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SOLVENT EXTRACTION STUDIES OF RERTR SILICIDE FUELS\*

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Abstract

Uranium silicide fuels, which are candidate RERTR fuel compositions, may require special considerations in solvent extraction reprocessing. Since Savannah River Plant may be reprocessing RERTR fuels as early as 1985, studies have been conducted at Savannah River Laboratory to demonstrate the solvent extraction behavior of this fuel. Results of solvent extraction studies with both unirradiated and irradiated fuel are presented along with the preliminary RERTR solvent extraction reprocessing flow sheet for Savannah River Plant.

Introduction

The Reduced Enrichment Research and Test Reactor (RERTR) Program is part of a national effort to reduce the enrichment of fuels used in research and test reactors at universities and research institutions in the United States and abroad. The United States Government is obligated to provide fresh fuel and accept spent fuel from 156 research reactors in 35 countries. At any one time, these reactors require a total inventory of about 5,000 kilograms of high-enriched uranium (HEU). Since HEU (>70%  $^{235}\text{U}$ ) could potentially be diverted to non-peaceful uses, it is desirable to convert these reactors to low-enriched uranium (LEU) fuels (<20%  $^{235}\text{U}$ ). However, to maintain reactor performance with the LEU fuels, the total amount of  $^{235}\text{U}$  in the fuel must be maintained. Thus, the total uranium content must be increased by about 4-1/2 times.

Uranium silicide compounds offer densities acceptable for this use. Currently three compounds in this category are being studied. These are  $\text{U}_3\text{Si}$ ,  $\text{U}_3\text{Si}_2$ , and  $\text{U}_3\text{SiAl}$ .

Silicon, however, can cause problems in the solvent extraction reprocessing of spent nuclear fuel.<sup>1-3</sup> These problems are in the form of hydraulic disruptions and incomplete phase separation during the solvent extraction process. A technique has been in use at Savannah River Plant (SRP) since the late 1950's that uses a dilute gelatin solution to polymerize and precipitate silicon species out of the dissolver solution before it is fed to the solvent extraction process.<sup>4</sup>

Since current planning is to reprocess the RERTR fuels at SRP, the reprocessibility of the silicide fuels at SRP must be demonstrated prior to general use of these fuels in research and test reactors. Further, a new flowsheet for reprocessing these fuels is required since they are significantly different from other fuels that are being processed at SRP.

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## SUMMARY

Solvent extraction of unirradiated RERTR silicide fuels has been demonstrated.  $U_3Si$ ,  $U_3Si_2$  and  $U_3SiAl$  fuel compositions were used. No hydraulic disruptions were observed during the course of these studies.

Two solvent extraction runs with dissolved, irradiated mini-plates have been completed. While a coalescence phase formed in the extraction section of the mixer-settler early during the first run (after roughly two hours), the thickness of this phase decreased as the run progressed and no disruption of operation was observed as a result of this phenomenon. Preliminary analytical results from this run were satisfactory. The second run was successfully completed without the appearance of any hydraulic problems. Two other solvent extraction runs were started, but were terminated after 5 and 1.5 hours, respectively, due to problems in the feed system. No hydraulic disruptions were observed prior to the termination of either run.

## DISCUSSION

### Flow Sheet

Figures 1-3 show the solvent extraction flow sheet that was used in these studies. Figure 1 shows the first solvent extraction cycle where initial separation from fission products and of uranium and plutonium is accomplished. Figure 2 shows the second uranium decontamination cycle. A nominal second plutonium decontamination cycle, described previously,<sup>5</sup> will be used for plutonium processing. This flow sheet was developed using the SEPHIS solvent extraction computer model developed at the Oak Ridge National Laboratory (ORNL).<sup>6</sup> For the purpose of these studies, only the first two mixer-settler banks of the first solvent extraction cycle were tested. Any hydraulic disruption caused by silicon would occur primarily in the first mixer-settler bank. Further, the separation of uranium and plutonium in the second mixer-settler bank is important for proper operation of the solvent extraction system at SRP. Sufficient confidence was placed in the SEPHIS code and prior operating experience at SRP such that testing of the uranium recovery bank and the uranium and plutonium decontamination cycles was not necessary.

Solvent extraction studies were done in the Intermediate Level Cells (ILC) Facility at the Savannah River Laboratory (SRL). While it was not necessary to conduct the work with unirradiated fuel in this facility, this was done to check equipment that would be needed for experiments using irradiated fuel.

### Unirradiated Fuel Studies

Three solvent extraction runs were made with unirradiated RERTR silicide fuels; one run with each of the three candidate fuel compositions. The first run was with a dissolved  $U_3SiAl$  miniplate. Feed solution data are shown in Table 1. This run lasted 18 hours and 20 minutes. During the course of this run, there was no evidence of any phase separation or hydraulic problems that might be indicative of interference with the solvent extraction process by silicon species.

Samples were taken of the aqueous and the organic phases in the even numbered stages of the 1A and 1B mixer-settler banks to generate a profile of the uranium and nitric acid concentrations in both phases of both banks. Figures 3 and 4 show the profiles for the 1A bank and Figures 5 and 6 for the 1B bank. These profiles are compared to those predicted by the SEPHIS computer code. The profiles are within the limits of analytical error and the confidence limits of the SEPHIS code.

A comparison of the analyzed endstreams and the SEPHIS predictions is shown in Table 2. The SEPHIS predictions are close for all of these except the low uranium levels, which the SEPHIS code consistently mispredicts. The uranium losses to both the 1AW and 1BP (plutonium product) stream are shown in Table 3. The losses to both of these streams are well below 0.01% and indicate excellent recovery of the uranium. The calculated uranium level in the plutonium product, if this had been an irradiated plate, was 1058 ppm.

A  $U_3Si$  miniplate was used for the second unirradiated plate run. The feed solution data is shown in Table 4. This run lasted 17 hours and 15 minutes. Again, no hydraulic disruption was observed during the course of this run.

Analyses of the endstreams and uranium losses are shown in Table 5. Again, the endstream concentrations are close to the expected values. The predicted uranium level in the plutonium product was calculated again and was estimated to be 640 ppm.

The last solvent extraction run with an unirradiated plate was made with  $U_3Si_2$  alloy. The analysis of the feed solution is shown in Table 6. This run lasted 17-1/2 hours. In the last few hours of the run, aqueous/organic "bubbles" formed at the interface of the settler section of the feed stage, indicating slow coalescence of the phases. Complete separation did occur, and no disruption of the operation resulted from this phenomenon. This might have resulted from the slightly higher silicon levels in this feed solution as compared to the previous runs (70 ppm versus 57 and 65 ppm), although this is doubtful due to the small differences involved.

Table 7 shows the endstream analyses and uranium losses. Again, all of the analyses are within a reasonable range of the expected values. The uranium/plutonium cross-contamination was calculated to be 1800 ppm uranium in the plutonium. This is slightly high, but is probably due to the lower uranium concentration in the feed.

#### Irradiated Fuel Studies

Two solvent extraction runs with irradiated RERTR silicide fuel have been completed and partial analytical information is available. Two other runs were started but were terminated due to problems with the feed system.

During the first run, a coalescence zone formed between the aqueous and organic phases in the settler of each stage in the 1A bank extraction section after about 2 hours of operation with irradiated feed solution. However, this condition began improving about 8 hours into the run and continued to improve until the run was terminated, about 17 hours after it was

started. Hydraulic operation of the banks was not disrupted. Analytical results are pending which will determine the effect of this phenomenon on the chemical operation of the system. Preliminary indications, based on the improvement of the condition as the run progressed, are that this should not pose a problem in reprocessing spent RERTR silicide fuels. The other complete run showed no evidence of a similar condition and was finished without incident.

The two incomplete runs with irradiated plates were conducted with  $U_3Si$  and  $U_3SiAl$  fuel alloys and lasted 5 and 1.5 hours, respectively, before they were terminated due to problems with the feed system. There was no evidence of any hydraulic phenomena similar to that observed on the first run prior to the termination of either of these two runs.

### Conclusions

Solvent extraction reprocessing of irradiated RERTR silicide fuels can be accomplished at the Savannah River Plant. Although complete results are still pending, the levels of silicon present in the feed solutions should not pose a problem in reprocessing.

### REFERENCES

1. Paige, B. E., G. W. Gibson, and K. L. Rohde, The Effect of Silicon on Fabrication and Reprocessing of Aluminum Alloy Reactor Fuels, U.S.A.E.C. Report IN-1194, Idaho Nuclear Corporation, National Reactor Testing Station, Idaho Falls, ID., November 1968.
2. Parrett, O. W. and K. L. Rohde, The Effect of Silicon in the Reprocessing of a Uranium-Aluminum Alloy, U.S.A.E.C. Report IDO-14441, Phillips Petroleum Co., Idaho Falls, ID, May 1958.
3. Cannon, R. D., The Characterization of Surfactants in Aluminum-Uranium Fuel Reprocessing Solutions, U.S.A.E.C. Report IDO-14489, Phillips Petroleum Co., Idaho Falls, ID, October 1959.
4. Groh, H. J., Removal of Silica from Solutions of Nuclear Fuels, U.S.A.E.C. Report DP-293, E. I. du Pont de Nemours & Co., Inc., Savannah River Laboratory, Aiken, SC, June 1958.
5. Hyder, M. L., 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, U.S.D.O.E. Report DP-1500, E. I. du Pont de Nemours & Co., Inc., Savannah River Laboratory, Aiken, SC April 1979.
6. Mitchell, A. D., SEPHIS-MOD4: A User's Manual to a Revised Model for the Purex Solvent Extraction System, U.S.D.O.E. Report ORNL-5471, Union Carbide Corporation, Oak Ridge National Laboratory, Oak Ridge, TN, May 1979.

TABLE 1

U<sub>3</sub>SiAl Unirradiated Plate

Feed Solution

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Uranium	-	25.8 g/l
Nitric Acid	-	3.9 M
Aluminum Nitrate	-	0.94 M
Silicon	-	57 ppm
Mercury	-	39 ppm

TABLE 2

U<sub>3</sub>SiAl Unirradiated Plate

Endstream Analyses

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Stream	HNO <sub>3</sub> , M		U, g/l	
	Actual	Predicted	Actual	Predicted
Waste	3.75	2.99	1.21 x 10 <sup>-4</sup>	1.9 x 10 <sup>-11</sup>
Pu Product	2.32	2.21	1 x 10 <sup>-3</sup>	2.24 x 10 <sup>-9</sup>
U Product	0.074	0.158	10.73	9.14

TABLE 3

U<sub>3</sub>SiAl Unirradiated Plate

Uranium Losses

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Waste Stream Losses (%)	-	5.7 x 10 <sup>-4</sup>
Pu Product Stream Losses (%)	-	1.4 x 10 <sup>-3</sup>
Estimated Content in Pu Product	-	1058 ppm

TABLE 4

U<sub>3</sub>Si Unirradiated Plate

<u>Feed Solution</u>	
Uranium	- 26.7 g/l
Nitric Acid	- 2.77 M
Aluminum Nitrate	- 1.23 M
Silicon	- 65 ppm
Mercury	- 74 ppm

TABLE 5

U<sub>3</sub>Si Unirradiated Plate

<u>Endstream Data</u>			
	<u>HNO<sub>3</sub>, M</u>	<u>U, g/l</u>	<u>U Losses, %</u>
Waste	3.0	2.59 x 10 <sup>-4</sup>	1.22 x 10 <sup>-3</sup>
Pu Product	2.41	3.86 x 10 <sup>-4</sup>	5.44 x 10 <sup>-4</sup>
U Product	0.08	8.03	-----

Calculated U Content in Pu Produce = 640 ppm

TABLE 6

U<sub>3</sub>Si<sub>2</sub> Unirradiated Plate

<u>Feed Solution</u>	
Uranium	- 12.4 g/l
Nitric Acid	- 3.47 M
Aluminum Nitrate	- 1.11 M
Silicon	- 70 ppm
Mercury	- 70 ppm

TABLE 7

U<sub>3</sub>Si<sub>2</sub> Unirradiated Plate

Endstream Data

<u>Stream</u>	<u>HNO<sub>3</sub>, M</u>	<u>U, g/l</u>	<u>U Losses, %</u>
Waste	3.21	2.5 x 10 <sup>-4</sup>	2.44 x 10 <sup>-3</sup>
Pu Product	2.54	5.5 x 10 <sup>-4</sup>	1.61 x 10 <sup>-3</sup>
U Product	0.08	2.99	-----

Calculated U Content in Pu Product = 1900 ppm

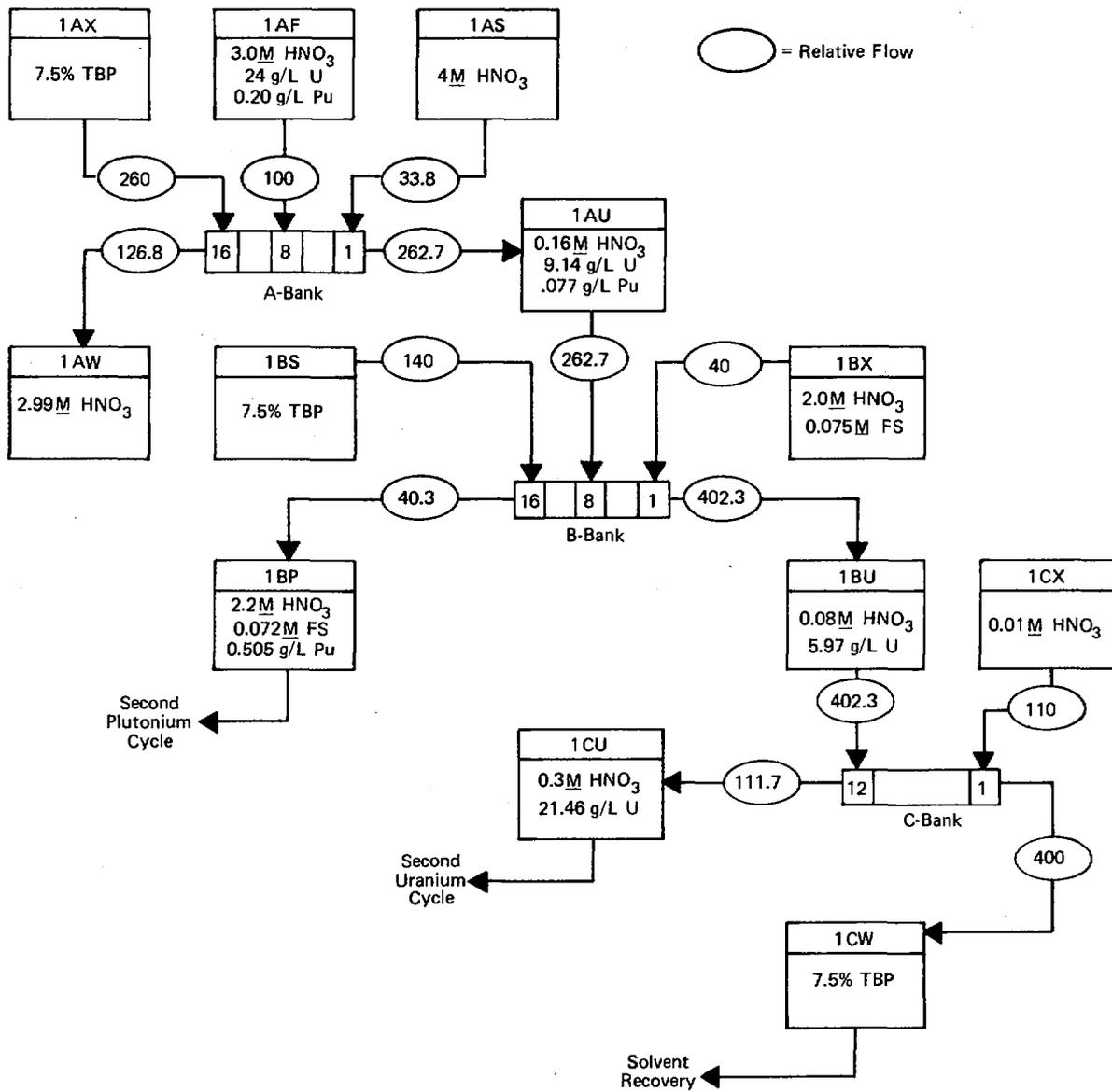


FIGURE 1. RERTR First Solvent Extraction Cycle

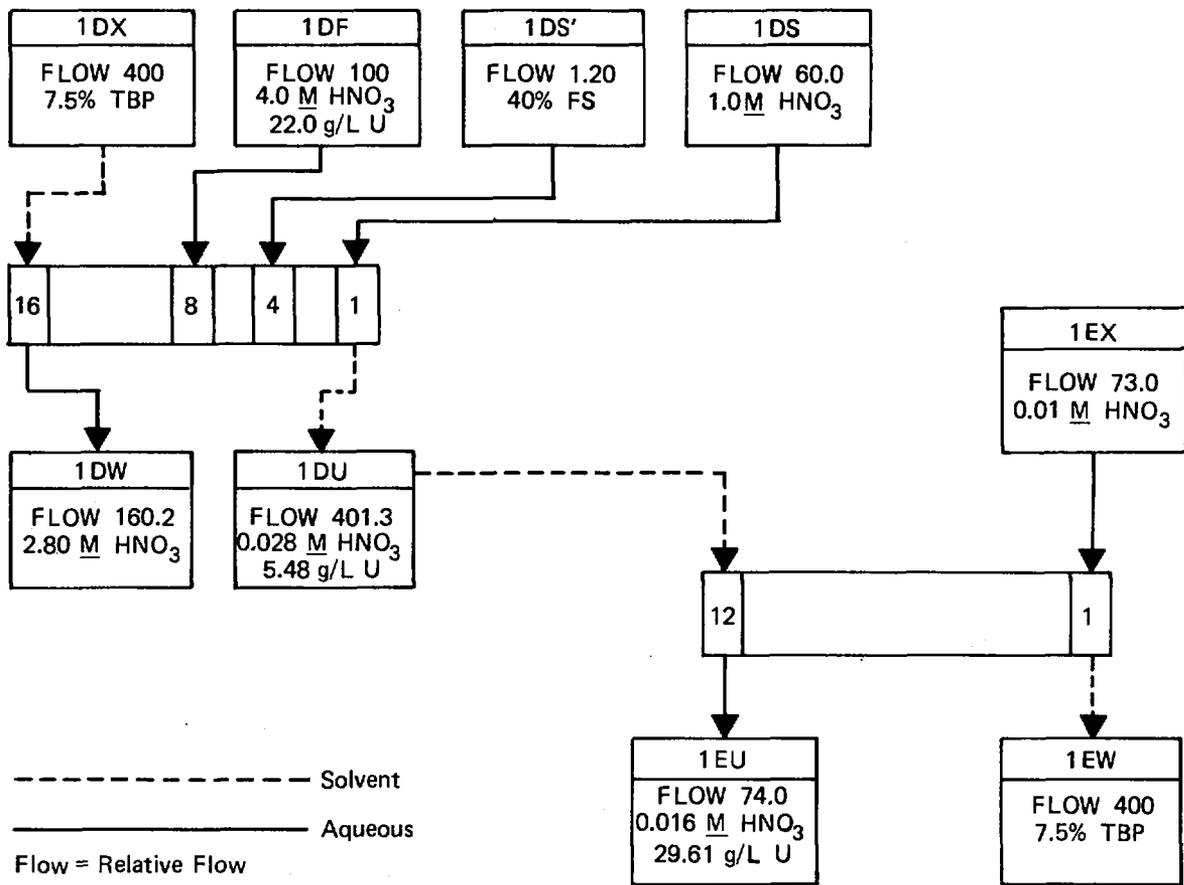


FIGURE 2. RERTR Second Uranium Decontamination Cycle

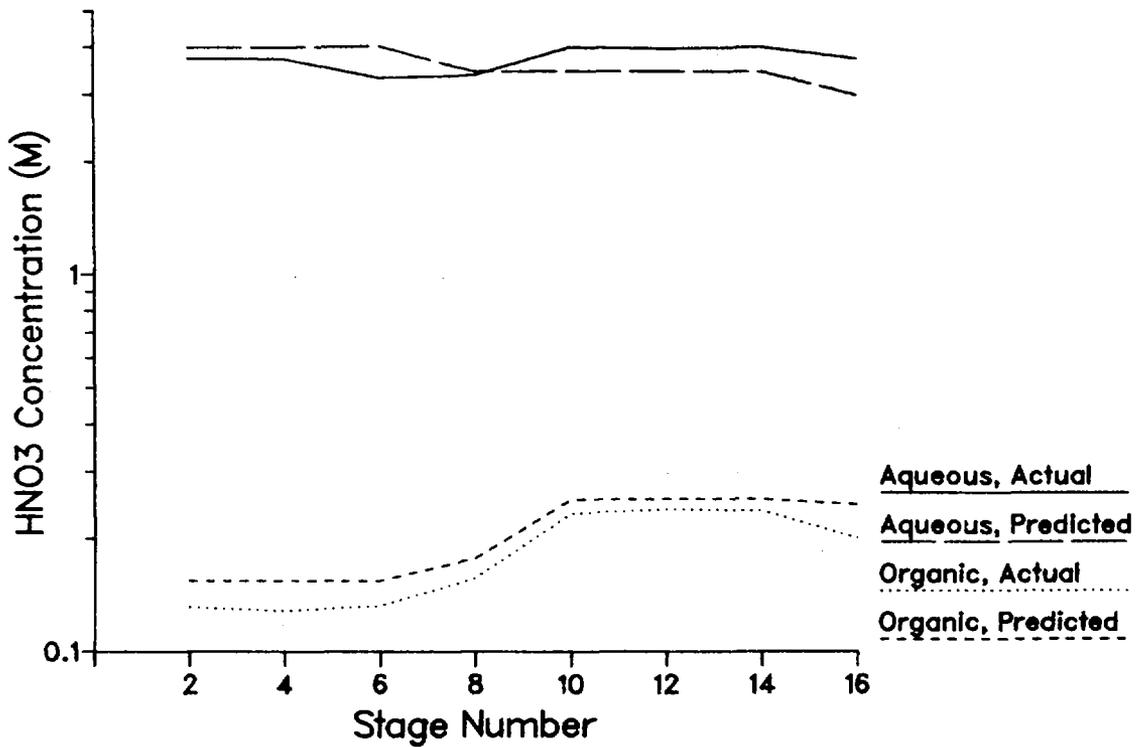


FIGURE 3. Acid Concentrations A-Bank

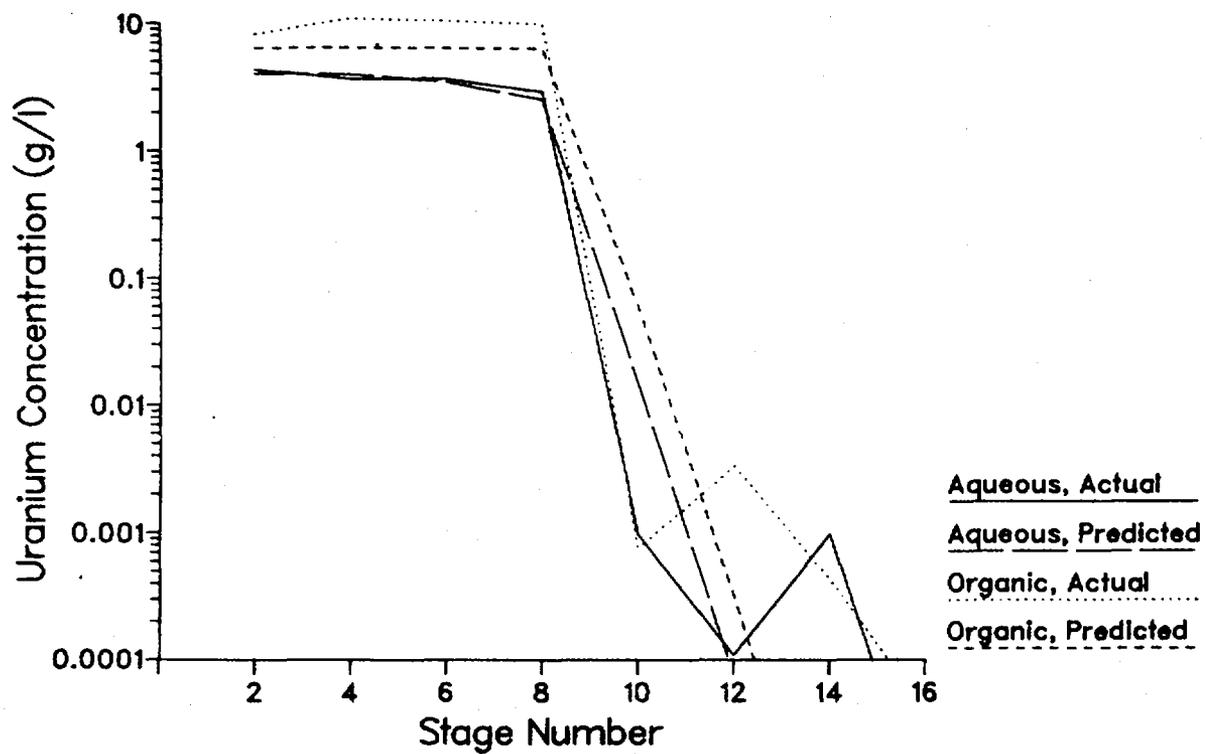


FIGURE 4. Uranium Concentrations A-Bank

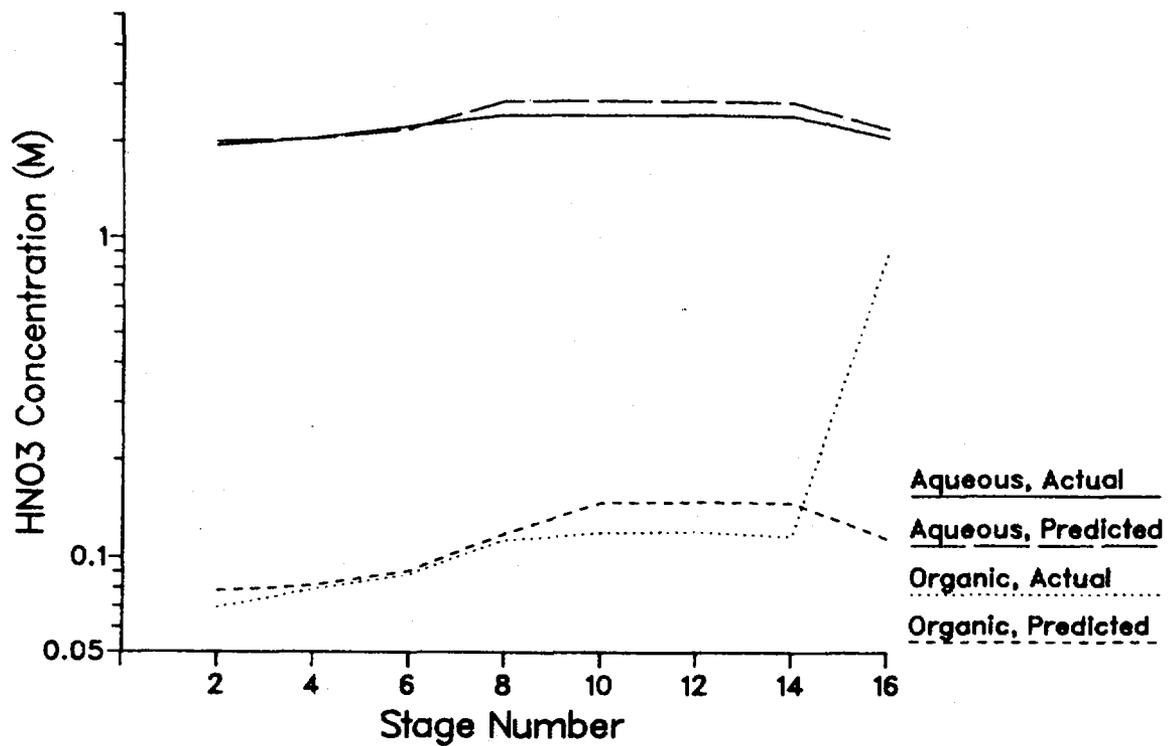


FIGURE 5. Acid Concentrations B-Bank

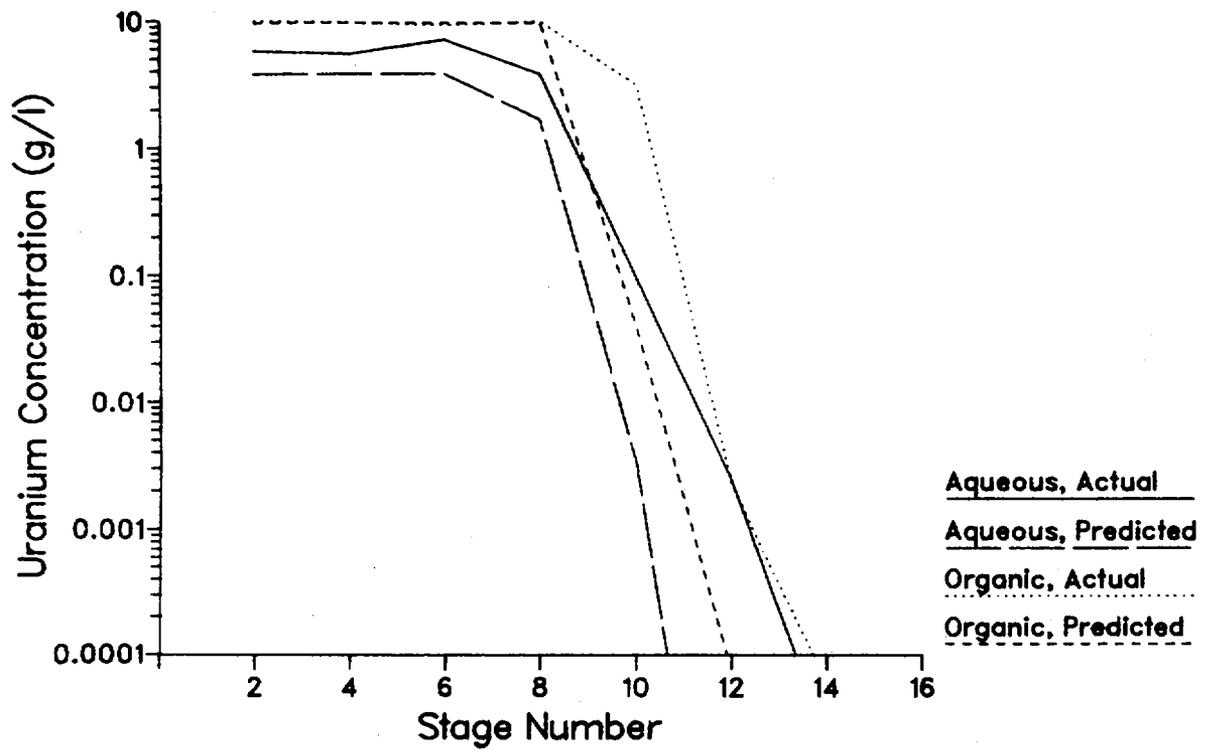


FIGURE 6. Uranium Concentrations B-Bank