

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Keywords: Aluminosilicate
Actinide
Criticality

Retention: Permanent

Fate of Uranium during Sodium Aluminosilicate Formation under Waste Tank Conditions

W. R. Wilmarth
J. T. Mills
V. H. Dukes
R. C. Sullivan

Publication date: June 22, 2005

SAVANNAH RIVER NATIONAL LABORATORY
WESTINGHOUSE SAVANNAH RIVER COMPANY
Savannah River Site, Aiken, SC 29808



Disclaimer

This report was prepared by Westinghouse Savannah River Company (WSRC) for the United States Department of Energy under Contract No. DE-AC09-96SR18500 and is an account of work performed under that contract. Neither the United States Department of Energy, nor WSRC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, or product or process disclosed herein or represents that its use will not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trademark, name, manufacturer or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring of same by WSRC or the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America

Table of Contents

Fate of Uranium during Sodium Aluminosilicate Formation under Waste Tank Conditions ...	1
List of Figures	3
List of Tables	4
Approvals	5
Summary	6
Introduction	6
Experimental Details	7
Task 1: Characterization of Uranium in Tank 49H Concentrate	7
Task 2: Characterization of Tank 49H Concentrate and High Aluminum-containing Waste	8
Task 3: Thermodynamic Modeling to Predict Solution Behavior	8
Task 4: NAS Co-Precipitation Testing	9
Task 5: Sub-Saturation Test	10
Results and Discussion	10
Determination of Uranium Distribution between Solid and Liquid Phases	10
Simulant Studies involving Uranium and NAS Formation	13
Solid State Characterization of Solids	18
Actual Waste Testing	21
Conclusions	24

List of Figures


Figure 1. Photograph of Tank 49 Samples	8
Figure 2. Plot of Added SiO ₂ versus NAS Formation	9
Figure 3. Uranium Concentration in 2H Evaporator Liquor	11
Figure 4. SRS Analytical Laboratories Data For Tank 43H	11
Figure 5. Uranium Concentrations in Filtered Tank 49H Supernate	12
Figure 6. Uranium Solubility Curves in Simulated Waste Solution	14
Figure 7. Effect of Aluminate Ion on Uranium Solubility	14
Figure 8. Results from the 50 mg/L Uranium Test	15
Figure 9. Results from the 25 mg/L Uranium Test	16
Figure 10. Results from Testing at 15 mg/L Uranium	17
Figure 11. Results from the 5 mg/L uranium Test	17
Figure 12. Results from 10 mg/L Uranium Test	18
Figure 13. Typical Powder Diffraction Spectrum from Solids Produced during Aluminosilicate Formation	19
Figure 14. SEM Images of Solids from Simulant Studies	20
Figure 15. SEM Image from Simulant Test with 50 mg/L Uranium	20
Figure 16. EDS Spectrum from Uranium-Containing Solid	21
Figure 17. Uranium Concentrations in the Actual Waste Test	23
Figure 18. X-Ray Diffraction Pattern from Actual Waste Test	23
Figure 19. SEM of Solids from Actual Waste Test	24


List of Tables

Table 1. Solution Composition	10
Table 2. Solution Compositions of Tank Samples.....	13
Table 3. Uranium Content of Simulant Solids.....	22

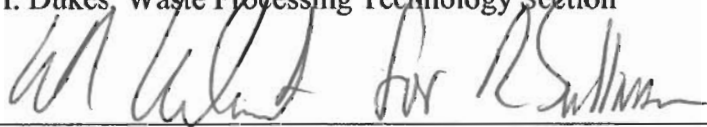
Approvals

Authors:

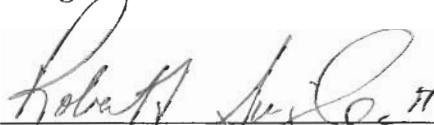
 9/2/05
 W. R. Wilmarth, Waste Processing Technology Section Date

 for JT Mills 9/2/05
 J. T. Mills, Waste Processing Technology Section Date

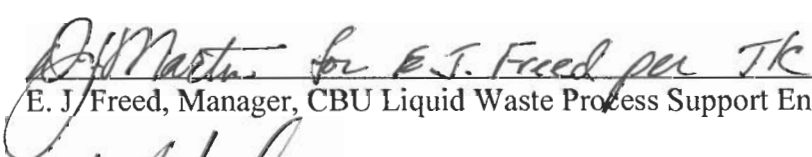
 9/7/05
 V. H. Duker, Waste Processing Technology Section Date


 for R Sullivan 9/7/05
 R. Sullivan, Shielded Cells Operations Date

Design Check:

 9/7/05
 R. F. Swingle, SRNL Waste Processing Technology Section Date

Approvals/Review:

 for E.J. Freed per JK 9/14/05
 E. J. Freed, Manager, CBU Liquid Waste Process Support Engineering Date

 9-2-05
 W. R. Wilmarth, Manager, SRNL Waste Processing Technology Section Date

 9/14/05
 J. C. Griffin, Manager, SRNL Waste Processing Technology Section Date

Summary

Experiments have been conducted to examine the fate of uranium during the formation of sodium aluminosilicate (NAS) when wastes containing high aluminate concentrations are mixed with wastes of high silicate concentration. Testing was conducted at varying degrees of uranium saturation. Testing examined typical tank conditions, e.g., stagnant, slightly elevated temperature (50 °C). The results showed that under sub-saturated conditions uranium is not removed from solution to any large extent in both simulant testing and actual tank waste testing. There are data supporting a small removal due to sorption of uranium on sites in the NAS. Above the solubility limit the data are clear that a reduction in uranium concentration occurs with the formation of aluminosilicate. This uranium precipitation is fairly rapid and ceases when uranium reaches its solubility limit. At the solubility limit, it appears that uranium is not affected, but further testing might be warranted.

Lastly, analysis of the uranium speciation in a Tank 49H set of samples showed the uranium to be soluble. Analysis of the solution composition and subsequent use of the Hobb's uranium solubility model indicated a uranium solubility limit of 32 mg/L. The measured value of uranium in the Tank 49H matched the model prediction.

Introduction

The Savannah River Site (SRS) stores high level nuclear waste in 49 underground storage tanks. The wastes are to be vitrified in the Defense Waste Processing Facility (DWPF) for permanent disposal. The available tank space must be managed to ensure viability of the separation canyons to support nuclear material stabilization and continued operation of DWPF. Under normal operations, the wastes are evaporated to reduce volume. The SRS has three operational atmospheric-pressure high-level waste evaporators. Two evaporators are located in H-Area and one is in F-Area. The 242-16H (or 2H) evaporator had not operated from October 1999 to September 2001 due to the presence of a large amount of sodium aluminosilicate scale that contained sodium diuranate.^{1,2,3} The scale is very similar to that observed in the aluminum and pulp paper industries^{4,5,6} and was produced at SRS by reaction of the aluminate supplied by the plutonium separations facilities and the silicate from recycle water from the DWPF. The chemistry of high level waste with elevated silicon levels thermodynamically favors the formation of aluminosilicates.⁷ The 2H Evaporator was scaled to the point that the concentrated evaporator bottoms could not be removed through normal steam lifting protocol.

As a result of the formation of aluminosilicates when elevated concentrations of silica are a concern, SRS changed the operational requirements for the site's High-Level Waste evaporators. Wastes containing high silicon concentrations, e.g., DWPF recycle would be concentrated in the 2H Evaporator. The criticality hazard for the 2H Evaporator was reduced by depleting the U-235 content of the waste below acceptable levels. Waste containing aluminate would be processed in the 2F or 3H Evaporator and acceptance criteria were established to monitor for the possible formation of sodium aluminosilicate.⁸

Operation of the Site's Evaporators in a segregated mode is acceptable to prevent issues associated with sodium aluminosilicate formation. However, the segregation does generate a problem when a need to de-inventory the high silicon-containing system. With tank space at a premium, the de-inventory process has the potential to mix high silicon-containing and high aluminum-containing wastes. Rosencrance⁹ examined the fate of uranium during testing involving mixing both types of wastes together. In this testing, uranium was found to precipitate in all cases. However, it should be noted that uranium was added at a concentration thought to be very near or above its solubility limit as evidenced by precipitation in the control samples.

Current plant operation has de-inventoried the 2H Evaporator system to Tank 49H. Plans call for this high silicon-containing waste to be moved to one of the Type IV tanks. However, a heel will remain in Tank 49H. A large inventory of dissolved saltcake from Tank 41H is scheduled to be moved into Tank 49H. This will bring a high aluminum-containing waste into contact with the high-silicon material. Therefore, SRNL has been asked to assess the fate of uranium during a simulation of this plant operation.¹⁰ Additionally, SRNL has been asked to determine if the uranium present in the Tank 49H material is soluble or colloidal.

Experimental Details

The work was divided into 5 separate tasks as described below:

Task 1: Characterization of Uranium in Tank 49H Concentrate

It has been reported that the uranium concentration in Tank 49H (formerly Tank 38H/43H concentrate) has risen well above historical levels.¹¹ This is well above that predicted by Hobbs and Karraker in their solubility models.¹² Therefore, SRNL determined if this uranium concentration represents a soluble uranium species or is the uranium in a colloidal form. SRNL used a filtration method described elsewhere¹³ to determine the nature of the uranium. Three samples were received from H-Tank Farm and were numbered HTF-073, -074, and -075 (Figure 1). The sample from the lowest depth in the tank (HTF-075) showed some sludge solids. The samples were combined and filtered sequentially through a 0.45, 0.2 and 0.02 μm filter units. Samples were taken from the as-received samples and from each filtration step. These samples were analyzed for uranium using a Fisons Plasmaquad PQS972 II Inductively Coupled Plasma Mass Spectrometer.



Figure 1. Photograph of Tank 49 Samples

Task 2: Characterization of Tank 49H Concentrate and High Aluminum-containing Waste

In order to perform thermodynamic modeling of the waste chemistry, a complete characterization of the liquid composition was needed. This included analysis of elemental compositions using a JY170C Inductively Couple Plasma Emission Spectrometer and anion analyses by ion chromatography and titration for free hydroxide of Tank 49H Concentrate but, also, the contents of wastes (referred to as Variable Tank Sample (VTS)) stored in a Satellite Accumulation Area in the Shielded Cells. These wastes were sent to SRNL for analyses during previous sampling campaigns.

Task 3: Thermodynamic Modeling to Predict Solution Behavior

A significant effort was expended to thermodynamically model the operation of the Site's High-Level Waste Evaporators.^{14,15} In this work, a commercially available computer software called Geochemist's Workbench was used. This software package is capable of performing a number of equilibrium thermodynamic calculations simultaneously. The program is equipped with the Lawrence Livermore National Laboratory extensive database for minerals and aqueous species. It has also been augmented with data on sodium aluminosilicate solubilities.¹⁶ This software package has undergone a thorough quality assurance validation process.¹⁷ Data on the solution compositions of the Tank 49H waste and the Variable Tank Sample (VTS) Composite were entered into the Geochemist Workbench program and modeled for aluminosilicate formation. In a 1:5 mixture of the Tank 49H supernate with the VTS supernate, the mixture was found to be subsaturated with

respect to aluminosilicate precipitation. Therefore, using the *REACT* command, 10 g of SiO_2 (aq) was added. The following Figure 2 shows the result of this addition in terms of NAS formation as a function of SiO_2 (aq) addition. The initial amount of solution is approximately 1 L. If one wanted to produce 20 g of NAS in 1 L of this solution, one would need to add approximately 7 g of SiO_2 (aq), or 3.25 g of elemental Si.

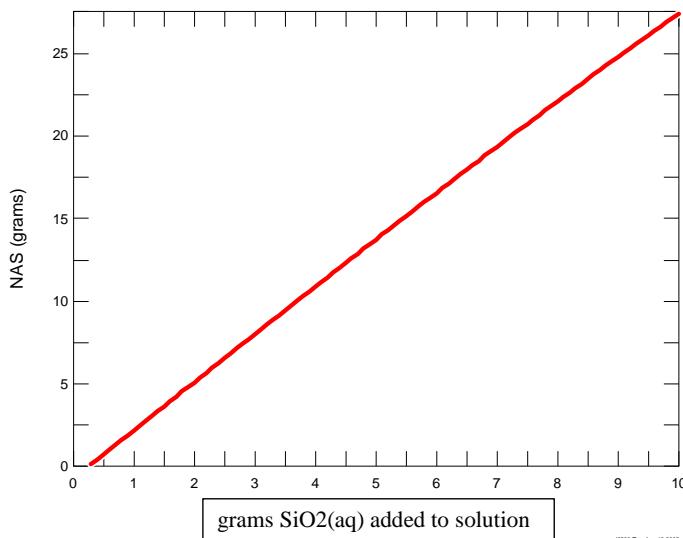


Figure 2. Plot of Added SiO_2 versus NAS Formation

Task 4: NAS Co-Precipitation Testing

Testing combined amounts of the Tank 49H (high silicon material) with characterized available VTS supernate (high aluminum material) in a 1:5 ratio, respectively. Using the graph in Figure 2, an addition of ~ 6.63 g of sodium metasilicate was added to the combined waste matrix at the beginning of the test. Testing was performed at 50 °C in Teflon bottles in duplicate on a 100 mL scale. Periodically during the test, the samples were removed from the oven allow to cool to ambient temperature and an aliquot was removed for analysis. A sub-sample of the aliquot was filtered through a cellulose 0.45 micrometer filter and gravimetrically diluted into 0.2 M nitric acid. Portions of the dilution acid were removed from the Shielded Cells and analyzed for silicon and aluminum by ICP-ES and uranium by ICP-MS.

Task 5: Sub-Saturation Test

In his sorption testing, Addai-Mensah^{18,19} established the uranium solubility in a 7 M sodium salt solution and the effect of increasing the aluminate concentration. The base solution concentrations are shown in Table 1.

Table 1. Solution Composition

Concentration	Component
4.0 M	NaOH
1.0M	NaNO ₃
1.0 M	NaNO ₂
1.7×10^{-3} M	SiO ₂
1.7×10^{-3} M	Al (III)

Testing was performed in duplicate in Teflon bottles with ~ 100 mL of solution. The aluminate concentration was raised to ~ 2500 mg/L and silicon was raised to over 1000 mg/l to promote aluminosilicate formation. The tests were spiked to a level of 5, 10, 15, 25 and 50 mg/L uranium(VI) dissolved in nitric acid. Periodically during the test, the samples were removed from the oven and allowed to cool to ambient temperature and an aliquot was removed for analysis. A sub-sample of the aliquot was filtered through a cellulose 0.45 micrometer filter and analyzed for silicon and aluminum by ICP-ES and uranium by ICP-MS.

Results and Discussion

Determination of Uranium Distribution between Solid and Liquid Phases

The uranium concentration in actual 2H Evaporator liquors have been measured over a span on many years. Wilmarth²⁰ reported a compilation of data from the feed and drop tanks of all three operating High-Level Waste Evaporators including data for Tank 43H, the feed tank to the 2H Evaporator, over the period of 1990 to 1997. Figure 3 shows these data along with 67 and 95 % confidence limits. The average uranium concentration was below 3 mg/L and the upper 95 % confidence limit was below 6 mg/L. These data are from acid diluted aliquots of samples removed from the actual waste tank. It is not known whether these liquors were saturated in uranium or not. Data were also obtained for a more extended timeframe from the SRS Analytical Laboratories and are shown in Figure 4. The timeframe for uranium is from May 1991 through November 1999. Typically, the uranium concentration is low,

agreeing with Wilmarth's compilation. However, beginning in 1996 a jump in the measured uranium concentration is observed. The timing of this increase coincides with the receipt of silicon-containing recycle water from the Defense Waste Processing Facility (DWPF). The uranium concentration measured around 15 mg/L with a large variance. The reason for this increase has not been examined. It could be that the recycle water that is known to contain uranium brings a uranium compound that dissolves into the Tank 43H liquor.

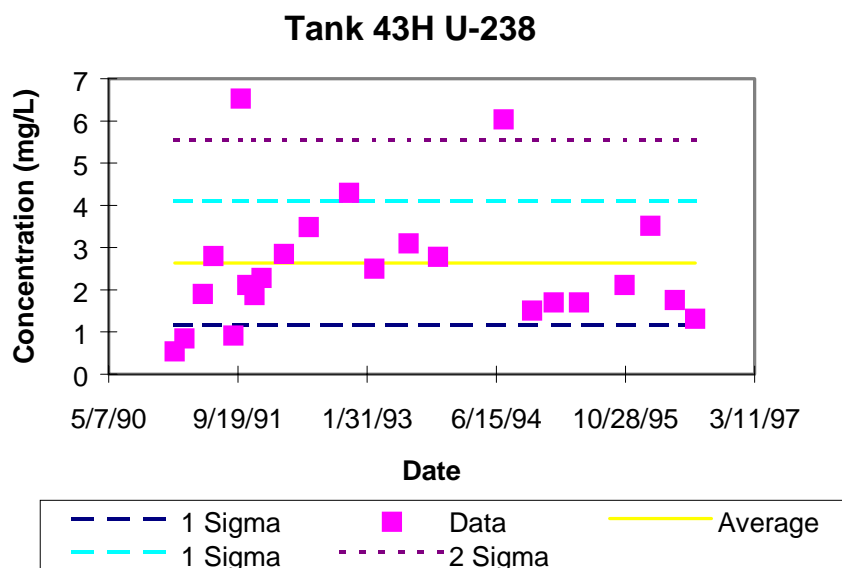


Figure 3. Uranium Concentration in 2H Evaporator Liquor

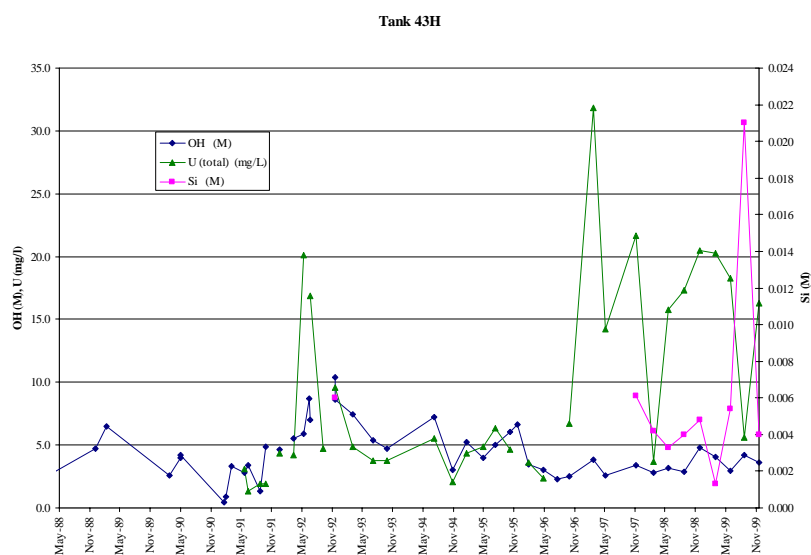


Figure 4. SRS Analytical Laboratories Data For Tank 43H

Periodically, liquor from evaporators must be purged from the system due to being saturated in key constituents. The 2H liquor was removed from the system and sent to Tank 49H. Samples had shown elevated uranium concentrations in the 2H system prior to de-liquoring. Therefore, samples were pulled from Tank 49H. Previously, a filtration method was used to ascertain the amount of insoluble silica in High-Level Waste samples.²¹ This method used a 0.45 μm filter to remove bulk solids, 0.2 μm filter to remove suspended solids and a 0.02 μm filter to remove colloidal solids.

Four sets of duplicate samples were prepared and included the As-Received composite and the filtrates from the sequential filtration at filter pore sizes of 0.45 μm , 0.2 μm and 0.02 μm . The averaged values and one standard deviation of the uranium concentrations are reported below:

As-Received	$33.5 \pm 0.5 \text{ mg/L}$
0.45 μm Filtrate	$31.8 \pm 0.5 \text{ mg/L}$
0.2 μm Filtrate	$29.6 \pm 1.9 \text{ mg/L}$
0.02 μm Filtrate	$31.5 \pm 0.4 \text{ mg/L}$

Shown below in Figure 5 is a graphical representation of the data and the associated error at 95 % confidence. These data indicate that the uranium is soluble and has an averaged value of $31.6 \pm 3.4 \text{ mg/L}$ at 95% confidence. The % U enrichment was 0.600 ± 0.2 at 95 % confidence. Hobbs and Edwards²² had published a report of the solubility of uranium in alkaline solutions and represented the solubility as a function of a number of anion concentrations. Shown in Table 2 are analytical data for the composite of the three tank samples. Using these concentrations, one predicts the uranium solubility to be 31.8 mg/L indicating that these solutions are saturated with uranium.

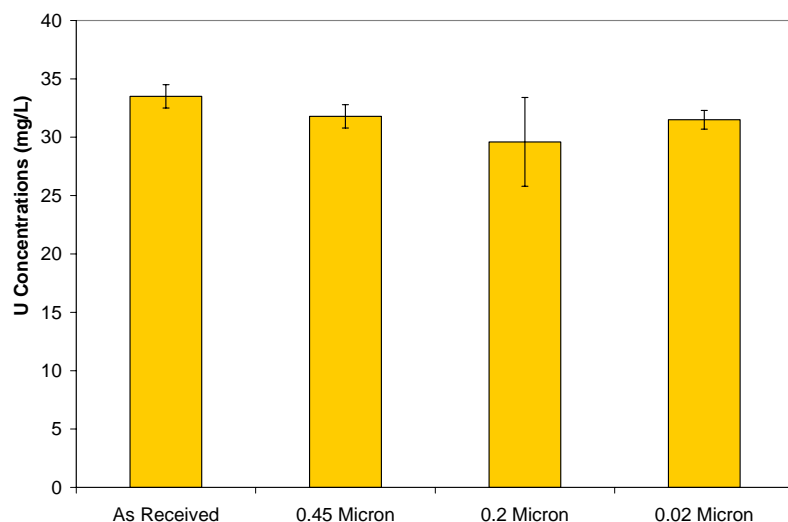


Figure 5. Uranium Concentrations in Filtered Tank 49H Supernate.

Table 2. Solution Compositions of Tank Samples

	Units	Tank 49	VTs
Al	M	0.14	0.42
Cr	M	0.0025	0.0047
K	M	0.04	0.06
Li	M	0.009	0.004
Na	M	9.53	7.85
P	M	0.01	0.01
Si	ppm	185	128
Carbonate	M	1.35	0.91
Formate	M	0.05	0
Nitrite	M	1.73	1.16
Nitrate	M	2.22	2.03
Sulfate	M	0.01	0.03
Free OH	M	5.13	3.49

VTs = Variable Tank Sample Composite

Simulant Studies Involving Uranium and NAS Formation

The past experience with the uranium incorporation into aluminosilicate phases causes concerns if the NAS formation occurs in the large waste tanks (~ 1M Gal) whereby large amount of uranium are available even though the absolute concentration is small. Previously, Rosencrance⁹ had studied the fate of uranium and found under all conditions studied that uranium precipitated. Rosencrance, however, initiated the study with relatively high uranium concentrations and may have been above the solubility limit for the base simulant composition. In performing his uranium sorption experiments on the different sodium aluminosilicate phases, Addai-Mensah^{23,24} established the uranium solubility in a 7 M sodium salt solution and the effect of increasing the aluminate concentration. Figure 6 and Figure 7 show the results of that work. Using the base simulant shown in Table 1 and adjusting the starting aluminate ion concentration, experiments were conducted at known uranium concentrations that were well below the solubility limit up to well beyond the solubility limit. A total of 5 uranium concentrations were explored from 5 mg/L to 50 mg/L.

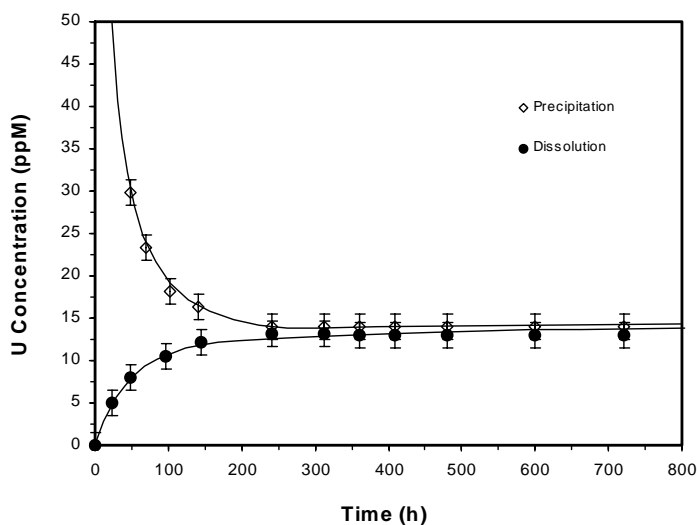


Figure 6. Uranium Solubility Curves in Simulated Waste Solution

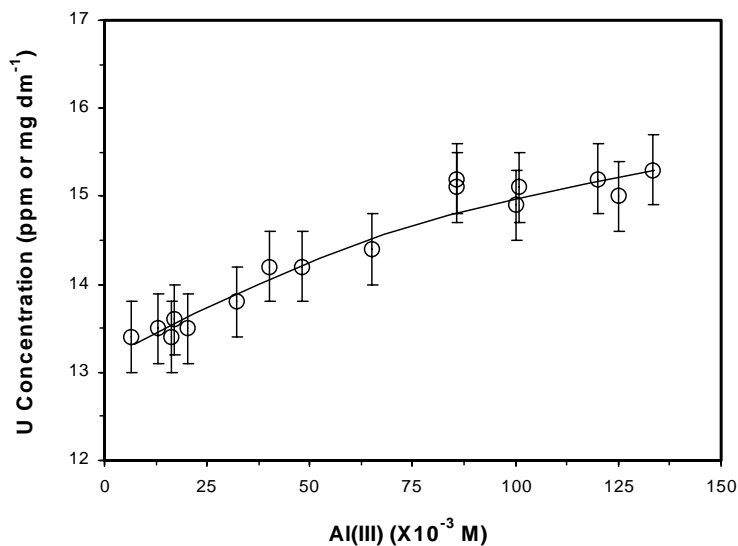


Figure 7. Effect of Aluminate Ion on Uranium Solubility

Using the above graphs to determine that the uranium concentration in the simulated waste was 14 – 15 mg/L, experiments were conducted at target uranium concentrations of 25 and 50 mg/L. In these experiments, the targeted uranium was spiked into the waste solution and held at temperature (50 °C) for 50h. Samples were taken very shortly after uranium addition (recorded as Time = 0 hours) and at 50 h to determine if the uranium had precipitated. An aliquot of reagent grade sodium metasilicate was added (~ 6.26 g) to the waste solution and a second sample was taken following the dissolution of the metasilicate. Lastly, samples were taken periodically over approximately 200 h.

Figure 8 shows the results for the test conducted with 50 mg/L uranium. The initial samples showed uranium concentrations of 53 and 61 mg/L. The first sample taken at 50 h measured 64 mg/L while the second sample taken, after the metasilicate was added, measured 21.6 mg/L. At the time of the second sample was taken during the 50th hour, a concomitant reduction in the aluminum concentration occurred indicating the formation of aluminosilicate had commenced. Evident from the silicon and aluminum data, aluminosilicate formation continued over the duration of the test. However, the uranium concentration plot does not indicate a continued loss of uranium from solution.

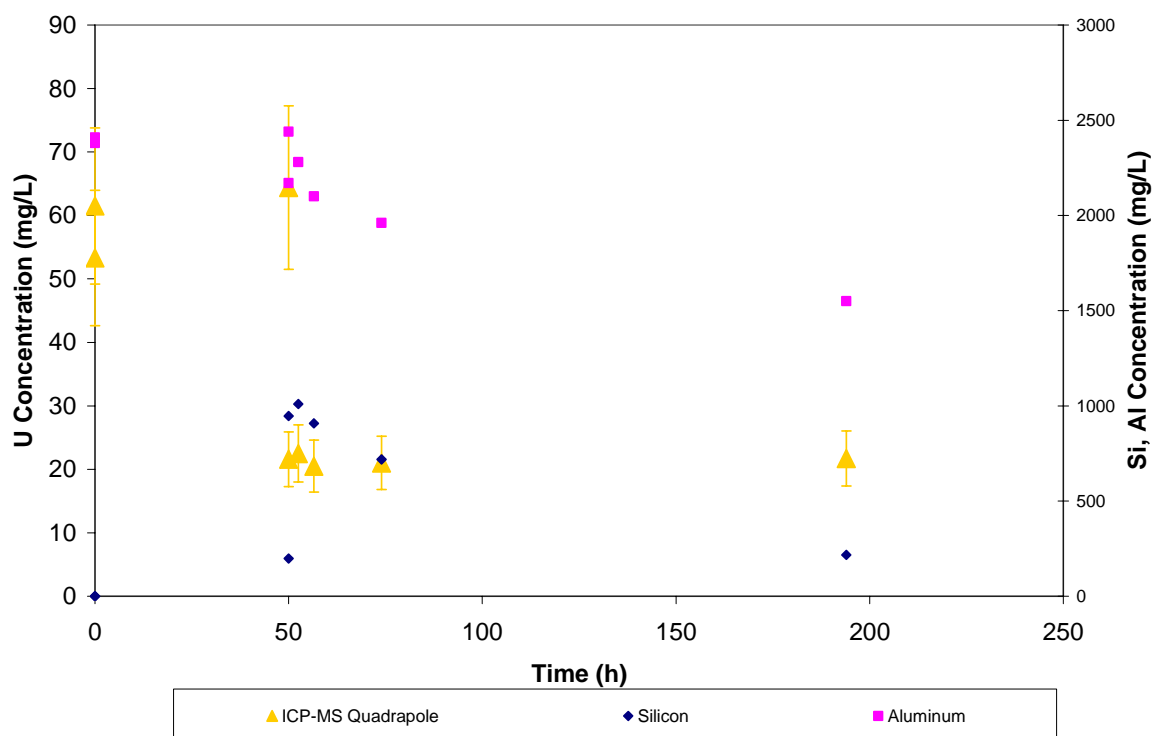


Figure 8. Results from the 50 mg/L Uranium Test

A second test was conducted at a uranium concentration of 25 mg/L with the expectation that similar solution chemistries would occur. The results from the 25 mg/L uranium test are shown in Figure 9. In this instance the starting uranium concentration was slightly higher than the 25 mg/L target and measured slightly above 30 mg/L. The supersaturated solution was stable at the 50 hour mark. When the silicon was added, the same phenomenon as in the 50 mg/L uranium test occurred. A drop in both uranium and aluminum concentrations are observed. This is followed by further reaction to produce additional aluminosilicate without a significant removal of uranium from solution.

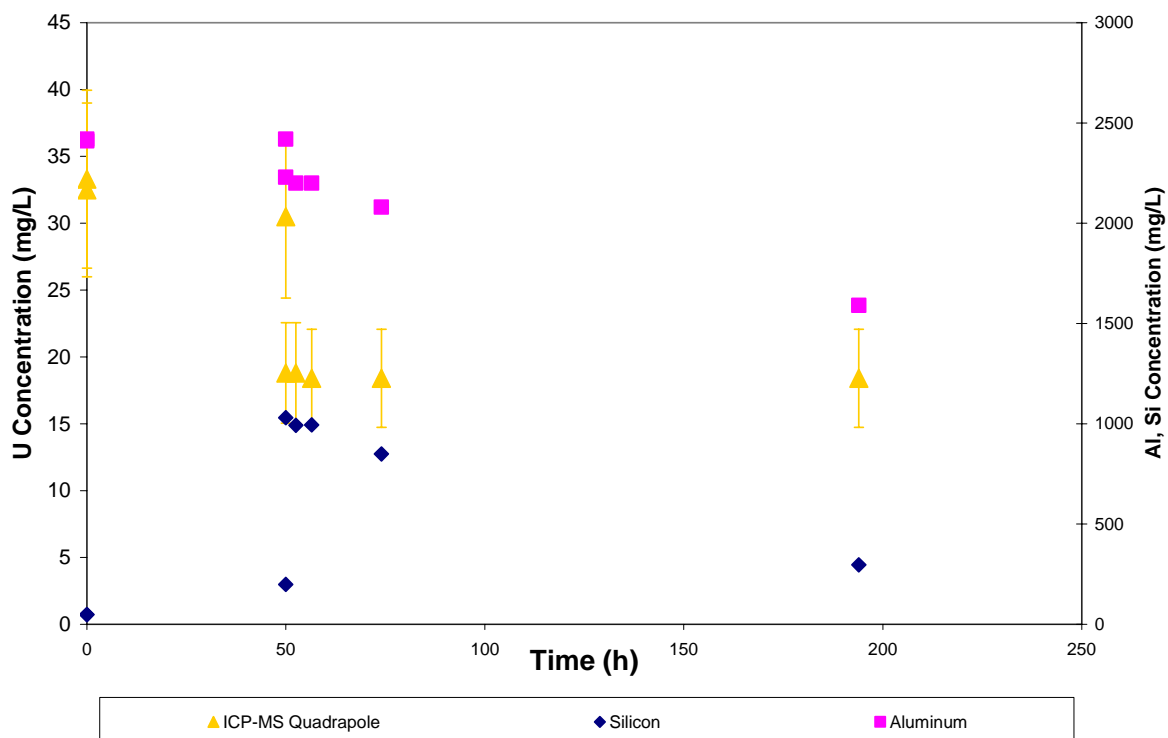


Figure 9. Results from the 25 mg/L Uranium Test

One experiment was conducted with a uranium concentration approximately at the uranium solubility limit. In this experiment, the targeted uranium concentration was 15 mg/L. Figure 10 shows the uranium, silicon and aluminum elemental analysis results. As observed in the tests conducted with uranium concentrations of 50 and 25 mg/L, silicon was added at the 50 h mark and reaction to form the sodium aluminosilicates occurs as evident by both aluminum and silicon concentrations declining with time. In this experiment, the starting measured uranium concentration was slightly higher than targeted and measured near 20 mg/L with an anticipated solubility limit of 15 mg/L. The uranium data suggests that at the point at which aluminosilicate starts to form that the uranium concentration is reduced. However, as indicated by the uncertainty bands, many of the measurements for uranium after the addition of metasilicate (at 50 h) many of the uranium measurements overlap the starting concentration. As in the other tests, there does not appear to a continual change with time after the addition of metasilicate.

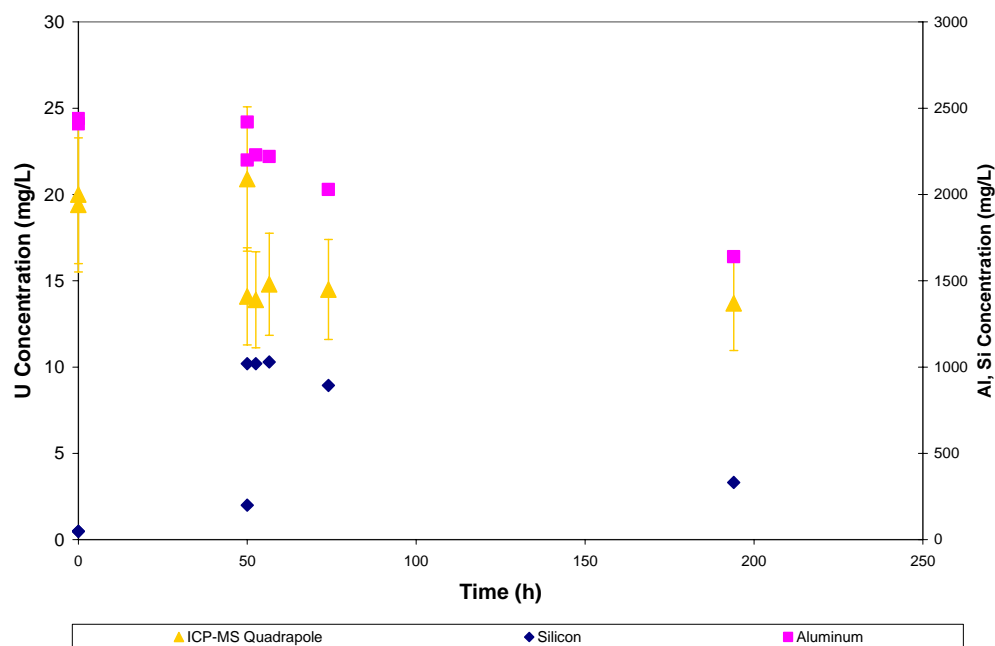


Figure 10. Results from Testing at 15 mg/L Uranium

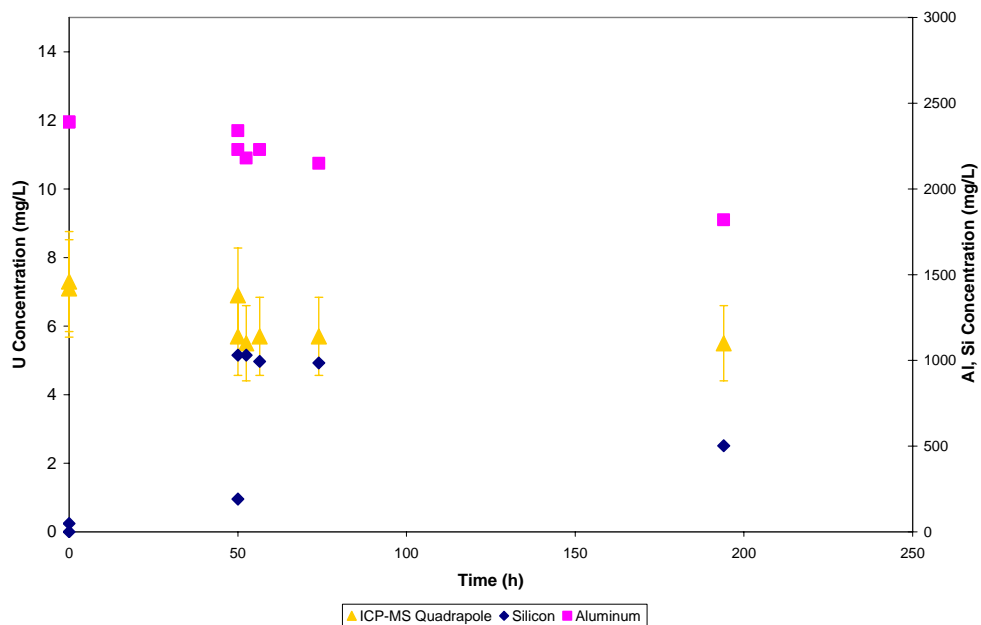


Figure 11. Results from the 5 mg/L uranium Test

It is evident from the results of the first three tests that the formation of sodium aluminosilicate will influence the level of supersaturated uranium causing removal of

uranium from solution. To examine the other extreme, a solution was prepared with uranium well below its solubility in this case at a concentration of 5 mg/L. The identical reaction sequence was followed including the thermal treatment of the solution prior to the silicon spike. The results of this test are shown in Figure 11. As in the previous tests conducted at higher uranium concentrations, aluminosilicate forms immediately upon the addition of metasilicate as evidenced by the drop in aluminum concentration and a continued reaction producing aluminosilicate solids for the remainder of the test. The uranium concentration appears to be constant throughout the test within the error associated with the uranium measurement. This indicates that when below the solubility limit uranium is unaffected during the formation of aluminosilicate. This was examined at a slightly higher uranium concentration as shown in Figure 12. In this experiment, the uranium concentration was raised to a target of 10 mg/L and measurements taken throughout the test indicate the uranium concentration is constant. The results from all five of these tests show that when the uranium concentration is at or below the solubility limit that the uranium is unaffected during aluminosilicate formation.

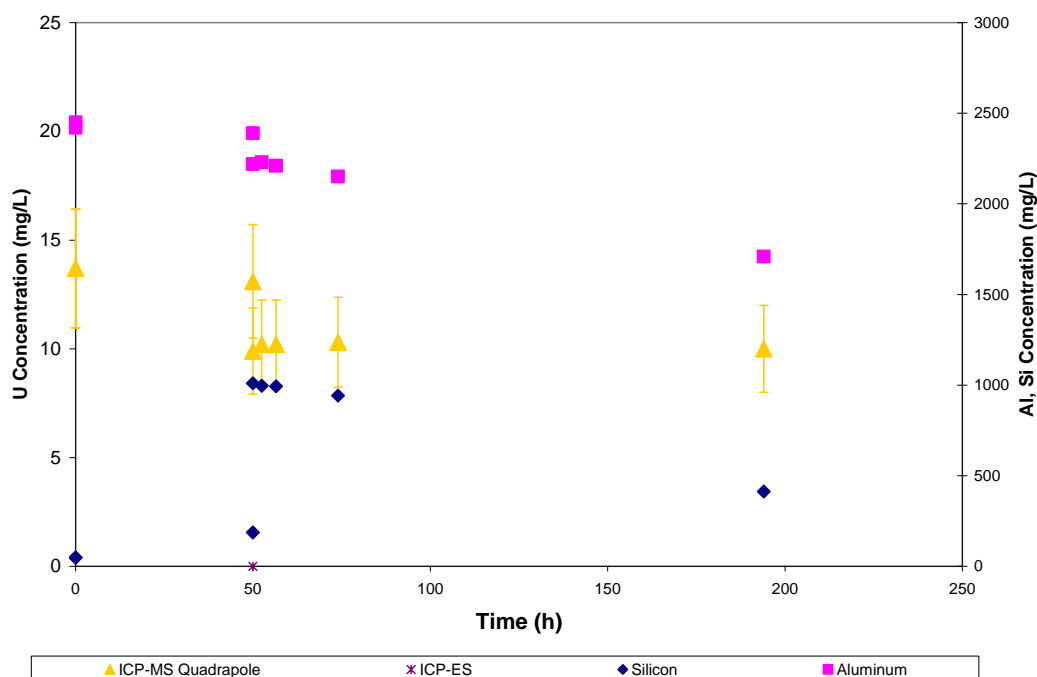


Figure 12. Results from 10 mg/L Uranium Test

Solid State Characterization of Solids

Solids were collected from the reaction vessels from each of the five aluminosilicate formation tests. The samples were characterized by powder X-ray diffraction and Scanning Electron Microscopy along with Energy Dispersive Spectroscopy. In addition, portions of the solid samples were digested in nitric acid and submitted for uranium analysis. The solids were white and flaky in color.

The results from the X-ray diffraction showed powder patterns typical of that shown in Figure 13. The pattern matches the reference pattern for a nitrated cancrinite typical of that observed in the 2H Evaporator. The pattern does show amorphous character as evidenced by the broad band in the 15 – 40 degree 2θ. Even in the test involving 50 mg/L, there was no indication of a crystallographic phase of a uranium compound. This is not unexpected due to the small amount of uranium present in each test.

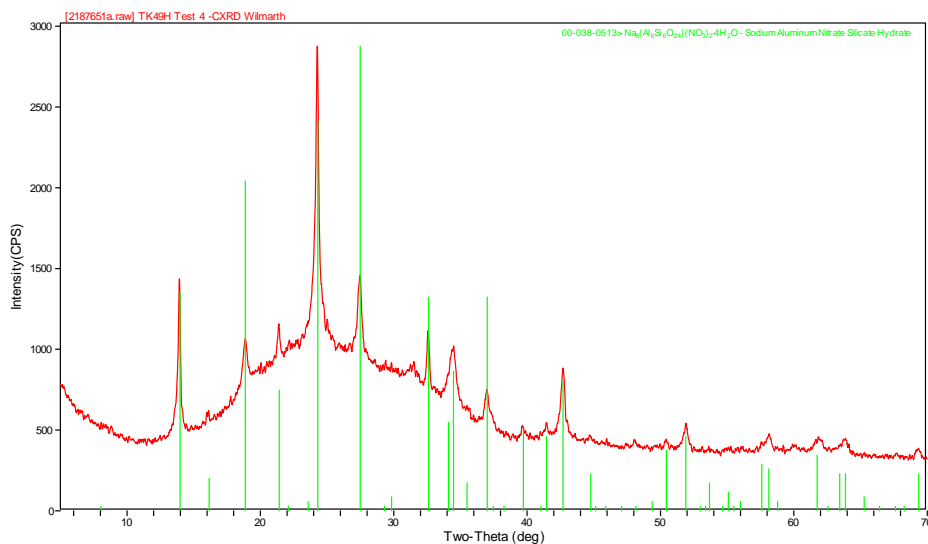


Figure 13. Typical Powder Diffraction Spectrum from Solids Produced during Aluminosilicate Formation

Several Scanning Electron Micrographs are shown in Figure 14. For all of the tests, the basic structure of the material is the zeolytic ball structure. The material is cancrinite based on the X-ray powder pattern and the scanning electron images agree with that published by Addai-Mensah.²⁵ This “yarn-ball” effect observed in the micrograph in the upper right of Figure 14 can be seen in higher magnification in all portions of the samples. The energy dispersive spectrum of the materials show peaks only for sodium, aluminum, silicon and oxygen.

In the test that was conducted with 50 mg/L uranium in the starting solution, a different image is observed and is shown in Figure 15. The backscatter image shows a few small bright images that contain uranium. This test is where uranium was well above the solubility limit and is expected to precipitate and precipitation was observed when aluminosilicate formed. The occlusion of these small uranium compounds into the aluminosilicate solids is similar to that observed in the 2H Evaporator scale.³ The energy dispersive spectrum of the solids is shown in Figure 16. The spectrum contains peaks characteristic of uranium at about 3 keV. These uranium solids were not observed in the solids from the tests with starting uranium concentrations of 5 to 25 mg/L.

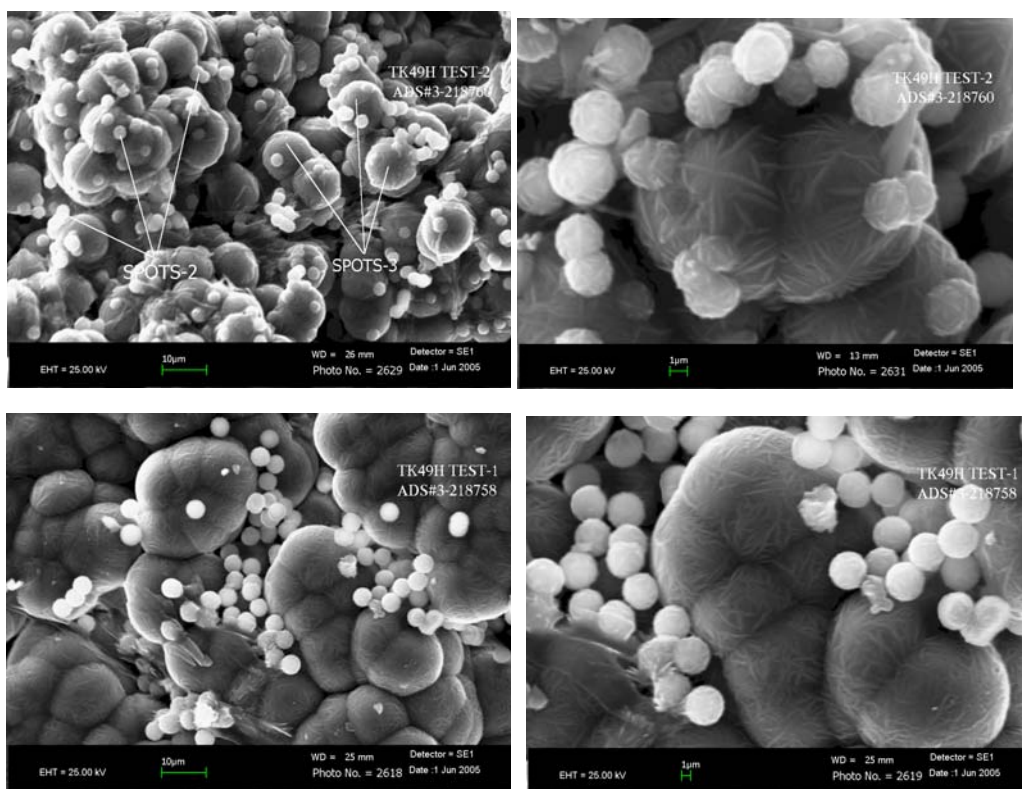


Figure 14. SEM Images of Solids from Simulant Studies

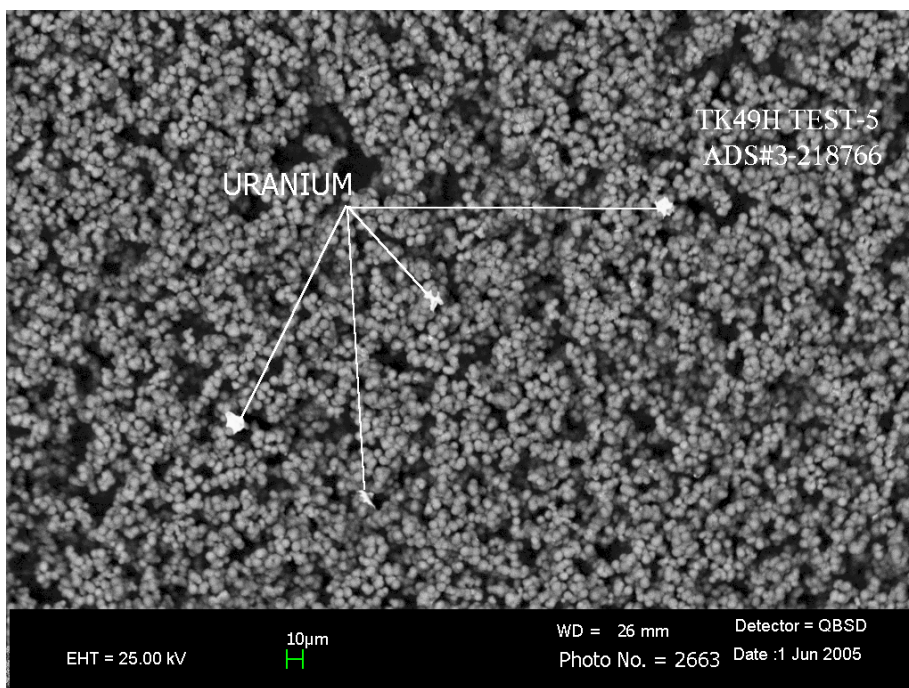


Figure 15. SEM Image from Simulant Test with 50 mg/L Uranium

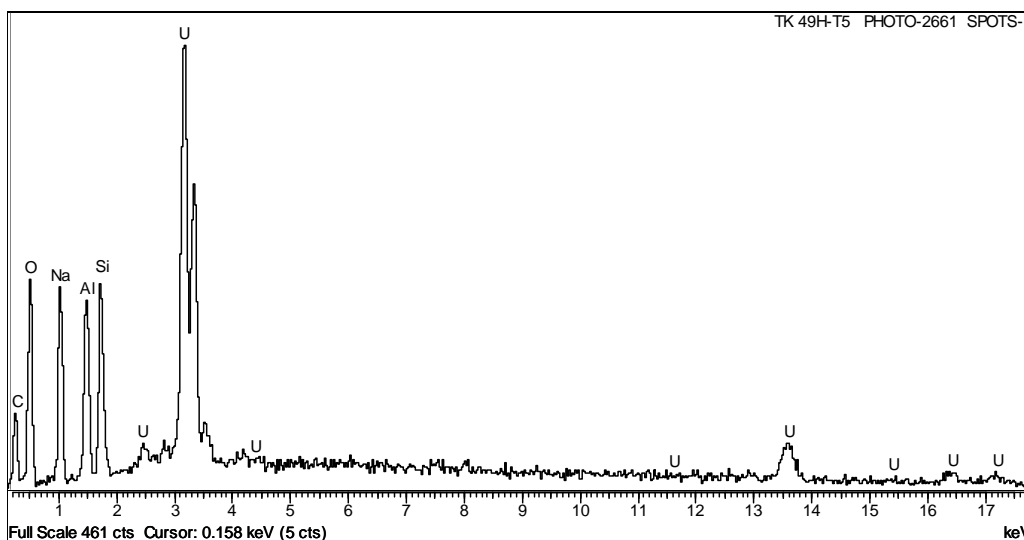


Figure 16. EDS Spectrum from Uranium-Containing Solid

The solids from each of the simulant studies with starting uranium concentrations of 5 to 50 mg/L were collected and washed with inhibited water three times. The washed solids were digested in nitric acid and submitted for uranium analysis. Table 3 displays the measured uranium concentration in the aluminosilicate solids. The uranium content of the solids increased with an increase in the starting uranium concentration. A distinctive jump in the uranium content was observed for the solids from the test with a starting uranium concentration of 25 mg/L. The uranium content of the solids increased from 370 $\mu\text{g/g}$ of NAS solids at 15 mg/L U to 1100 $\mu\text{g/g}$ for the solids from the 25 mg/L U. This is expected due to the presence of uranium above the solubility limit. The uranium content of the 15 mg/L solids was also high and may have resulted from precipitation of uranium due to the uranium spike was high for that test. The starting uranium concentration was above 20 mg/L with a target of 15 mg/L. The uranium content from the sub-saturated tests was 23 and 110 $\mu\text{g/g}$ for the tests starting with 5 and 10 mg/L uranium, respectively. These values are in the range of that observed from sorption tests.¹⁸ The measured sorption values for cancrinite were lower and were less than 10 $\mu\text{g/g}$. These elevated levels may result from inefficient washing of the test solution from the solids or small amounts of precipitation or uranium from solution.

Actual Waste Testing

In order to confirm that the formation of sodium aluminosilicate would not influence the uranium concentration if the uranium concentration was at or below the uranium solubility, a test was conducted in duplicate with a 1:5 mixture of waste removed from Tank 49H and some high aluminum-containing waste that was previously stored in the Shielded Cells. Table 2 shows the chemical composition of the wastes used in the testing. As mentioned the tests were conducted in duplicate. The testing was similar to the simulant testing; however, the heat pretreatment was not performed. Silicon in the form of sodium metasilicate was

added to the waste mixtures and the solutions were heated to 50°C. Figure 17 shows the results for aluminum, silicon and uranium from the first of two actual waste tests. The data from the second test are very similar to these results. With the addition of elevated levels of silicon to the waste, an immediate reaction is observed with the measured silicon and aluminum concentrations declining throughout the 500 h of the test. The uranium concentration, on the other hand, remains constant at about 6 – 7 mg/L. This is the expected result based on the simulant studies

Table 3. Uranium Content of Simulant Solids

Test Condition	Uranium (µg/g)	Uranium Wt %
5 mg/L	22.5 ± 4	0.0023 ± 0.0004
10 mg/L	110 ± 16	0.011 ± 0.002
15 mg/L	370 ± 36	0.04 ± 0.004
25 mg/L	1100 ± 1	0.11 ± 0.0001
50 mg/L	3140 ± 1200	0.31 ± 0.12

The solids produced during the testing were collected and thoroughly washed with distilled, de-ionized water to remove the interstitial supernate. The samples were examined for crystal structure, imaging and uranium content. Figure 18 shows the X-ray powder pattern from the first of two samples. The result from the second sample agreed with the first. The powder pattern is that of cancrinite identical to the pattern obtained from the simulant studies. No other forms of the sodium aluminosilicate are observed. This is reasonable since the solids were heat treated for several hundred hours at 50 °C. There is, however, a large band typically associated with amorphous material observed in the powder pattern.

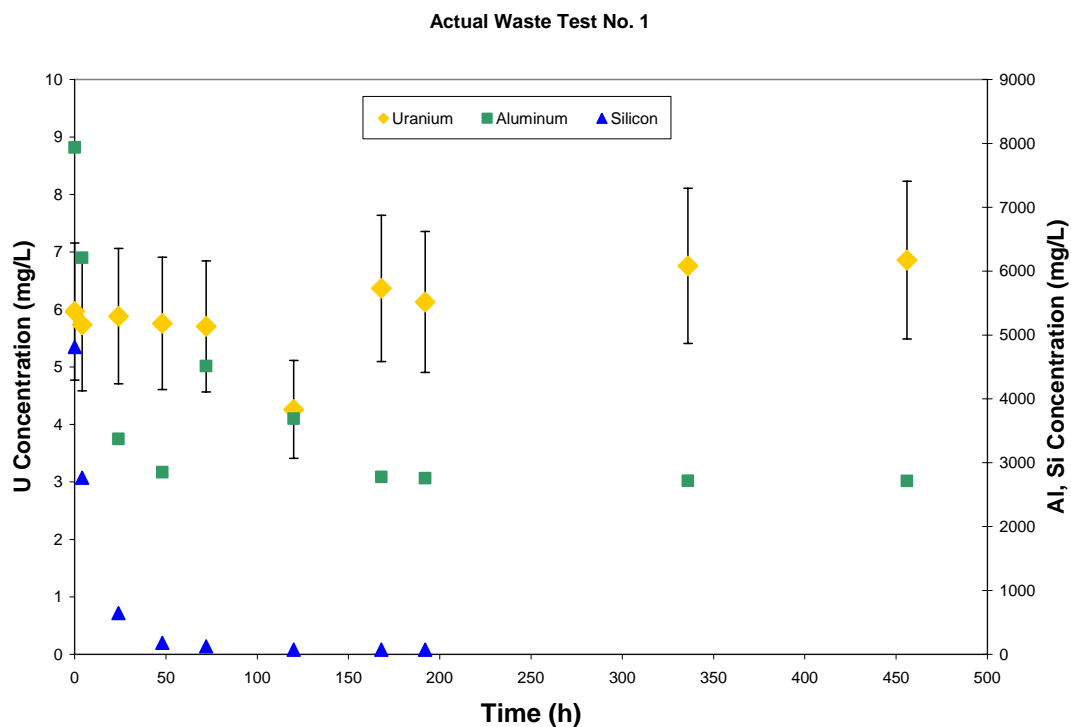


Figure 17. Uranium Concentrations in the Actual Waste Test

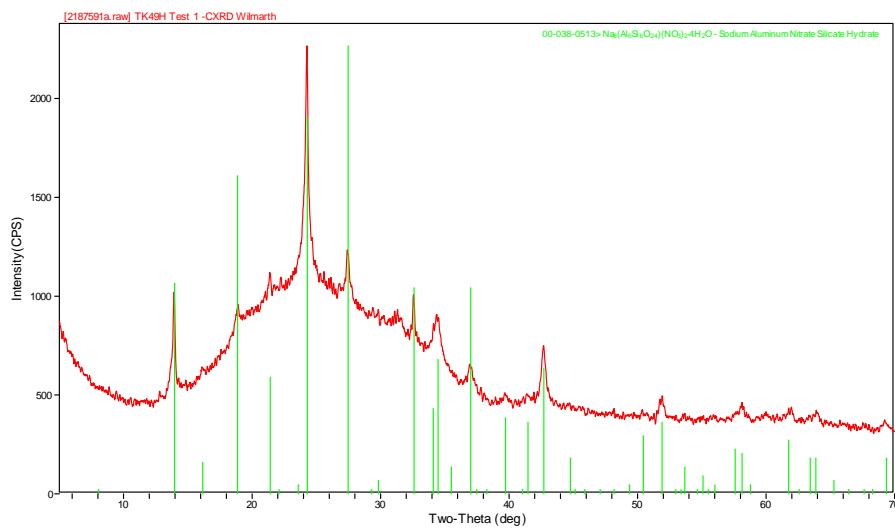


Figure 18. X-Ray Diffraction Pattern from Actual Waste Test

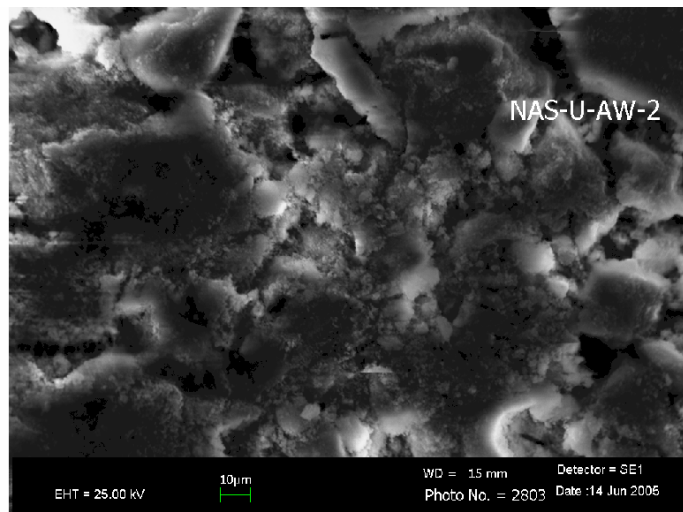


Figure 19. SEM of Solids from Actual Waste Test

Figure 19 shows a typical scanning electron micrograph of the solids collected from the second actual waste test. The morphology of these samples is less defined than the simulant studies. The “yarn ball” structure is not observed in the actual waste solids indicating that the material consists primarily of the amorphous form of the NAS which is not detected by the X-ray diffraction measurement. Both sets of solids from the actual waste have the same appearance. The energy dispersive spectra from the solids show sodium, silicon, aluminum and oxygen from the sodium aluminosilicate. Some spots within the samples showed evidence of iron and manganese typical of sludge solids. Others showed evidence of barium, calcium, and other elements which are likely contaminants of the sample from sample handling in and out of the Shielded Cells. The uranium content of the solids was determined by digesting an aliquot of the sample and measuring the uranium using ICP-MS. The measured uranium concentrations in the actual waste samples were 5.2 and 6.0 µg/g of NAS solid. This indicates that employing a better washing procedure removed the interstitial supernate. The magnitude is in better agreement with sorption data for cancrinite.¹⁸

Conclusions

The focus of this work was to determine if the formation of sodium aluminosilicate occurred when wastes containing high aluminate concentrations are mixed with wastes containing high silicate concentrations could cause the precipitation of uranium-containing phase. Similar phenomenon has occurred in the 2H Evaporator. The testing has shown that if the uranium concentration is above the solubility limit, i.e., the solution is supersaturated with uranium, and then the formation of sodium aluminosilicate can act as a means to reduce the degree of supersaturation. The exact mechanism for the removal of uranium from solution was not examined. The data from simulant studies showed a concomitant reduction in

uranium, silicon and aluminum. Testing at the highest degree of uranium supersaturation demonstrated that a separate uranium phase can be formed in the aluminosilicate matrix.

Testing with waste simulants and actual tank wastes have shown that if the solution is sub-saturated with uranium, then the formation of aluminosilicates does not influence the uranium concentrations. Analysis of the uranium content in these solids show levels typically observed during sorption experiments.

Lastly, analysis of the uranium speciation in a Tank 49H set of samples showed the uranium to be soluble. Analysis of the solution composition and subsequent use of the Hobb's uranium solubility model indicated a uranium solubility limit of 32 mg/L. The measured value for uranium in the Tank 49H matched the model prediction.

References

- ¹ W. R. Wilmarth, M. C. Thompson, C. J. Martino, V. H. Dukes, J. T. Mills, C. Boley, and B. L. Lewis, "Nitric Acid Cleaning of a Sodalite – Sodium Diuranate Scale in High Level Waste Evaporators," WSRC-MS-2001-00741, Sep. Sci and Tech., **38**, 3249, 2003.
- ² W. R. Wilmarth, C. J. Coleman, J. C. Hart, and W. T. Boyce, "Characterization of Samples from the 242-16H Evaporator Wall," WSRC-TR-2000-00089, March 20, 2000
- ³ W. R. Wilmarth, C. J. Coleman, A. R. Jurgensen, W. M. Smith, J. C. Hart, W. T. Boyce, D. Missmer, and C. M. Conley, "Characterization and Dissolution Studies of Samples from the 242-16H Evaporator," WSRC-TR-2000-00038, Rev. 0, January 31, 2000.
- ⁴ Barnes, M. C.; Addai-Mensah, J.; Gerson, A. R. J., Crystal Growth, 200 (1999), 251-264.
- ⁵ Gasteiger, H. A.; Fredrick, W. J.; Streisel, R. C., J. Eng. Chem. Res., Vol 31, 1992, 1190.
- ⁶ Buhl, J.; Löns, J., J. Alloys and Compounds, 235 (1996), 41.
- ⁷ Kumada, N.; Wetrum, E. F.; Hemingway, B. S.; Zolotov, M. Y.; Semenov, Y. V.; Khodakovskiy, I. L.; Anovitz, L. M., J. Chem. Thermodynamics, **1995**, 27, 1119.
- ⁸ W. R. Wilmarth, "Technical Requirements for Dispositioning Tank 40H Decants, SRT-LWP-2001-00032, Rev. 1, March 20, 2001.
- ⁹ S. W. Rosencrance, T. B. Edwards, D. P. Healy and E. J. Coleman, "Concentrate Interaction Testing," WSRC-TR-2002-00232, June 28, 2002.
- ¹⁰ J. Jeffrey, "Tank 49 Co-Precipitation of NAS and Uranium," Technical Task Request, HLE-TTR-2005-038, December 17, 2004.
- ¹¹ W. R. Wilmarth, "High Level Waste Evaporator Sample Analysis," WSRC-TR-98-00223, Rev. 0, June 16, 1998.
- ¹² D. T. Hobbs and D. G. Karraker, Nucl. Tech. **114**, p. 318, 1996.
- ¹³ W. R. Wilmarth, J. T. Mills, V. H. Dukes, and R. C. Sullivan, "Characterization of Surface and Variable Depth Samples from the 3H Evaporator Feed (32H) and Drop (30H) Tanks – Re-Baseline of Silicon Concentration and Aluminosilicate Formation," WSRC-TR-2001-00514, Rev. 0, October 24, 2001.
- ¹⁴ C. M. Jantzen, J. E. Laurinat, and K. G. Brown, "Thermodynamic Modeling of the SRS Evaporators: Part 1. The 2H and 2F Systems (U)," WSRC-TR-2000-00293, Rev. 1, April 4, 2002.
- ¹⁵ C. M. Jantzen, J. E. Laurinat, and K. G. Brown, "Thermodynamic Modeling of the SRS Evaporators: Part 2. The 3H System (U)," WSRC-TR-2001-00155, Rev. 1, April 8, 2002.
- ¹⁶ C. M. Jantzen, J. M. Paraeizs, and T. B. Edwards, "Thermodynamic Modeling of the SRS Evaporators: Part IV. Incorporation of High Caustic Aluminosilicate Solubility Data (U)," WSRC-TR-2002-00330, Rev. 0, March 15, 2003.
- ¹⁷ J. M. Paraeizs and C. M. Jantzen, "Thermodynamic Modeling of the SRS Evaporators: Part V. Validation", WSRC-TR-2002-00331, April 15, 2003.
- ¹⁸ J. Addai-Mensah, J. Li, M. Zbik, and W. R. Wilmarth, "Uranium Sorption on Solid Aluminosilicate Phases under Caustic Conditions", J. Sep. Sci. and Tech., **40**, 267, 2005.
- ¹⁹ W. R. Wilmarth, "Memo on Report by J. Mensah," SRT-LWP-2004-00056, April 13, 2004.

²⁰ W. R. Wilmarth, “High Level Waste Evaporator Sample Analysis,” WSRC-TR-98-00223, Rev. 0, June 16, 1998.

²¹ W. R. Wilmarth and R. A. Peterson, “Analyses of Surface and Variable Depth Samples from Tanks 30H and 32H,” WSRC-TR-2000-00112, April 3, 2000.

²² D. T. Hobbs and T. B. Edwards, “Solubility of Uranium in Alkaline Salt Solutions,” WSRC-TR-93-00454, March 1994.

²³ J. Addai-Mensah, J. Li, M. Zbik, and W. R. Wilmarth, “Uranium Sorption on Solid Aluminosilicate Phases under Caustic Conditions”, J. Sep. Sci. and Tech., 40, 267, 2005.

²⁴ W. R. Wilmarth, “Memo on Report by J. Mensah,” SRT-LWP-2004-00056, April 13, 2004.

²⁵ M. C. Barnes, J. Addai-Mensah, and A. R. Gerson, J. Crystal Growth, 200 (1999) p. 251.