL), respectively. The corrected concentrations for each experiment are given in Table B.3.

Table B.2. Estimated Dissolver Volume Prior to Sample Removal

Sample Time (h)	Expt. No. 1 Dissolver Volume (mL)	Expt. No. 2 Dissolver Volume (mL)	Expt. No. 3 Dissolver Volume (mL)	Expt. No. 4 Dissolver Volume (mL)	Expt. No. 5 Dissolver Volume (mL)
0	500	500	500	500	500
1	495	497	498	497	495
2	488	493	494	494	489
3	482	490	491	490	483
3					482
4	476	486	488	487	476
5	470	482	484	483	470
6	463	478	481	479	464
7	457	474	478	476	457
8		470	474	472	451
8		469	473	471	
9		466	470	468	445

10		462	466	464	439
11		458	463	460	433
12		454	460	457	427
13			456	453	
14			453	450	
15				446	

Table B.3. Corrected Neptunium Concentrations for Dissolving Experiments

Dissolution Time	Expt. No. 1 Corrected Neptunium Concentration	Expt. No. 2 Corrected Neptunium Concentration	Expt. No. 3 Corrected Neptunium Concentration	Expt. No. 4 Corrected Neptunium Concentration	Expt. No. 5 Corrected Neptunium Concentration
(h)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)
1	0.62	0.08	0.09	0.09	0.07
2	2.00	0.32	0.28	0.45	0.20
3	2.22	0.66	0.64	0.77	0.40
3					0.45
4	2.27	1.13	1.11	1.11	0.60
5	2.29	1.49	1.42	1.39	0.91
6	2.30	1.71	1.80	1.61	1.35
7	2.28	1.81	1.98	1.69	1.59
8		1.84	2.08	1.72	1.63

8		1.80	2.07	1.75	
9		1.85	2.09	1.77	1.81
10		1.82	2.06	1.74	1.80
11		1.82	2.11	1.74	1.80
12		1.80	2.11	1.77	1.74
13			2.07	1.74	
14			2.07	1.78	
15				1.70	