Test Dissolution of Hanford Scrap Oxide, HRA-40

by

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TO: J. L. ADAMS, 221-F, B-LINE

FROM: H. P. HOLCOMB, 772-F *HPH*

Key Words

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TEST DISSOLUTION OF HANFORD SCRAP OXIDE, HRA-40

INTRODUCTION AND SUMMARY

Two portions from a single sample of Hanford scrap plutonium oxide (12% Pu²⁴⁰), account HRA-40, were dissolved in the Separations Technology Laboratory as you requested. Test conditions, including oxide-to-dissolvent ratio were very similar to those used in the process. Both test portions dissolved quite readily in 14M HNO₃ - 0.2M HF in a boiling water bath. Efficient agitation of the oxide in the dissolvent was instrumental in ensuring quick, thorough dissolution.

Small residues of siliceous materials appeared in both tests. These residues were produced from a combination of the silica dissolved from the test container, a Kimax® graduated centrifuge cone, plus the silica impurity in the oxide itself. The former was the primary source of the silica in the first of our tests. Siliceous solids can build up in the process dissolver as a result of continued dissolution of Hanford material containing silica as an impurity. A previous study¹, following the dissolution of HRA-37 in 1986, showed silicon to be the primary constituent of actual process residues analyzed by SEM/XRF.

Laboratories Department emission spectrographic analysis found 65 ppm silicon in the HRA-40 sample provided me. Hanford reported an average silicon content of 12 ppm in the six batches of HRA-40 sent to SRP.

Plutonium accountability in the test dissolver solutions, based on weight of oxide dissolved and volumes of the dissolver solutions, was in good agreement with that analyzed by diode array spectrometry by Laboratories Department. Agreement was excellent between diode array data and the plutonium content calculated from isotopic data from gamma pulse height analysis in F B-Line together with alpha and alpha pulse height analysis.

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EXPERIMENTAL

Procedure

Two dissolutions were made from the single 5 g sample of HRA-40 provided. The first was 3.012 g (approx. 2 mL volume on lightly tamping) of oxide placed in 15.0 mL of dissolvent, 14M HNO_3 -0.2M HF in a 30-mL Kimax® graduated centrifuge cone. The second test was with 1.650 g (about 1.0 mL tamped) of oxide with 8.5 mL of dissolvent in a different cone. The tests, conducted in the glove box in the Sep Tech Lab, were run in sequence and not concurrently. Heating was done in a boiling water bath, which generally results in a maximum temperature of 95°C in the cone's liquid phase. All mixing was by vigorous, frequent hand shaking of the tightly capped (PVC-lined) cone and its contents.

Test #1

For the first test, the contents of the capped cone were well mixed, then placed in the boiling water bath. The cone's contents were subsequently mixed every 5 minutes. After 20 minutes, only 0.5 mL of solids remained. After 40 minutes, no settled solids were noted. Total time in the boiling water bath was 70 minutes. The cone and its contents were allowed to cool for 2½ hours prior to sampling of the dissolver solution (16.0 mL) for Pu analysis. No settled solids were noted on sampling. The solution was not centrifuged.

Some 72 hours after dissolution (over a weekend), 600 µL of 60% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ANN) was added to a 10-mL aliquot of the dissolver solution. This is the approximate volume ratio now used in the process. On centrifuging, some 200 µL of solids were noted in the cone bottom. Thinking they might be due to ANN crystallization, the cone and contents were reheated in a boiling water bath for one hour. The solids persisted. On removing the mother liquor, the solids were found to be insoluble in 1M HNO_3 . Upon further washing, the solids appeared to be hydrated silicic acid, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. They were colorless, indicating that plutonium was probably absent.

Test #2

Since the solids in Test #1 appeared on centrifugation after some 3 days contact with the Kimax® cone, Test #2 was conducted differently, being completed during one 8-hour shift. The 1.650 g of oxide from HRA-40 was placed into a clean cone and 8.5 mL of dissolvent added. The cone's contents were mixed vigorously by hand and placed in a boiling water bath. The container's contents were well mixed every 5 minutes during the heating cycle. After

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one hour, the tube and its contents were centrifuged. Some 250 μ L solids persisted, but most appeared, because of its texture and color, to be undissolved oxide.

The tube and contents were left in the boiling water bath for an additional hour and then recentrifuged. At this point, some 50 μ L of siliceous solids appeared in the cone bottom. After cooling to less than 60°C, a 5-mL aliquot of the 8.5 mL solution was removed and 0.5 mL of 60% ANN added to it. The solution was thoroughly mixed. No solids were noted on centrifugation of the separate dissolver solution aliquot containing ANN. Therefore, addition of the more concentrated ANN to such dissolver solutions did not create a solids problem.

The siliceous solids remaining in the original tube were washed several times with 1M HNO_3 . They appeared to be quite similar to those remaining after Test #1.

Blank Test for Si

Into a clean 30-mL Kimax® centrifuge cone was placed 15 mL of 14M HNO_3 - 0.2M HF dissolvent. The cone and its contents were heated in a boiling water bath for 1.5 hours and then allowed to stand at the ambient temperature of the laboratory for 72 hours. An aliquot of the dissolvent was removed for silicon analysis by Laboratories Department using DCAP spectrometry. The blank test solution contained 580 ppm Si. Therefore, the 15 mL of dissolvent contained a total of almost 9 mg silicon, equivalent to 19 mg of silica, SiO_2 .

The bulk of siliceous solids produced in Test #1 originated from silica dissolution from the Kimax® cone. Those resulting in Test #2 probably resulted mainly from the silica impurity in the oxide.

Analysis of HRA-40 Oxide for Si

A small portion of the original sample furnished the Sep Tech Lab was given to Laboratories Department for emission spectrographic analysis of the silicon content of the oxide as furnished by Hanford. This analysis showed the oxide, as received, to contain 65 ppm Si, or the equivalent of 139 μ g SiO_2 per g oxide. Hanford analysis of the 6 batches of HRA-40 for silicon were: <10, 15, 12, 14, 13, and 18, for an approximate average of 12 ppm Si, or the equivalent of 26 μ g SiO_2 per gram of oxide, a factor of five less than SRP's findings.

Formation of Siliceous Solids in the Dissolver

From a single nominal charge of HRA-40 oxide to the process, based on the SRP silicon results, 56 mg of SiO_2 solids could form in

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the dissolver. If we assume that the 50 μ L of solids in Test #2 totally resulted from the Si impurity (65 ppm) in the 1.65 g of oxide, then a maximum of 12 mL of siliceous materials could form in the dissolver from each charge of similar scrap oxide.

ACCOUNTABILITY AND MATERIAL BALANCE

For accountability purposes and mass balance agreement, we wished to compare data from the alpha plus gamma analyses with that from diode array spectrometric analysis of the dissolver solution, discussed later, as well as with the weight of oxide (theoretically considering it to be pure $\text{Pu}^{239-40}\text{O}_2$) dissolved in a given volume of solution.

Pu Isotopic Analysis of HRA-40

L. B. Baker of Laboratories furnished the following isotopic analysis for plutonium in HRA-40, obtained from gamma ray pulse height spectrometry conducted in F B-Line. The sample analyzed was identified as "Seal #FC1407" by F B-Line.

<u>Pu Isotope</u>	<u>Wt %</u>
238	0.05250
239	87.5238
240	11.4032
241	0.8394
242	0.1811
(Am ²⁴¹	5123 ppm)

Alpha Analysis of Test #1 Dissolver Solution

Replicate alpha analyses produced a total alpha activity of 4.14×10^{10} d/m/mL in the 16.0 mL of Test #1 dissolver solution. From alpha pulse height analysis, the alpha percent of Pu^{239-40} was 75.76%. Therefore, the Pu^{239-40} alpha activity in the Test #1 dissolver solution was 3.14×10^{10} d/m/mL.

Pu Content of Test #1 Dissolver Solution From Alpha & Gamma Data

To obtain the plutonium content of the Test #1 solution, the wt% Pu^{239} and Pu^{240} must first be normalized to represent 100% of the isotopic content of HRA-40 since almost 100% of the total Pu alphas come from these two isotopes alone. The following table shows how the normalization was done.

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<u>Pu Isotope</u>	<u>Wt% by Gamma</u>	<u>Normalized</u>	<u>Specific Activity²</u>
239	87.5238	88.4731	1.361×10^{11} d/m/g
240	11.4032	11.5269	5.057×10^{11} d/m/g
Total	98.9270	100.0000	

Using this data, in 1 gram of Pu²³⁹⁻⁴⁰ material with the normalized composition, there should be:

<u>Pu Isotope</u>	<u>Alpha d/m/g</u>	<u>Alpha %</u>
239	1.204×10^{11}	67.38
240	0.583×10^{11}	32.62
Total	1.787×10^{11}	100.00.

With this data, calculated exclusively from the gamma isotopic analysis, and combining it with the alpha data, we can calculate the total plutonium 239-240 content of the dissolver solution, as:

- 1) total d/m/ml Pu²³⁹⁻⁴⁰ from alpha = 3.14×10^{10} .
(Determined previously.)

Using the alpha percentages calculated from the foregoing data, the dissolver solution from Test #1 should have contained:

- 2) Pu²³⁹ = $3.14 \times 10^{10} \times 0.6738 = 2.12 \times 10^{10}$ d/m/mL &
Pu²⁴⁰ = $3.14 \times 10^{10} \times 0.3262 = 1.02 \times 10^{10}$ d/m/mL.

On converting these activities to weight using the specific activities listed above, then in 1 mL of Test #1 dissolver solution there should have been:

- 3) Pu²³⁹ = $2.12 \times 10^{10} / 1.36 \times 10^8$ d/m/mg = 156 mg Pu²³⁹/mL
+ Pu²⁴⁰ = $1.02 \times 10^{10} / 5.06 \times 10^8$ d/m/mg = 20 mg Pu²⁴⁰/mL,
or g/L Pu²³⁹⁻⁴⁰ in Test #1 Diss. Soln. = 176 g/L

Analysis of Test Dissolver Solutions by Diode Array Spectrometry

Samples of the dissolver solution from Test #1 and Test #2 were sent to Laboratories Department for analysis of their total plutonium content using the Pu⁺³ method with diode array spectrometry. Results were:

	<u>Test #1 Diss. Soln</u>	<u>Test #2 Diss. Soln</u>
Total Pu g/L	175.0	174.5

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Agreement between the accountability numbers calculated from the alpha plus gamma data with that from diode array analysis is excellent. Test #2 dissolver solution was not subjected to alpha analysis.

Data From Weight Oxide Dissolved in Dissolver Solution Volume

Based on weight of oxide dissolved in Test #1, 3.012 g (or 2.656 g Pu, then if the oxide were 100% $\text{Pu}^{239}\text{O}_2$, the plutonium content of the Test #1 dissolver solution should have been 166 g Pu/L.

For Test dissolution #2, based on weight of oxide dissolved, 1.650 g (or 1.455 g Pu), and again if the oxide were 100% $\text{Pu}^{239}\text{O}_2$, the plutonium content of the Test #2 dissolver solution should have been 171 g Pu/L.

Even fairly good agreement results from comparing these data, the worst accountability case because of assumptions made, with those obtained from the more reliable scientific methods, described above.

CONCLUSIONS

Plutonium oxide in HRA-40, tested in the Separations Technology Laboratory under conditions similar to those in the process, dissolved without difficulty. Efficient mixing of the oxide with the dissolvent was an absolute necessity to effect complete dissolution.

Residues of silicon solids resulted from silica impurity in the Hanford scrap plutonium oxide plus that dissolved from the Kimax® glass cones used as test containers. SRP emission spectrographic analysis of the oxide showed a silicon impurity level some five times greater than Hanford analytical data. Silica residues from continued dissolutions of such oxides will build up in the dissolver and will be difficult to remove since such solids are relatively intractable to the usual chemicals permitted in SRP processes. Similar residues from a previous Hanford oxide shipment, HRA-37, were characterized in an earlier Sep Tech Lab study¹ and found to be mostly silicon.

Plutonium content of the oxide, as determined by diode array spectrometric analyses of the dissolver solutions from the two test dissolutions, was in excellent agreement with data determined from alpha analysis of the solutions combined with the plutonium isotopic analysis by SRP gamma ray spectrometry.

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I wish to recognize the assistance provided by Laboratories Department in getting necessary information for this report. J. T. Coleman did the emission spectrometric analysis for Si in the oxide. DCAP analyses were overseen by B. K. Mitchell. Laboratories' shift personnel conducted the alpha counting and performed the diode array spectrometry. M. K. Holland was helpful in analyzing this data. L. B. Baker assisted by supplying the plutonium isotopic composition for this batch of Hanford material.

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