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THE DISSOLUTION OF DESICOOLER RESIDUES IN H-CANYON DISSOLVERS

John H. Gray
Westinghouse Savannah River Company
Aiken, SC 29808

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SUMMARY

A series of dissolution and characterization studies has been performed to determine if FB-Line residues stored in desicooler containers will dissolve using a modified H-Canyon processing flowsheet. Samples of desicooler materials were used to evaluate dissolving characteristics in the low-molar nitric acid solutions used in H-Canyon dissolvers. The selection for the H-Canyon dissolution of desicooler residues was based on their high-enriched uranium content and trace levels of plutonium.

Test results showed that almost all of the enriched uranium will dissolve from the desicooler materials after extended boiling in one molar nitric acid solutions. The residue that contained uranium after completion of the extended boiling cycle consisted of brown solids that had agglomerated into large pieces and were floating on top of the dissolver solution. Addition of tenth molar fluoride to a three molar nitric acid solution containing boron did not dissolve remaining uranium from the brown solids. Only after boiling in an eight molar nitric acid-tenth molar fluoride solution without boron did remaining uranium and aluminum dissolve from the brown solids. The amount of uranium associated with brown solids would be ~1.4 percent of the total uranium content of the desicooler materials. The brown solids that remain in the First Uranium Cycle feed will accumulate at the organic/aqueous interface during solvent extraction operations.

Most of the undissolved white residue that remained after extended boiling was aluminum oxide containing additional trace quantities of impurities. However, the presence of mercury used in H-Canyon dissolvers should complete the dissolution of these aluminum compounds.

INTRODUCTION

One of the approaches the Savannah River Site has selected to reduce fissile inventories is to recover enriched uranium from residues to blend with uranium before shipment off-site. Previous laboratory characterization and dissolution studies (Reference 1) established that enriched uranium found in FB-Line desicooler residues will dissolve in the eight molar nitric acid-tenth molar fluoride solutions used in HB-Line Phase I dissolvers. The complete dissolution of uranium from desicooler residues in nitric acid solutions without mercury was established during the HB-Line Phase I dissolution studies. However, since the HB-Line dissolver solution acid concentrations are not easily adjusted for subsequent processing operations in H-Canyon First Uranium Solvent Extraction cycles, additional laboratory characterization and dissolution studies became necessary using the adjusted H-Canyon dissolver flowsheet conditions.

Reference (1) J. H. Gray, “Analysis of FB-Line Desicooler Solids (U)”, SRT-ATS-2002-00084, April, 2003.

The one molar nitric acid solution containing boron was selected as the minimum bounding nitric acid concentration to be used during the laboratory study. The presence of mercury, higher starting nitric acid concentrations, and the generation of nitrite ions during dissolution of iron and aluminum metals will only improve the dissolving of uranium metal and/or alloys that are present in the desicooler materials.

EXPERIMENTAL PROGRAM

Two types of solids are present in desicooler residues that contain the enriched uranium (Figure 1). These solids are the small, black, loose particles and the larger black chunks. Both have similar compositions. Two types of desicooler solids do not contain enriched uranium. The few flat, half-moon particles contain iron and silicon and the silver slivers are just aluminum metal.

The first series of laboratory studies focused on dissolution of small, black, loose particles in boiling one molar nitric acid solutions with two grams of boron per liter. The mass-to-volume ratio used during experiment #1 represents the actual ratio expected to be present during dissolution of desicooler residues in H-Canyon dissolvers. The undissolved white solids settled to the bottom of the dissolver and were analyzed using Scanning Electron Microscopy (SEM) to determine if any uranium and aluminum remained undissolved. The nitric acid product solutions were analyzed using Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) to calculate how much uranium and aluminum had dissolved. Additional analyses of the product solutions used Rad Screen and gamma scans to confirm that only trace quantities of plutonium were in desicooler residues.

The second series of laboratory dissolution studies involved the addition of a large black chunk to the same dissolver solution from experiment #1. Although this increased the mass to volume ratio significantly, an additional extended boiling cycle was conducted until dissolution of uranium was complete. After experiment #2, a black sponge material remained that was separated and boiled in nitric acid solutions to determine how much of the total uranium inventory was associated with this residue; experiments #9 and #10. The same analytical methods were used to characterize solids and to analyze solutions.

Brown solids were observed to be floating on top of the dissolver solutions after experiments #1 and #2. The brown solids were analyzed by SEM to identify their chemical compositions. After removal from the dissolver solutions following experiment #2, additional attempts were made to dissolve the uranium and aluminum present in the brown floating solids. A description of the additional attempts to dissolve the brown solids are presented in experiments #5 through #8.

Figure 1. The photograph of the desicooler solids is attached at the end of the report.

DISCUSSION OF EXPERIMENTAL RESULTS

Dissolution of Small, Black, Loose Particles and Large Black Chunks

The first two series of experiments combined the dissolution of small, black, loose particles and a large black chunk into the boiling, one molar nitric acid solution containing two grams of boron per liter. Results from experiments #1 through #4 and the conditions used during the first two series of experiments are presented in Table I.

Table I. The Dissolution of Small, Black, Loose Particles and a Large Black Chunk

Experiment Number	Sample Weight (grams)	Hours at Temp. (95-104ºC)	Percent U in Solution	Wt.% U Dissolved in Desi-Materials	Wt.% Al Dissolved in Desi-Materials	Materials Left, Composition
#1)Small, Black, Loose Particles	1.34	3	98+	11.53 (12.1)[2]	27.6	White:Al, (U)[1] Brown:U, Al
#2)Large, Black Chunk	+3.51	+3	75.4	14.4	39.9	Sponge[3]:U, Al White:U, Al Brown:U, Al[6]
#3) #1+#2 Continued	4.85	+4	83.1	15.9	45.3	White:U, Al
#4) #3 Continued	4.85	+3 (13 total)	98+	19.1[7] (21.82)[4] (22.10)[5]	50.9	White: Al

(U)[1] , Only trace uranium left in settled white solids.
(12.1)[2] , Wt.% uranium found in small black particles during previous FB-Line study.
Sponge[3] , Black sponge found and removed after dissolution of large black chunk.
(21.82)[4] , Calculated wt.% uranium found in large black chunk.
(22.10)[5] , Wt.% uranium found in large black chunk during previous FB-Line study.
Brown: U, Al[6], Brown solids removed after experiment #2.
19.1[7], The 19.1 wt.% U includes the uranium from the black sponge material.

The first experiment involved the dissolution of 1.34 grams of small, black, loose particles for three hours in 500 ml of the boiling nitric acid solution. Approximately 98+% of the available uranium in the small, black, loose particles had dissolved. This amount of uranium represents 11.53 wt.% of the solids sample. A previous result obtained for the small, black, loose particles during the FB-Line characterization study (Ref. #1) found 12.1 wt.% uranium was present. No brown solids were floating on top of the dissolver solution during this previous study.

Two types of solids were left at the end of experiment #1: brown floating solids and the white solids that had settled to the bottom of the beaker. Results from SEM scans confirmed that only a trace of uranium remained in the white solids. The remaining white solids were predominantly aluminum, assumed to be aluminum oxide. The brown solids contained about 1.4 percent of the uranium found in desicooler materials.

Experiment #2 involved the addition of a 3.51 gram large, black chunk to the remaining dissolver solution. The black sponge solids that appeared after experiment #2 and the agglomerated floating brown solids were now separated and treated separately. Only after experiments #3 and #4 were completed, had all the uranium dissolved from the large black chunk. The 19.1 wt.% uranium in the combined loose particles and large chunk represents essentially 98+% dissolution of the available uranium in this particular sample. Based on the 19.10 wt.% uranium, the wt.% uranium in the large black chunk is 21.82. This wt.% uranium compares favorably with the 22.10 wt.% uranium obtained during the previous FB-Line characterization study of large black chunks.

Dissolution of Floating Brown Solids

Results from the dissolution of floating brown solids are presented in Table II. These solids were separated from the main dissolver solution after experiment #2 was completed.

Table II. The Dissolution of Floating Brown Solids

Experiment Number	Sample Weight (grams)	Hours at Temp. (95-104ºC)	Percent U in Solution	Percent Al in Solution	Solids Left Composition
#5) in 1M+2g/1 B	0.128	4	none	none	U, Al trace:Si,Ti,Fe,Ni ,Pu
#6) plus $NaNO_2$	0.128	+3	none	none	same
#7) in 3M-0.1M F	0.128	3	none	none	same
#8) in 8M-0.1M F	0.128	3	all	some	Al, trace:Si,Ti,Fe,Ni

Experiments #5 through #7 showed that the three different solution conditions examined were unsuccessful in dissolving any of the uranium or aluminum from the brown floating solids. After the SEM scan confirmed that all uranium had dissolved from the brown solids in experiment #8, analysis of the nitric acid solution for uranium by ICP-ES indicated that a maximum of 1.4 percent of the total uranium could be present in these solids. For each kilogram of uranium in the desicooler material, about 14 grams of uranium could remain undissolved in the floating brown solids. The desicooler residue could contain up to 2.64 wt.% brown solids.

A separate experiment was conducted to determine the behavior of brown solids during solvent extraction operations. The brown solids were vigorously mixed with equal volumes of 30% tributyl phosphate/n-paraffin and one molar nitric acid solutions. The two phases easily separated and the brown solids remained intact at the organic/aqueous interface (Figure 2).

Dissolution of Black Sponge Solids

The composition of the black sponge is identical with the bulk of the desicooler material. The SEM scans could only identify uranium and aluminum. Results from dissolution of the black sponge are presented in Table III. The black sponge was observed only after dissolution of the large, black chunk.

Table III. The Dissolution of Black Sponge Material

Experiment Number	Sample Weight (grams)	Hours at Temp. (95-104ºC)	Percent U in Solution	Percent Al in Solution	Solids Left Composition
#9) in 1M-2.0g/1 B	0.50	3	78.2	some	U, Al
#10 plus $NaNO_2$	0.50	+4	100[1]	some	Al

100[1], About 8.7 percent of the total uranium in desicooler materials was associated with the black sponge.

After seven hours at boiling in the one molar nitric acid solution, essentially 100% of the uranium had dissolved. The amount of uranium plus aluminum in solution after seven hours represents about 85 wt.% of the black sponge. The SEM scan could only find aluminum left undissolved.

Figure 2. The photograph of brown solids sitting at the aqueous/organic interface is attached at the end of the report.

C0NCLUSIONS

1) Extended boiling in a one molar nitric acid solution containing two grams of boron per liter should result in dissolution of at least 98+% of the uranium inventory.

2) The brown floating solids that may not dissolve in H-Canyon dissolvers could contain up to 1.4 percent of the total uranium inventory.

3) The presence of mercury used in H-Canyon dissolvers should complete the dissolution of all aluminum materials and should reduce the amount of uranium associated with the brown floating solids.

4) The brown floating solids will remain at the organic/aqueous interface during solvent extraction operations. This conclusion assumes the brown floating solids will stay with the aqueous solution after the evaporation, gelatin strike, and centrifugation process steps.

5) All of the uranium associated with the black sponge will dissolve during the extended boiling cycle.

Figure 1

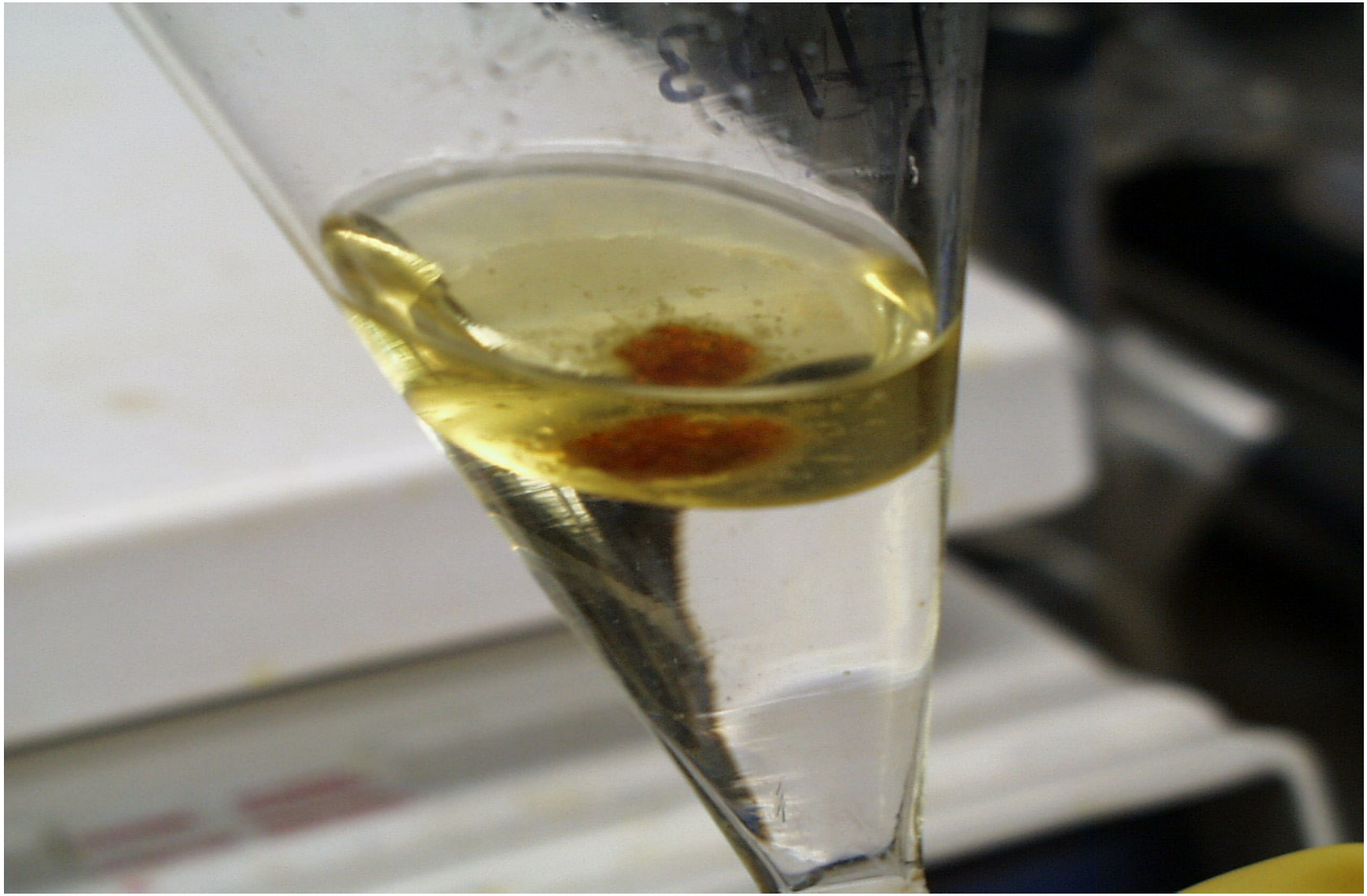

Figure 2