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WSRC-MS-2003-00361

Evaluation of Uranium Co-precipitations with Sodium Aluminosilicate Phases.

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ABSTRACT

This paper describes batch laboratory experiments performed to evaluate uranium incorporation into aluminosilicate structures during synthesis. This research was conducted in response to plant problems related to the accumulation of uranium with aluminosilicates in low-level radioactive waste evaporators. We have found that conditions which favor precipitation of aluminosilicates also foster uranium solid precipitation, so it is difficult to attribute problems with uranium accumulation to say just the formation of the aluminosilicates. Infrared spectra shows that sodium uranates, uranium silicates and other uranium solids are formed during the synthesis of sodium aluminosilicates structures in the presence of uranium. Both amorphous and sodalite aluminosilcate phases, unlike zeolite A phase, show appreciable affinity for uranium incorporation during their formation in the presence of uranium.

Keywords: Evaporator scaling, aluminosilicates, uranates, amorphous, zeolite A, sodalite.

I. INTRODUCTION

The High-Level Waste Tank Farms at the Savannah River Site (SRS) stores and processes high-level liquid wastes from a number of sources including F and H area canyons and a recycle stream from the Defense Waste Processing Facility. The waste is relatively dilute as received and is concentrated in one of several evaporators to minimize the space required to store the waste. The concentrated waste is transferred to one of several concentrate receipt tanks for storage. Recently, the 2H-Evaporator was shut down due to crystallization of sodium aluminosilicates (NAS), such as zeolite A ($Na_6Al_6Si_6O_{24}{\cdot}nH_2O_{(s)}$), sodalite ($Na_8(AlSiO_4)_6{\cdot}nH_2O_{(s)}$) and cancrinite ($Na_8(AlSiO_4)_6{\cdot}nH_2O_{(s)}$) in the evaporator and the precipitation of enriched uranium with the NAS[1,2,3]

The aluminosilicates, such as zeolites, are complex crystalline cages of tetrahedron oxygen atoms which encase either silicon or aluminum atoms. The oxygen atoms can be shared by only two tetrahedrons, and no two aluminum atoms can share the same oxygen atom. This restriction means that the Al/O ratio is always equal to or less than one. The crystal structures that result are complex 3-D frameworks of aluminosilicates with precisely dimensioned channels and cages as in the case of sodalite running through them. These channels and cages enable the crystals to be selectively permeable to various gases and liquids as molecular sieves. As in the case of zeolites, for every aluminum atom in the unit cell made up of these tetrahedrons, there will be one free electron and hence a negative charge. The negative charges are compensated for by incorporating cations (usually, but not limited to Na^+, K^+, Ca^{2+}, Mg^{2+}). These cations are not part of the actual framework of tetrahedrons, but reside at the internal channels. When these crystals absorb fluids in the channels, it is possible for one type of cation to be exchanged for another without affecting the electrical neutrality or crystal structure.

In the evaporator, several processes may contribute to the concentration of uranium. Uranium species, cations, solids, anion complexes etc, may be incorporated and concentrated in the NAS channels or cages as hosts as a result of uranium co-precipitation during the formation of the aluminosilicates structures. Uranium may also be concentrated by adsorption on NAS surfaces, by precipitation with NAS minerals and by co-precipitation with the NAS minerals. Here we define the co-precipitation of uranium as the uptake of weighable amounts of uranium impurities (soluble or insoluble) into NAS phases during formation of NAS precipitates. The formation of NAS precipitates from supersaturated solutions of the reagents is extremely rapid. Under these conditions, uranium impurities may be unable to escape from the neighborhood of the crystal growth, so they become entrapped in pockets or crystal defects of the NAS particles.

This uranium and NAS interaction research is part of an ongoing effort to understand the mechanisms for uranium accumulation with the aluminosilicates in the 2H Evaporator. The information from this study would enable High Level Waste personnel identify operational strategies to avoid or minimize formation of NAS forms with high affinity for uranium. In this paper we present experimental results from studies conducted at the Savannah River Technology Center (SRTC) to examine uranium co-precipitation with sodium aluminosilicate structures sodalite, zeolite A, and amorphous phases during isothermal batch synthesis of these silicates in the presence of depleted uranium. The main objective of this study was to determine how much uranium, if any, is incorporated in NAS structures and to determine which of the silicate structures (sodalite, zeolite A, and amorphous phases) has the highest affinity for uranium as a result of co-precipitation.

II. EXPERIMENTAL

A description of the methods[4] and reagents used for the aluminosilicates synthesis is summarized in Tables I and II. After synthesis, the three silicate structures were washed and their identities were confirmed by X-ray diffraction (XRD) patterns, scanning electron microscopic (SEM) techniques and diffuse reflectance infrared-Fourier-transform (DRIFT) spectroscopic techniques. To determine when the uranium should be added during the aluminosilicate syntheses, precipitation timing studies (referred to as “reference” uranium curves) were performed with uranium and aluminum containing caustic salt solutions using the same experimental conditions as those required for the individual NAS syntheses. A “reference” uranium curve for each of the NAS was generated without added silica in the reaction mixtures. The synthesis of each NAS was then repeated in the presence of 50 mg uranium as summarized in flow diagram in Figure 1. The source of the depleted uranium used in this study was a stock solution of uranyl nitrate hexahydrate.

The sequence of analytical procedures used to account for uranium concentrations in solid NAS structures, by mass balance, in the unwashed NAS solids, reaction filtrate and structurally trapped uranium, if any, is summarized below and in Figure 1.

II.A. Uranium mass balance summary.

The experimental approach used to account for the amount of uranium co-precipitated per gram of each NAS synthesized in the presence of uranium is summarized in the steps below; where the letters denote the amount of uranium or uranium content removed in each step.

A. Initial uranium mass (50 mg).

B. Soluble uranium concentration in post NAS synthesis liqueur (filtrate),

C. Uranium from DI water (distilled and de-ionized water) washed NAS solid cake (filtrate).

D. Uranium from ethylenediaminetetraacetic acid (Na_4EDTA) wash of post DI water washed and dried NAS solid.

E. Uranium from acid digestion, post-Na_4EDTA washed NAS solid.

The sum of uranium from steps C, D and E above is C+D+E. Thus, the total mass of uranium used in synthesis (50 mg) is equal to C+D+E + uranium from step B. Where C+D+E is total mass of uranium trapped in each NAS solid (unleacheable uranium including surface bound uranium) and uranium from step B is the uranium in each post-synthesis filtrate. After the synthesis of each NAS solids in the presence of 50 mg depleted uranium (step A above), the mass of uranium in the filtrate was determined (step B). The quantitative difference in the mass of uranium between the initial 50-mg uranium and the filtrate uranium concentration is the amount of uranium in the solid fraction of the wet and unwashed NAS solid. Each NAS solid is now suspended in DI water and washed three times with DI water (step C) and the filtrates analyzed for uranium content.

A known quantity of the air-dried solid is washed with Na_4EDTA solution to strip the NAS of all traces of surface bound uranium from the solid (step D) and air-dried to constant weight. A known amount of this air-dried Na_4EDTA washed sample was acid digested and analyzed for its uranium content (step E).

Based on the above information the uranium mass in the solid NAS (unwashed and washed parts) was calculated. The uranium detected in step E above, if any, is considered to be uranium incorporated with that particular NAS form. In summary, if there is no uranium remaining in the Na_4EDTA-washed NAS solid, then (A = B + C + D) E = 0. If E > 0, then E represents the amount of uranium that was resistant to Na_4EDTA leaching and thus was not removed. The forms of uranium remaining in E would be that which was structurally incorporated with NAS solids during synthesis. Hence by using this information, the amount of uranium per gram of each of the three NAS from step D was calculated and the comparative affinity for uranium by each of the NAS phases determined by calculating the ratio of uranium trapped per gram of NAS product yield. The magnitude of the above ratio defines which of the three NAS phases has the greatest affinity for uranium during formation in the supersaturated liqueur. Other complementary ways used for comparing the uranium affinity by each NAS phase includes the following:

- Characterization of the uranium “stripping efficiency” from each NAS phase, to determine the ease with which both DI water and the chelating agent can be used to easily remove all surface-bound uranium,
- The presence of infrared signatures for uranium solids, like sodium uranates, uranium silicates or hydroxides, in post DI water and Na_4EDTA washed solids and

- The local structure characterization of the uranium by the use of Extended X-ray Absorption Fine Structure (EXAFS) techniques[5]

II.B. Uranium reference curve

In a high caustic reaction environment, such as the one the aluminosilicates were synthesized in, the reaction kinetics for the formation of the aluminosilicates was expected to be quite different from that for the formation of uranium solids such as the sodium uranates ($Na_2U_2O_7$ and Na_2UO_4) and uranium silicates or hydroxides. Therefore, the reaction times for the formation of the silicates and the uranium solids had to be synchronized, if needed, to enhance the chances for uranium incorporation into NAS during the batch silicate synthesis in the presence of uranium. This approach would also ensure that this laboratory-based batch silicate synthesis does mimic the plant continuous process, which produces NAS containing uranium in the evaporator.

In the laboratory batch synthesis process for these silicates, we attempted to synchronize these two main reactions by first generating a uranium curve. From the uranium reaction profile we determined the definite time,τ_u, when uranium starts forming solids in the reaction mixture. The generation of each uranium reference curve involved the withholding of one of the reagents for NAS formation, in this case the silicate solution. Changes in ionic strength of the final reaction mixture, due to the withholding of silicate solution, were compensated by adding equimolar concentration of sodium hydroxide. In these uranium reference curve reactions, the reactions were performed at the same reaction conditions already established for the formation of each NAS. No aluminosilicates are formed because of the absence of the silicate solution. In effect, only reactions leading to the formation of uranium solids were observed. After determining this uranium time, $\tau_{u,}$ for each of the precipitation timing studies, and if found significantly different from that of NAS synthesis without uranium, we then introduced the reagents into the reaction mixture. Reagents were introduced in such a manner as to ensure simultaneous reactions for the formation of each NAS and the uranium solids.

In these synchronized batch reactions for the production of each NAS in the presence of uranium, all the reagents for NAS synthesis and uranium solids were expected to be initially present except, of course, the silicate solutions again. The required amounts of silicate solutions were to be injected into the reaction mixture at time, τ_u, corresponding to each NAS uranium reference curve. In this approach, both the formations of each NAS and uranium solid will start rapidly at the same time. Thus, on a reaction time scale, if we assume that the reaction for the formation of uranium solids is further along than that of the formation of NAS, this approach is simply a delay for the initiation of the reaction for the formation of each NAS.

II.C. Preparation and composition of NAS synthesis solutions

Research grade reagents were used throughout this study. The sodium aluminosilicate structures (amorphous, zeolite A and sodalite phases) were precipitated at various temperatures and reaction times from supersaturated caustic solutions as summarized in Tables I and II. The solutions used for the synthesis of the amorphous and sodalite NAS phases were reaction mixtures consisting of equal volumes of solutions A and B from Table I and the resulting concentrations for reagents is summarized in solution C in Table I. The reaction temperatures and duration of reaction for each synthesis is summarized in Table II and are, respectively, 40•C for 1.0 hour and, 80•C for 1.5 hours.

The reagents and solutions used for the synthesis of zeolite A were different from the nitrated precursor solutions in Table I. Because nitrated zeolite A is a metastable aluminosilicate and thus readily converts to sodalite, a caustic solution without nitrates or nitrites was used for zeolite A synthesis[6]. Zeolite A synthesis solution (Table II) was based on sodium silicate solution (14% NaOH and 27% SiO_2-, (Aldrich chemical)) and sodium aluminate hydrate (54% Al_2O_3). The reaction temperature and synthesis duration were, respectively, 60°C and 12 hours.

The reaction vessel used for this isothermal aluminosilicate synthesis consisted of a one-liter stainless steel reaction vessel with a Pyrex® glass lid cover, which was machined to bear an O-ring grove. The domed glass lid, bearing an o-ring rubber seal, was secured onto the one-liter reaction vessel with an adjustable clamp assembly (Duran reaction clamp). The top portion or lid contained appropriate glass receptacles and ports for a reflux condenser unit, an electric stirrer shaft in the center, a thermocouple and a covered reagent/sampling port. The digital read-out overhead electric stirrer (Fisher) featured two variable speed ranges (60 to 500 and 240 to 2000 rpm). A 46-cm long plastic stirring shaft, rotating at 400 ± 5 rpm, was used to keep the reactor contents well mixed. During the NAS synthesis, the reaction vessel was placed in a heated circulator water bath equipped with a multi-step temperature controller and water re-circulator (Cole-Parmer). Since the synthesis mixtures involved the mixing of two solutions, all initially brought to the same temperature, two heated circulator water baths were used.

II.D. Preparation of sodium aluminosilicates phases for characterization.

After the synthesis of each aluminosilicate the solid fraction was separated from the liquid fraction by filtration and the filtrate submitted for uranium and silicon analysis (Figure 1). The solid fraction from each NAS synthesized was vacuum dried to constant weight after several days in the hood at room temperature (25 ± 1° C). A known weight of each dry solid fraction, usually 20-30 grams, was washed three times (three DI water leaching cycles) with a volume of DI water equivalent to a total of 50 ml DI water per gram of dry solid NAS. For example, a 30-gram solid NAS will be washed with a total of 1500 ml DI water at the end of the three water leaching cycles; that is 500 ml DI water per leach cycle. During each wash cycle the solid is dissolved in the appropriate amount of liquid inside a 500-ml Teflon bottle, which was tightly capped and put into an orbital shaker (set at 200 rpm), for 2 hours. After each wash cycle, a solid liquid separation, using a 0.25-micron Nylon membrane filter, was performed and the filtrate for that cycle saved for latter characterization for uranium content. During the second wash cycle, the solid fraction from the first wash was again suspended in DI water and the second wash cycle started and so on. At the end of the three DI water-washing cycles, three liquid fractions were submitted for uranium characterization and the water leached solid vacuum dried to constant weight. Fractions of the DI water leached and dried solid sample from each NAS synthesis was saved for the following characterizations, DRIFTS, acid digestion for uranium and silicon content, XRD and SEM in some cases.

The DI water washed and dried solids from each NAS material formed the starting material for the Na_4EDTA and carbonate washes. From each DI water washed and dried solid, about 5 to 10 grams of the material was used for Na_4EDTA or in some cases sodium carbonate wash. The procedure described above for DI water uranium leaching from the solid was also used for all uranium leaching with Na_4EDTA or sodium carbonate solutions. The dry solids resulting from the three Na_4EDTA leaching was also characterized for its uranium content (DRIFTS, and ICP-MS). The three-filtrate fractions from the leach cycles were also analyzed for uranium. Based on the uranium concentration from each of the washes involving DI water, Na_4EDTA, we obtained a plot of the percent uranium removed per leach cycle. The uranium content in each dry solid NAS material synthesized was also determined from acid digestion and subsequent analysis by ICP-MS and ICP-ES. The sum of uranium from the leaching cycles (DI water and Na_4EDTA) and acid digestion analysis together constitute the total uranium, α, in the solid NAS phase under study.

III. RESULTS and DISCUSSION

III.C. Synthesis and Confirmation of aluminosilicate structures

Figure 2 shows the infrared spectra of amorphous, zeolite A, and sodalite phases, including the overlay spectra for specific wavelength regions, of the sodium aluminosilicates synthesized for this study. The XRD spectra for these NAS materials are shown in Figure 3. Both the FT-IR and XRD spectra of all the NAS synthesized here matched those from literature[7]

III.B. Reference Curve generation

Figure 7 shows the overlay uranium reference curves for the amorphous and the sodalite reaction mixture. In both curves, the precipitation of uranium in the absence of silicon is complete within an hour. Therefore, since uranium precipitation starts at the instant when the amorphous and sodalite phases are formed, we added all reagents, including uranium and silica at the beginning of the synthesis. The uranium reference curve for zeolite A is shown in Figure 8. No significant evidence for uranium precipitation at the start of the reaction was observed. The reason for this behavior can be attributed to the reagent solution composition for the zeolite A formulation. At this caustic composition and uranium composition of 50 mg/L, uranium will not precipitate out of solution because of solubility limits (Uranium is probably not supersaturated in this particular solution). However, we went ahead and synthesized the zeolite A in the presence of 50 mg uranium by adding all the reagents, which includes uranium and silica at the beginning of the synthesis as we did before.

III.C. Sodium aluminosilicate synthesis in the presence of uranium.

The three NAS materials were each synthesized in the presence of 50 mg uranium per liter of NAS synthesis reagent solution of supersaturated caustic solutions. The choice of 50 mg uranium was based on the fact that we needed an NAS synthetic environment, saturated with uranium to ensure a greater probability of forming detectable uranium solids during synthesis and the generation of uranium reference curve. During the synthesis of the three NAS materials in the presence of uranium, samples were collected at selected intervals, which were based on the duration of each synthesis (Table II).

The overlay uranium concentration profile from the synthesis of these NAS materials is shown in Figure 9. The overlay plot in Figure 9 does not include the synthesis data for zeolite A because of its longer reaction time The plot for zeolite A is shown in Figure 10. From Figure 10 plot for the zeolite A synthesis not much uranium precipitated during the synthesis period. The mass of soluble uranium dropped down to only 48.4 mg at the end of the synthesis.

From the overlay plots in Figure 9 for the synthesis of both amorphous and sodalite NAS phases, there is a distinct loss of soluble uranium from the two reaction mixtures. At the end of the amorphous phase synthesis, the soluble uranium mass was 12.96 mg, meaning that about 37 mg of the uranium was held in some fashion on or in the solid amorphous solid matrix. Similarly, at the end of the sodalite phase synthesis the soluble uranium concentration was 12.0 mg, which corresponds to about 40 mg of uranium trapped in the sodalite solid matrix. Overall, the sodalite synthesis showed the largest uranium drop compared to the synthesis of the other NAS materials. In less than 10 minutes into the reaction for the sodalite synthesis in the presence of uranium, the amount of soluble uranium had dropped below the average uranium mass of 11.3 mg, down to about 5 mg and then started creeping up again with time. This may indicate a re-dissolving of the insoluble uranium solids formed during the initial phase of the synthesis.

III.D. Silicon profile during synthesis of sodium aluminosilicates.

Figure 11 shows the overlay plot for soluble silicon disappearance of in the reaction mixture during synthesis of amorphous and soldalite phases in the presence of uranium. A similar plot is shown in Figure 12 for the synthesis of zeolite. Again, the two figures could not be combined because of significant differences in synthesis time; 11 hours at 60 °C for zeolite A and less than 2 hours each for the other NAS phases. The overlay plots show that in less than10 minutes into the reaction for the sodalite formation, the soluble silicon in the reaction mixture drops down to an equilibrium concentration level. The time for soluble silicon concentration in the synthesis mixture to drop to the equilibrium level for the amorphous phase was about 40 minutes.

From Figures 9 and 11, we see that both silicon and uranium are depleted from the reaction mixture during the synthesis of both the amorphous and sodalite phases. There is depletion of silicon but not much of uranium from zeolite A reaction mixture (Figures 9, 10, 11 and 12). Due to analytical cost, the silicon depletion plots for the NAS synthesis without uranium additives was not performed for comparison.

III.E. Uranium leaching from NAS solids

Figures 13 and 14 show, respectively, the percent uranium leached or removed from the surface of amorphous, zeolite A and sodalite phases bearing uranium solids with DI water and Na_4EDTA solutions. The successive washing or leaching cycles with these solutions was performed three times with each NAS solid as described earlier. Each solid NAS was first leached three times with DI water and the recovered dry solid material leached with Na_4EDTA to remove all the remaining surface bound uranium solids which could not be leached by water. After these two washes, we conclude that any uranium recovered from the solid NAS by acid digestion is uranium incorporated in the NAS matrix during synthesis. The leaching of uranium with water from all the NAS materials with the exception of the amorphous phase, Figure 13, shows that only about 5 to 20 % of the surface uranium were removed. After the second wash of the amorphous phase with DI water, the percent uranium leached thereafter stayed fairly constant. The other NAS materials, again, with the exception of the amorphous phase, after leaching with water and Na_4EDTA three times each, resulted in the removal of most of the surface bound uranium (Figure 14). The asymptotic nature of both the water and Na_4EDTA leaching curves for amorphous phase, especially after the second washes, indicates that all the surface bound uranium are not easily removed with these two leacheates (See Figures 13, 14 and 15). As a result, further leaching was performed with 0.4M solution of sodium carbonate. This solution still did not remove all the surface uranium as seen on infrared spectra on the post sodium carbonate washed solid (See IR spectra of amorphous solid washed with leaching solutions, Figure 15). Any uranium solids bound on the surface of the zeolite A synthesized in the presence of uranium were easily removed after washing with water and Na_4EDTA. As earlier mentioned, any uranium recovered from acid digestion of NAS solids from which surface bound uranium have been leached with DI water and Na_4EDTA for several hours in an orbital shaker, is considered to be trapped or incorporated uranium. Analytical digestion results from post Na_4EDTA leached solids are summarized in Table III. Table III data provides the total uranium content in unwashed solid NAS fraction (column 3), DI water washed and dried NAS solid fraction yields (column 2). The total incorporated uranium for each NAS from post leaching digestions is shown in column 4 and the ratio of total uranium in unwashed NAS solid fraction per gram of DI water washed NAS solid fraction is in column 5.

The amorphous NAS phase has the largest product yield and on the other hand, the sodalite phase, with the lowest product yield, showed the most uranium loading for the unwashed solid fraction. Zeolite A phase did not trap significant amounts of uranium. The ratio of incorporated uranium per gram of washed NAS product for the amorphous phase (0.36) is lower than the same ratio for the sodalite phase (1.16) Table III. This same ratio for the zeolite A phases is significantly lower (0.07). Thus, the uranium trapped in zeolite A phases, if any, is not significant and depends on the amount of sodalite impurity in the zeolite A phase.

The zeolite A phases synthesized in this study contained sodalite material as an impurity, although XRD and infrared characterizations in most cases confirmed the existence of only the zeolite A phase. From SEM micro-photos of the zeolite, about 5% of the material was sodalite (Figure 5). We estimated the level of sodalite impurity from SEM micro-photos by visually counting the number of visible sodalite aggregate materials, which looked spherical in appearance and the number of cubical zeolite A phases. From the number of spherical sodalite aggregates and cubical zeolite phases we calculated the total surface area for each materials. The ratio of the total surface areas was used as an approximation of the level of sodalite impurities.

III.F. Infrared characterization of uranium bearing NAS solids.

The overlay spectra in Figures 15, 16 and 17 show, respectively, the infrared spectra of unwashed and washed solids from amorphous, sodalite and zeolites A solid. The unwashed NAS solids showed infrared bands which can be assigned to uranium solids[8,9,10], such as uranium silicates, uranium hydroxides and sodium uranates (di-and mono-uranates). The unwashed amorphous phase from synthesis with uranium showed a broad infrared absorption band from about 850 to 725 cm^{-1} with the main peak centered at 801 cm^{-1}. There are other subtraction infrared bands at 668 and 565 cm^{-1} (Figure 15 and Table IV). As earlier mentioned, the washing of the solid amorphous solid with DI water and Na_4EDTA was followed with an extra wash with sodium carbonate because the uranium bands persisted after leaching with water and Na_4EDTA only. The final leaching with sodium carbonate still failed to remove all the uranium solid bands. Two major infrared bands corresponding to uranium solids at 865 and 829 cm^{-1} were observed with the unwashed uranium loaded sodalite. Other minor peaks are observed at 720 cm^{-1} (Figure 16 and Table IV). The zeolite A had two infrared bands for uranium solids at 865 and 565 cm^{-1} (Figure 17 and Table IV).

IV. CONCLUSIONS

We have used batch laboratory testing to evaluate the potential for the incorporation of uranium into sodium aluminosilicate structures during synthesis. These experiments were designed to provide insight into the possibility of physically or chemically trapping of uranium as solids or otherwise into NAS structures during synthesis in a supersaturated and high caustic environment. The following conclusions are based on the observations and results obtained in this laboratory-scale investigations detailed.

- Conditions that foster NAS precipitation are likely to foster uranium solid (uranium silicate, sodium uranates and uranium hydroxide) precipitation, so it is difficult to attribute problems with uranium accumulation to say just the formation of the aluminosilicates,

- Infrared spectral evidence shows that sodium uranate and other uranium solids are formed during the synthesis of these NAS phases in the presence of uranium.
- Uranium solids are found on the surface and the internal cavities of both sodalite and amorphous phases of NAS,
- Uranium solids may be physically trapped within the internal structures of both amorphous and sodalite phases,
- Not all uranium solids bound on NAS surfaces are easily removed by agitation with DI water,
- The order of total uranium loading during synthesis in the unwashed alumninosilicates solid phases are sodalite>amorphous>>Zeolite A and the order of measurable uranium, which could not be leached out with water and chelating solution and thus considered trapped inside the NAS phases, is Amorphous>sodalite>>Zeolite A.

These studies support the basis for continued operation of evaporators at the Savannah River Site.

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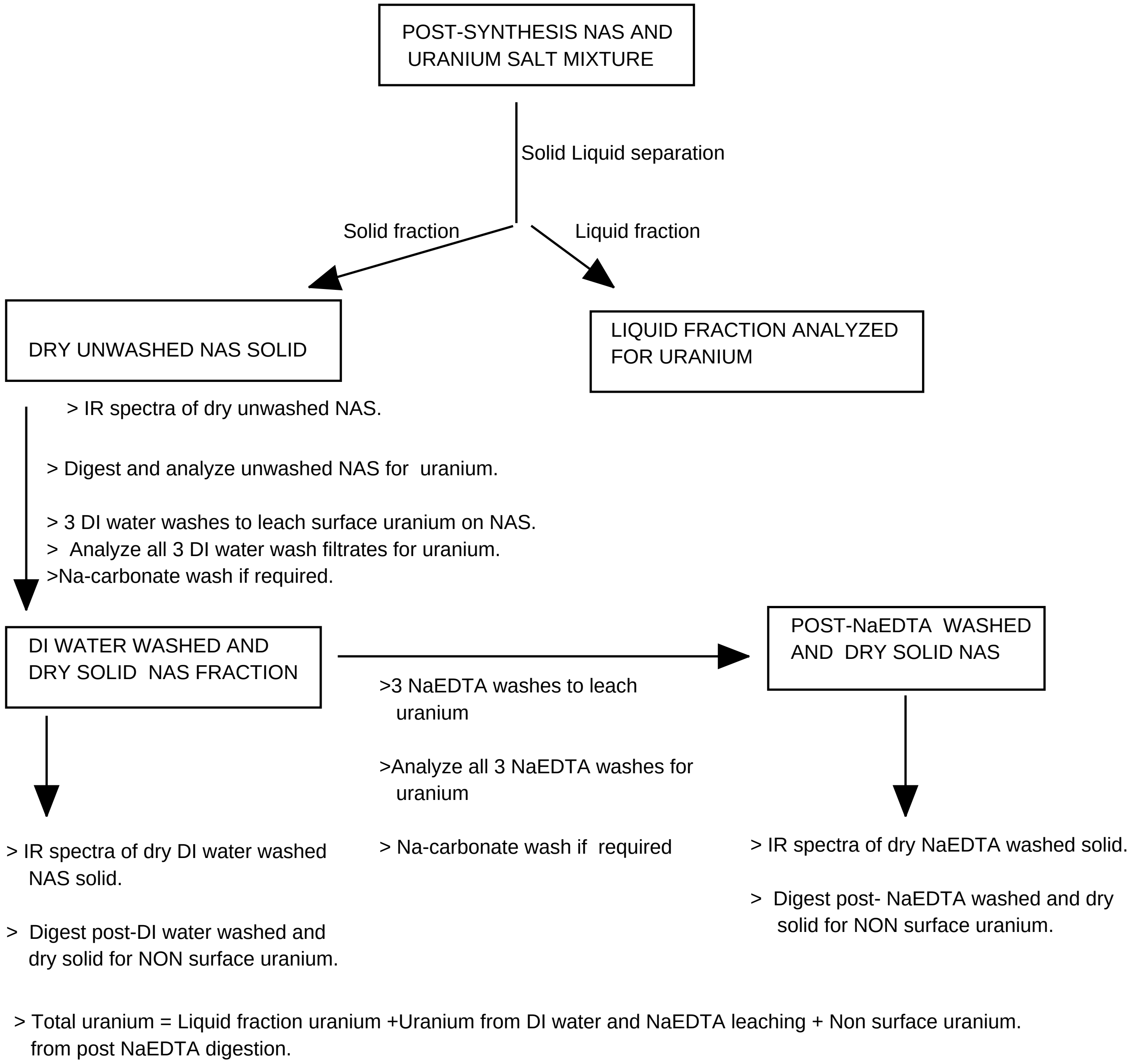
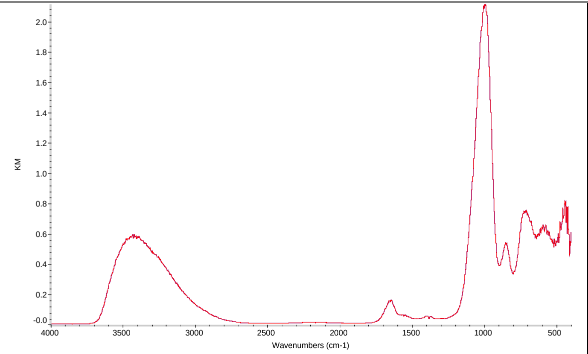
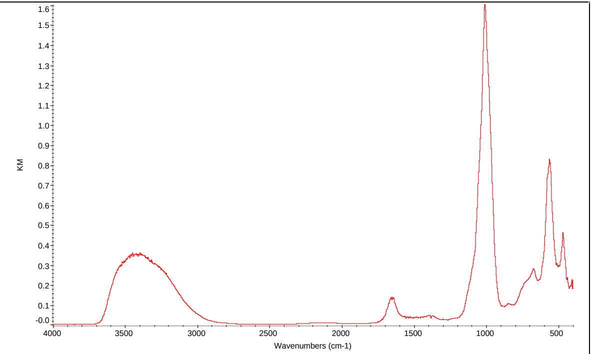


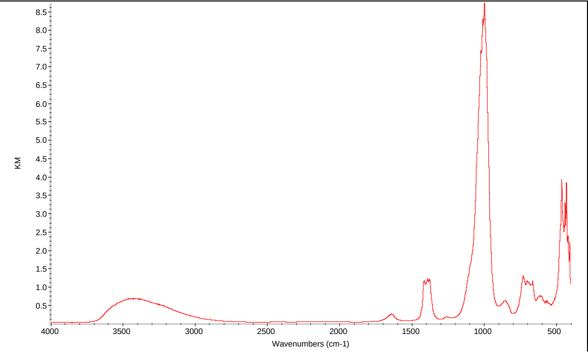
Figure 1. Uranium mass balance flow diagram.



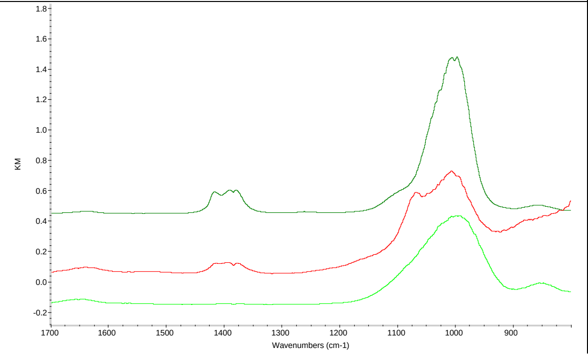
Amorphous



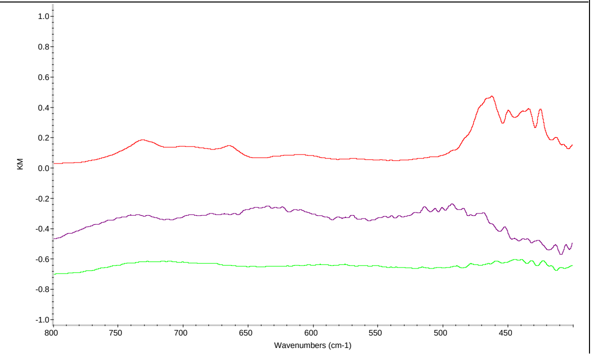
Zeolite A



Sodalite



Overlay IR spectra for amorphous, zeolite A and sodalite phases: 2000 to 900 cm^{-1}



Overlay IR spectra for amorphous, zeolite A and sodalite phases: 900- to 400 cm^{-1}

Figure 2. Confirmatory infrared spectra for the aluminosilicates.

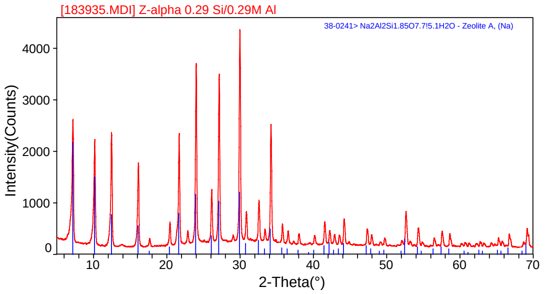
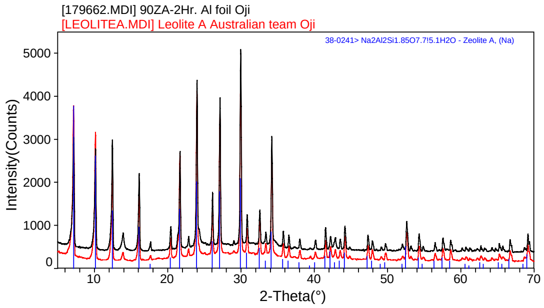
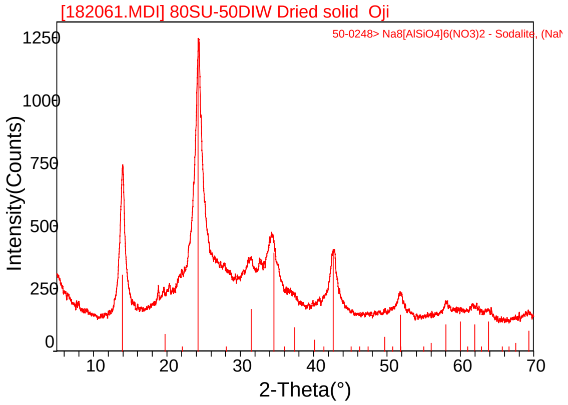
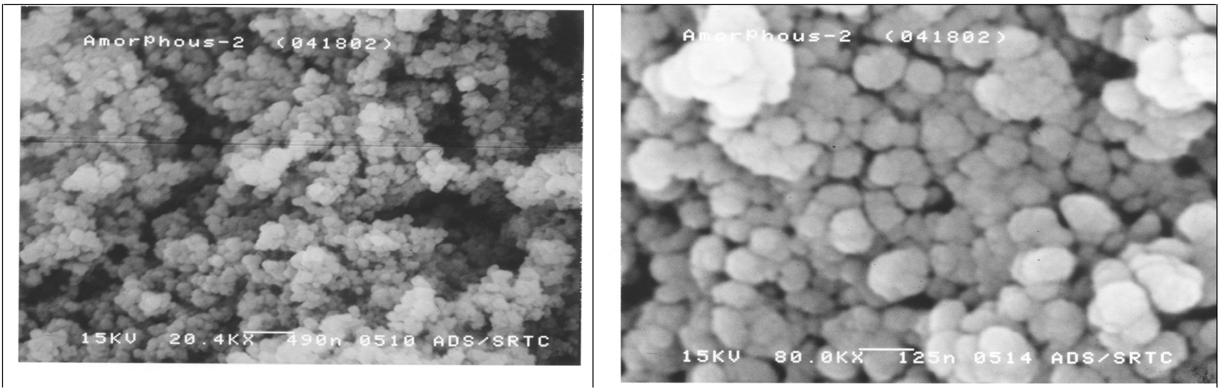
	
Zeolite A	Overlay spectra for zeolite A with reference
	
Sodalite	

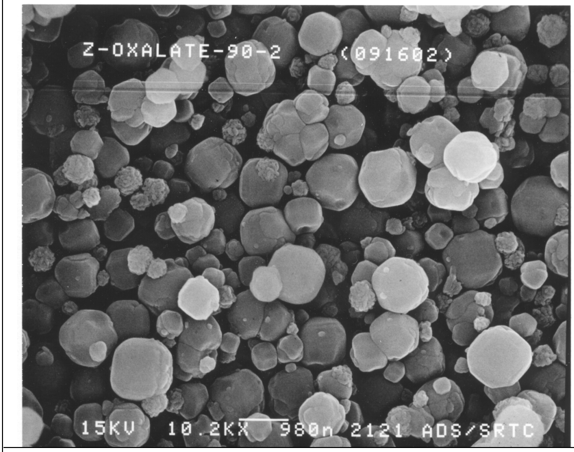
Figure 3. .Confirmatory XRD spectra for the Aluminosilicates.



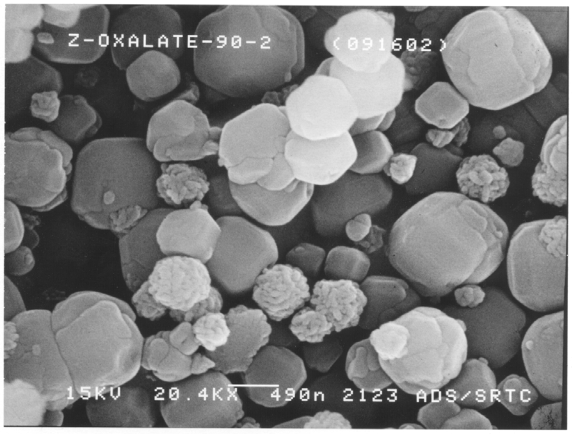
Amorphous phase at 20, 000 X magnification

Amorphous phase at 80, 000 X magnification

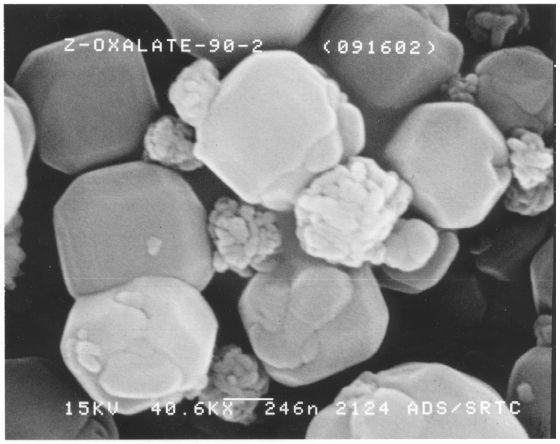
Figure 4. SEM microphotographs for amorphous phase at two magnifications



Zeolite A at 10, 000 X magnification



Zeolite A at 20, 000 X magnification



Zeolite A at 40, 000 X magnification

Zeolite A at 60, 000 X magnification

Figure 5 SEM microphotographs for zeolite A at various magnifications

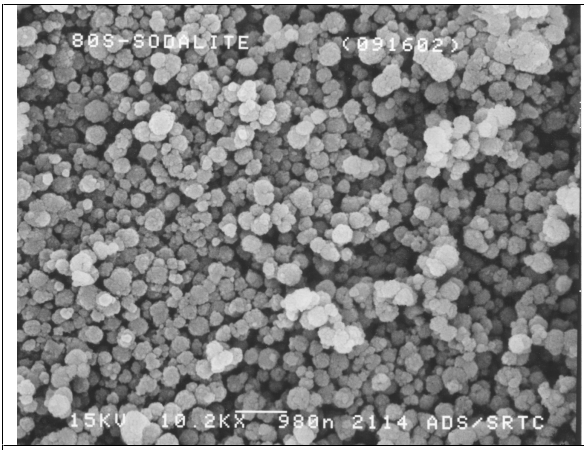
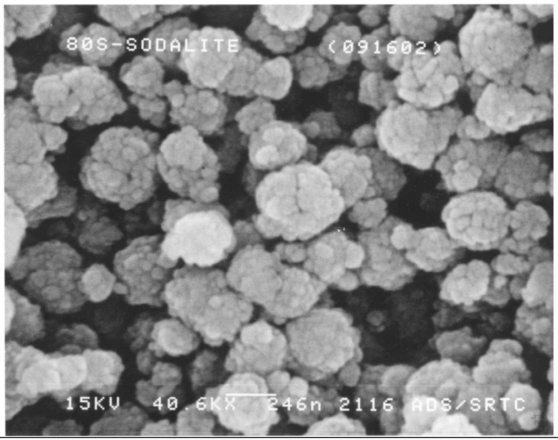
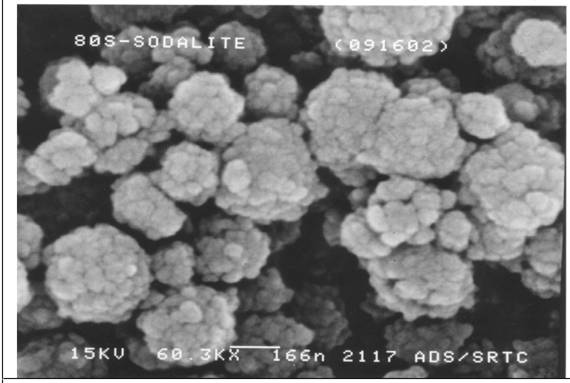
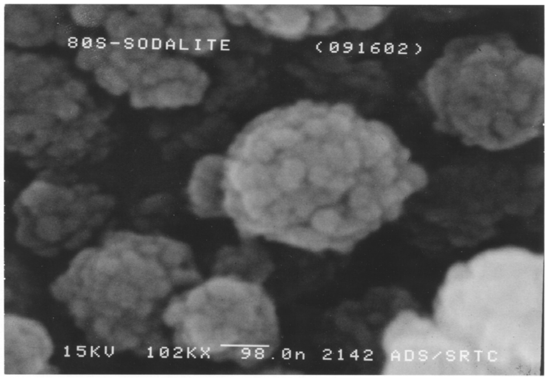
 	
Sodalite at 10, 000 X magnification	Sodalite at 40, 000 X magnification
 	
Sodalite at 60, 000 X magnification	Sodalite at 102, 000 X magnification

Figure 6. SEM microphotographs for sodalite at various magnifications

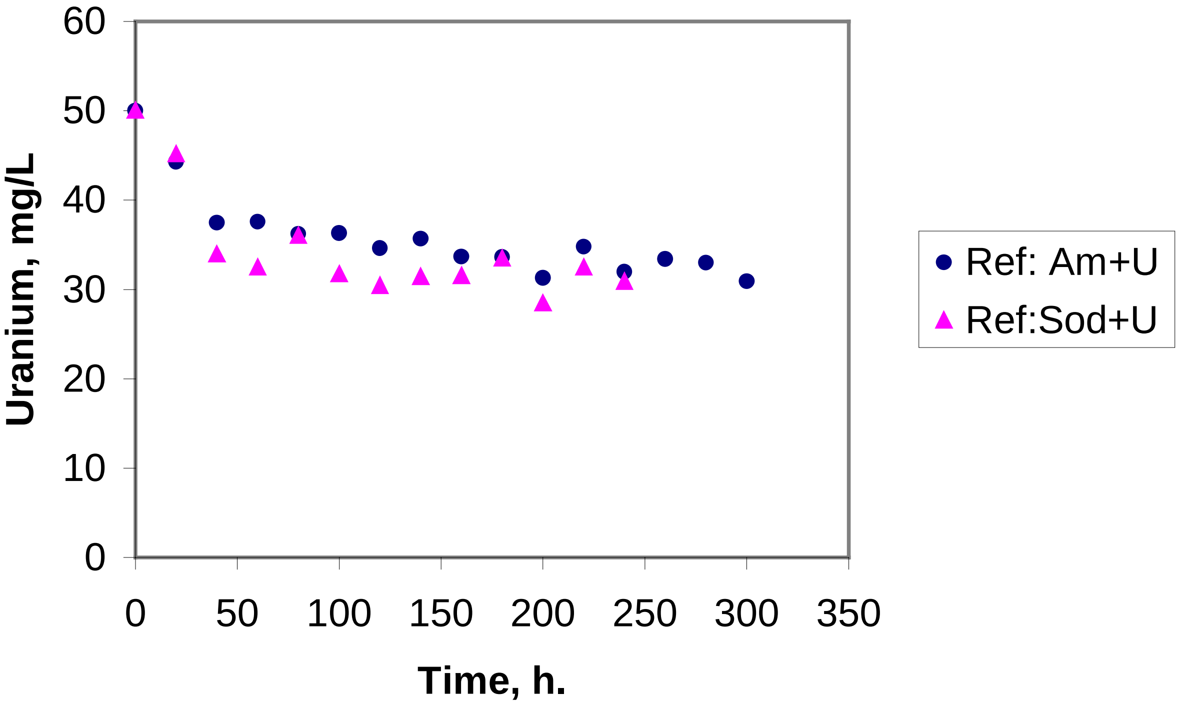


Figure 7. Overlay plot of amorphous and sodalite NAS reference curves at 50-mg uranium loading.

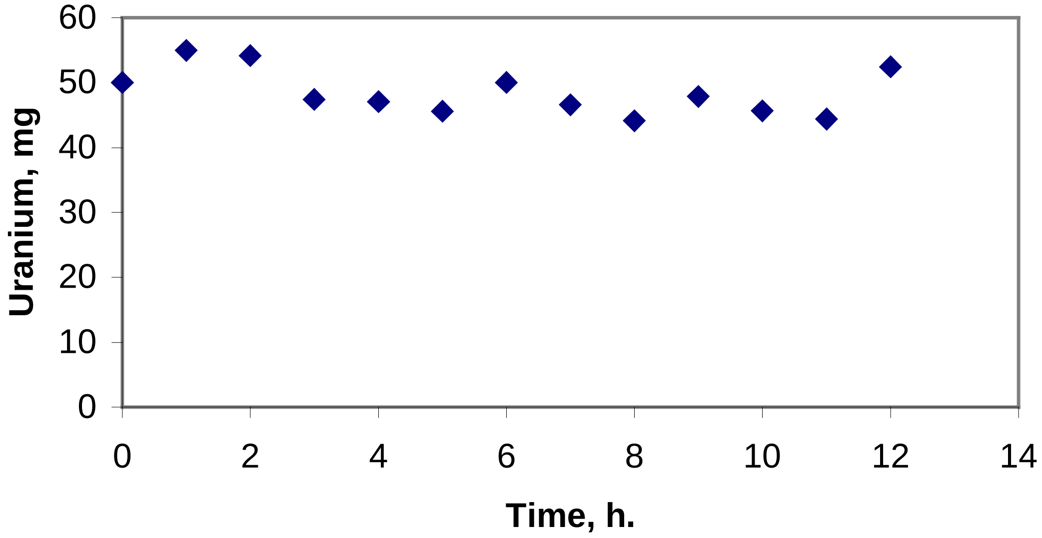


Figure 8. Zeolite A reference curves at 50-mg uranium loading.

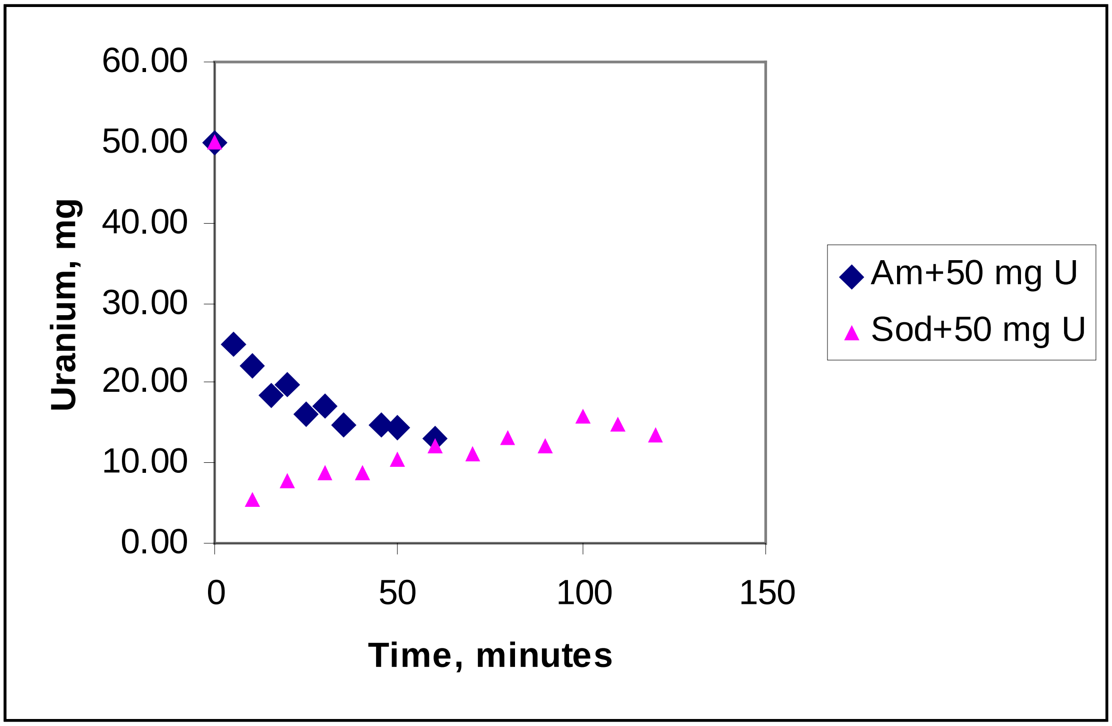


Figure 9. Amorphous, and sodalite synthesis in the presence of uranium. Filtrate uranium concentration profile.

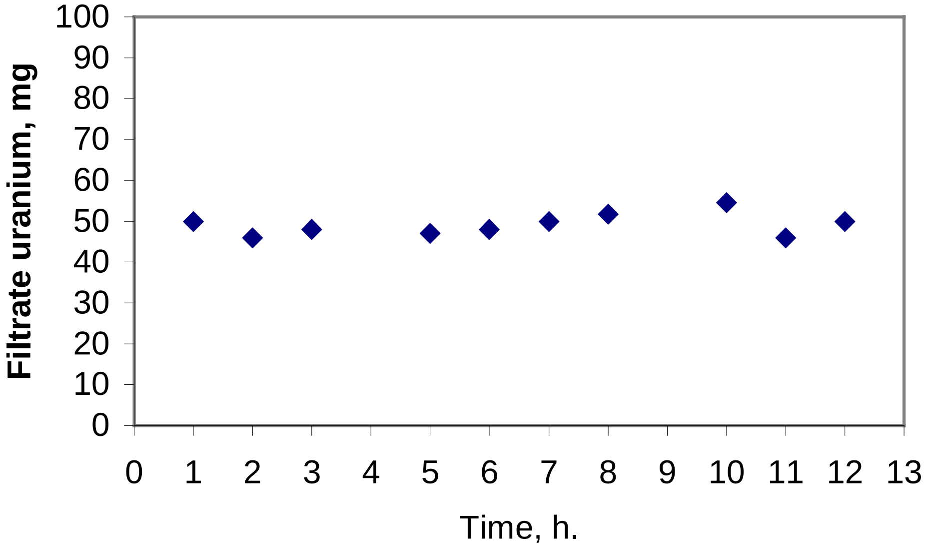


Figure 10. Zeolite A synthesis in the presence of uranium: Filtrate uranium concentration profile.

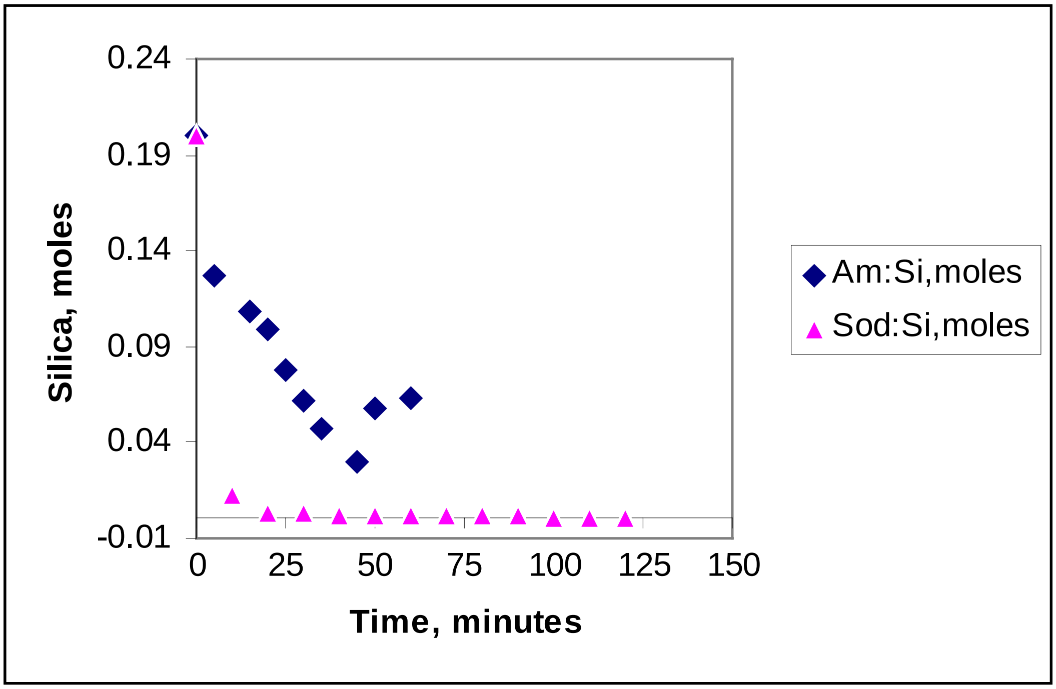


Figure 11 Silica depletion profile for amorphous and sodalite phases during synthesis in the presence of uranium.

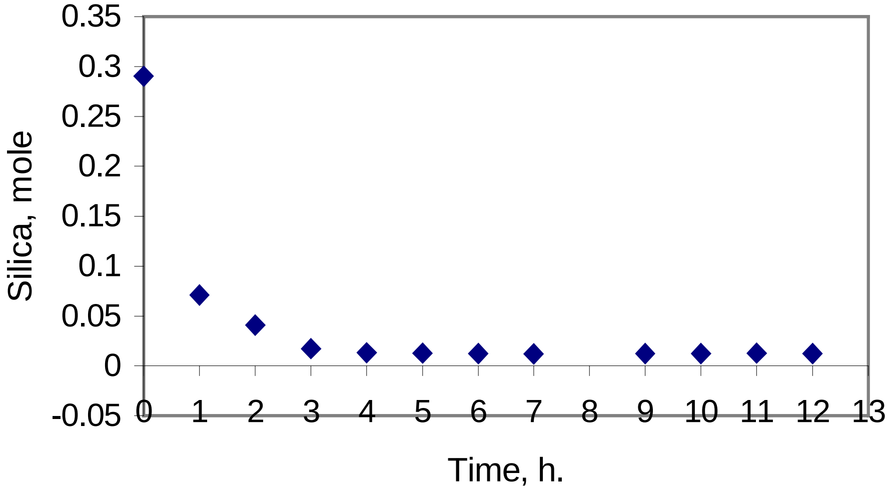


Figure 12. Silica depletion profile during zeolite A synthesis

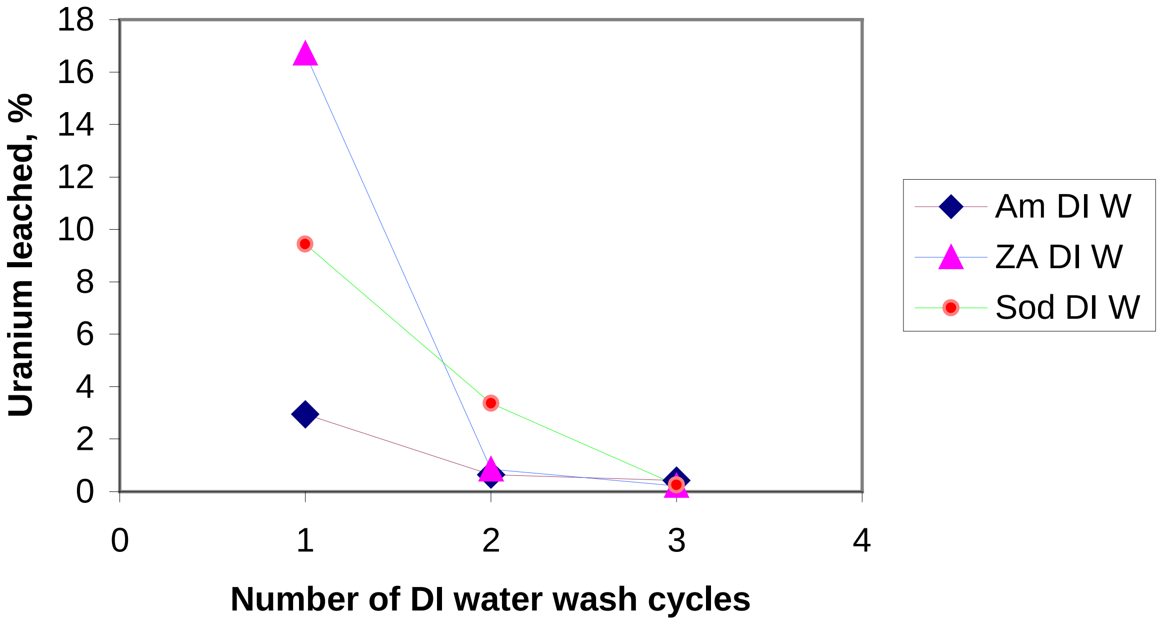


Figure 13. Amorphous, zeoliteA, and sodalite uranium concentration changes with number of distilled water wash cycles. Only a 5-20 % of the uranium removed with DI water washes.

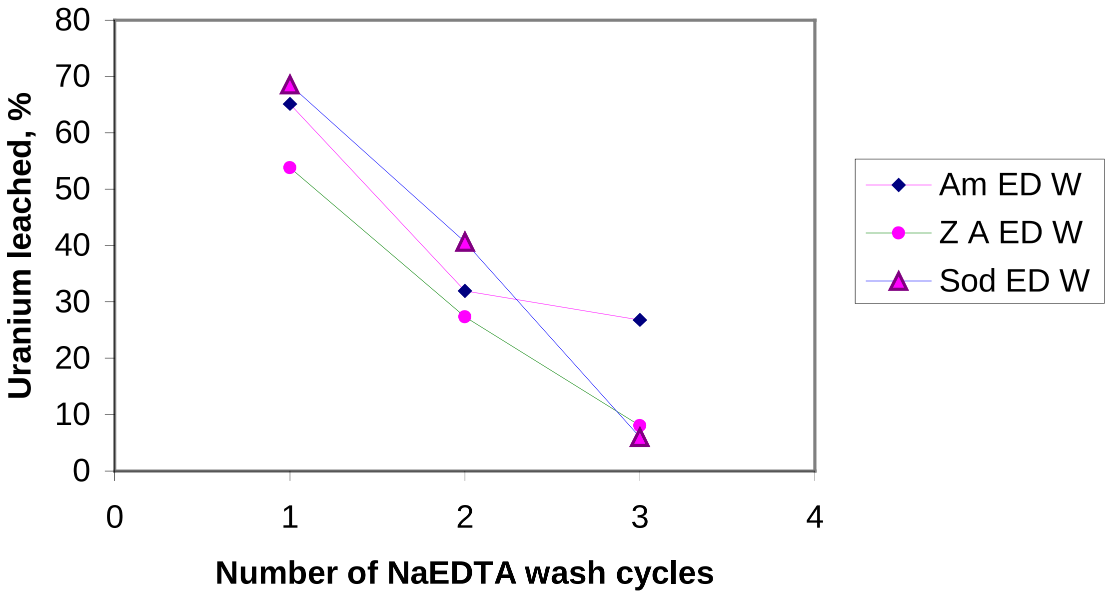
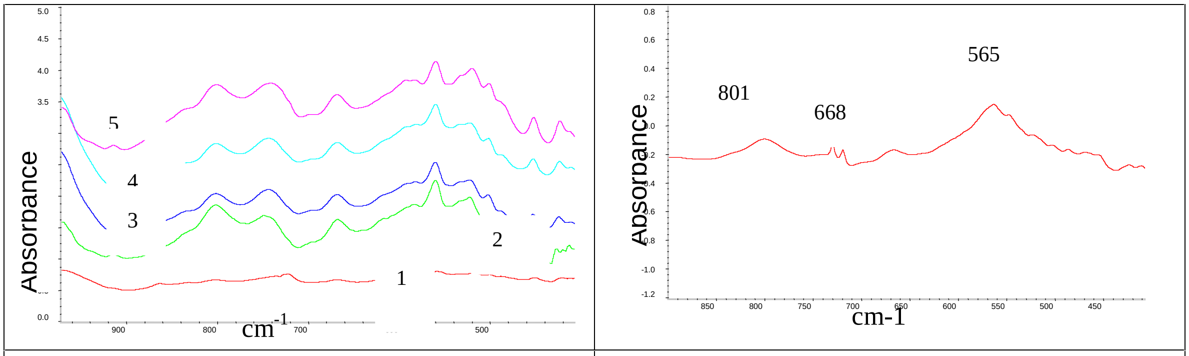


Figure 14. Changes in uranium concentration in post Na_4EDTA leaching of amorphous, zeolite A, and sodalite NAS solids.



1 = Spectrum w/o uranium
2 = Spectrum with uranium
3 = DI washed IR spectrum
4 = Na_4EDTA washed IR spectrum
5 = Carbonate washed IR spectrum

Uranate band at 801, 668 and 565 cm^{-1}

A: Overlay spectra

B: Subtraction spectra

Figure 15. Overlay IR spectra for amorphous washes. Broad uranate absorption bands from 825 to 725 cm^{-1} still visible after all washes.

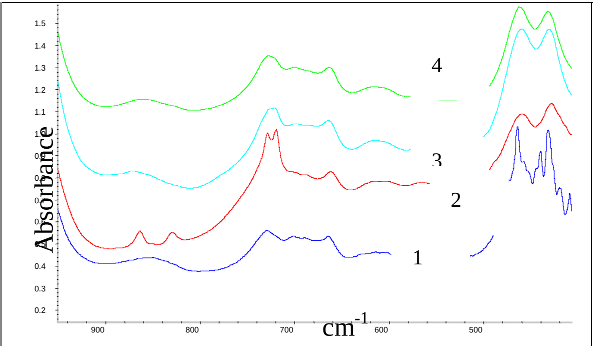
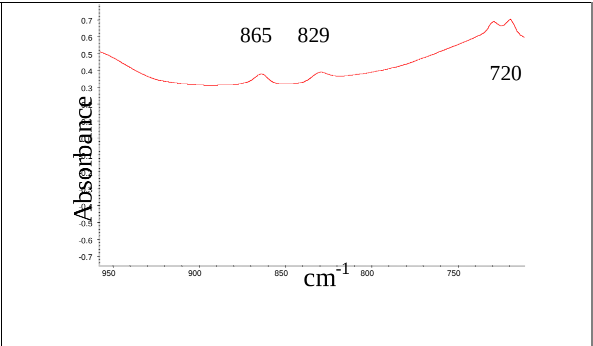
	
1 = Spectrum w/o uranium 2 = Spectrum with uranium 3 = DI washed IR spectrum 4 = Na_4EDTA washed IR spectrum	Sodalite uranate peaks at 865, 829 and 720 cm^{-1}
A: Overlay spectra	B: Subtraction spectra

Figure 16. Overlay IR spectra for sodalite wash. Uranate peaks at 864, 829 and 720 cm^{-1} for unwashed sodalite and no uranate bands after washes.

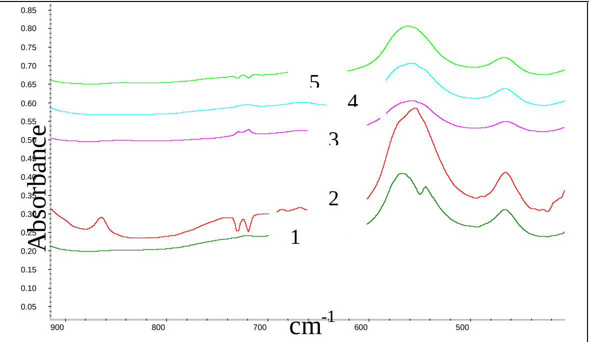
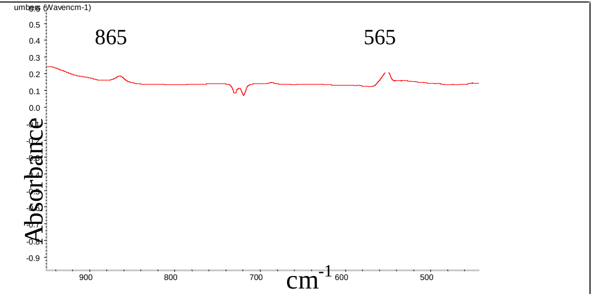
	
1 = Spectrum w/o uranium 2 = Spectrum with uranium 3 = DI washed IR spectrum 4 = Na_4EDTA washed IR spectrum 5 = Carbonate washed IR spectrum	Uranate band at 865 and 565 cm^{-1}
A: Overlay spectra	B: Subtraction spectra

Figure 17. Overlay IR spectra for zeolite A washes. Uranate peak present at 865 and 565 cm^{-1} for the unwashed zeolite A. No uranate peaks after washes.

Table I.

Reagent concentrations for amorphous and sodalite synthesis.

	Solution A	**Solution B**	**Solution C (50% solution A+50% Solution B**
	Moles/L	Moles/L	Moles/L
NaOH	4.0	4.0	4.0
$NaNO_3$	2.0	----	1.0
$NaNO_2$	2.0	---	1.0
$Al(NO_3)_3.9H_2O$	0.94	----	0.47
$Na_2\,siO_3.5H_2O$	------	0.75	0.38

Table II.

Summary of reagent concentrations and synthesis conditions for all NAS

Reagents	**Amorphous** **(moles/Liter)**	**Zeolite A** **(moles/Liter)**	**Sodalite,** **(moles/Liter)**
NaOH	4.0	4.7	4.0
$NaNO_3$	1.0		1.0
$NaNO_2$	1.0		1.0
$Al(NO_3)_3.9H_2O$	0.47		0.47
$NA_2SO_3.5H_2O$	0.38		0.38
$Na_2CO_3.H_2O$			
Sodium silicate solution (14% NaOH and 27% SiO2)		0.29 SiO_2 (65.0g)	
Sodium aluminate hydrate (54% Al_2O_3)		0.29 Al^{3+} (57.42 g)	
Synthesis temperature, °C	40	60	80
Duration of reaction, hours	≤ 1.0	12	≤ 1.5

Table III.

Summary of NAS product yields and uranium masses.

	Post-DI water Washed NAS solid weight, g	**Uranium in <u>unwashed</u> NAS solid fraction, mg**	**Incorporated uranium , mg**	**Total uranium in solid phase/ washed NAS (mgU / g NAS)**	**Total uranium in solid phase/ NAS solid + salt (unwashed NAS) (mgU / g NAS)**
Amorphous	101.75	37.04	21.10	0.36	0.20
Zeolite A	62.68	4.59	1.72	0.07	0.05
Sodalite	34.56	40 0	4.79	1.16	0.63

Table IV.

Uranium solid IR bands in NAS solids.

Leacheate	**Amorphous**	**Zeolite A**	**Sodalite**
Unwashed NAS	801, 668 and 558 cm^{-1}	865 and 565 cm^{-1}	865, 829 and 720 cm^{-1}
DI water/Na_4EDTA	Broad band	None	None
Carbonate	Broad band	-	-

Figure Captions.

Figure 1**.** Uranium mass balance flow diagram.

Figure 2. Confirmatory infrared spectra for the aluminosilicates.

Figure 3. .Confirmatory XRD spectra for the Aluminosilicates.

Figure 4. SEM microphotographs for amorphous phase at two magnifications

Figure 5 SEM microphotographs for zeolite A at various magnifications

Figure 6. SEM microphotographs for sodalite at various magnifications

Figure 7. Overlay plot of amorphous and sodalite NAS reference curves at 50-mg/L uranium loading.

Figure 8**.** Zeolite A reference curves at 50-mg uranium loading.

Figure 9**.** Amorphous, and sodalite synthesis in the presence of uranium. Filtrate uranium concentration profile.

Figure 10. Zeolite A synthesis in the presence of uranium: Filtrate uranium concentration profile.

Figure 11 Silica depletion profile for amorphous and sodalite phases during synthesis in the presence of uranium.

Figure 12. Silica depletion profile during zeolite A synthesis

Figure 13. Amorphous, zeoliteA, and sodalite uranium concentration changes with number of distilled water wash cycles. Only a 5-20 % of the uranium removed with DI water washes.

Figure 14. Changes in uranium concentration in post Na_4EDTA leaching of amorphous, zeolite A, and sodalite NAS solids.

Figure 15. Overlay IR spectra for amorphous washes. Broad uranate absorption bands from 825 to 725 cm^{-1} still visible after all washes.

Figure 16. Overlay IR spectra for sodalite wash. Uranate peaks at 864, 829 and 720 cm^{-1} for unwashed sodalite and no uranate bands after washes.

Figure 17. Overlay IR spectra for zeolite A washes. Uranate peak present at 865 and 565 cm^{-1} for the unwashed zeolite A No uranate peaks after washes.