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Conditions Conducive to Forming Crystalline Uranyl Silicates in High Caustic Nuclear Waste Evaporators.

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ABSTRACT

The laboratory conditions used to synthesize the uranyl silicate minerals are almost identical to the evaporator conditions under which high caustic nuclear wastes are processed to reduce total liquid waste volume. The only significant difference lies in the sodium ion concentration in such caustic nuclear wastes, which typically averages around 5.6 M Na^+. In this investigation, synthetic uranyl silicate minerals (sodium weeksite, sodium boltwoodite and uranophane) were produced only under low Na^+ concentration (<0.02 M), while attempts to synthesize these same uranyl silicates minerals in the presence of high Na^+ concentration (high ionic strength reacting media), which is typical of caustic nuclear waste evaporator processing conditions proved unfruitful. In the presence of high Na^+ concentration the main product for the same soluble silica-uranium reaction mixture shifts towards the formation of mainly clarkeite ($Na[(UO_2)O(OH)](H_2O)_{0-1}$), a hydrated sodium uranate and not towards the formation of uranyl silicates.

Thus, the presence of high Na^+ concentration in the reaction mixture of dissolved uranium and silica inhibits or suppresses the formation of crystalline uranyl silicates. We therefore conclude that evaporator fouling by uranyl silicate minerals is not easily produced under nuclear waste processing conditions because of the high Na^+ concentration in the liquid wastes.

I. INTRODUCTION

Nuclear waste in a typical large high-level nuclear waste storage tank is relatively dilute as received and is concentrated in one of several nuclear waste evaporators to minimize the space required to store extra waste. One of the problems with processing such nuclear waste through an evaporator is the occasional crystallization of sodium aluminosilicates (NAS) in the evaporators and the precipitation of enriched uranium (U) with the NAS.[1, 2, 3] This often leads to the eventual shut down of nuclear waste evaporation processes. One option for controlling the crystallization of NAS in such evaporators requires a segregation of silicon-containing waste fed to the evaporators from those containing aluminum. But in the absence of aluminosilicates, there still exists the potential for the formation of other evaporator clogging solids from the interaction of dissolved uranium with dissolved silica to form insoluble uranium silicates.

In nuclear waste evaporator storage feed tanks, which are hydrated and oxidizing environments, U exists in the U^{+6} oxidation state as the uranyl cation (UO_2^{2+}) and secondary U^{+6} minerals such as the uranyl oxide hydrates like schoepite ($UO_3 \cdot 2H_2O$) and sodium uranates (Na_2UO_4 or $Na_2U_2O_7$).

In nature, uranium silicates are formed in silica-rich ground water where dissolved uranium is present. The natural conditions for the precipitation of uranium silicate can vary from low to high pH conditions and from low parts per billion levels of divalent or univalent transition metals to the mg levels. At higher pH conditions, the uranyl ion may hydrolyze into a number of aqueous hydroxide complexes. These polymeric hydroxy uranyl complexes, under moderate temperatures conditions will combine with soluble silica to form various insoluble uranyl silicate minerals.[4] Whereas, insoluble uranium silicate minerals are readily formed under natural conditions, the question which needs to be addressed deals with the extent to which these evaporator-clogging minerals can also be formed under evaporator operating conditions. Although evaporator conditions are quite similar to the natural conditions for uranium silicate formation there is one important condition which is unique to the evaporator system; the high sodium ion concentration averaging about 5.6 moles.

Essentially, three general approaches have been used by researchers to produce synthetic uranyl silicates under laboratory conditions. By far the most widely used technique involves the direct reaction between dissolved silica and uranyl ion species[5, 6, 7] This normally involves the aging of the reaction mixture for several hours or even days, with pH adjustment in some cases, followed by isothermal treatment of the mixture at temperatures usually between 80 and 150 °C for several days to enhance the crystallographic features of the synthetic mineral. After thermal treatment and solid-liquid separation, the material is washed with distilled and de-ionized water and dried at room temperature. A third technique involves vapor phase hydration experiments[8] on uranium-doped borosilicate waste glass at elevated temperatures of about 200 °C.

The operational conditions for a typical nuclear waste evaporator are summarized in Table 1. The maximum operation temperature is about 150 °C. Our interest lies only in those synthetic crystalline uranyl silicate phases, which can be made and exist at or below this maximum temperature in a high caustic, oxidizing environment of the evaporators.

Uranyl silicates selected for laboratory synthesis under conditions, which are similar to those of nuclear waste evaporators are thus required to meet the following criteria:

- Minerals where the uranium atom is in the oxidized uranyl ion form
- Molecular structures containing one or several of the predominant cations present in the evaporators.
- Can be synthesized at high pH and exist at either low or high pH conditions.
- Can be synthesized even at low temperatures
- Can be synthesized at low and high Na^+ concentrations

Sodium boltwoodite ($Na(H_3O)(UO_2) SiO_4 \cdot H_2O$),[9] is synthesized at moderately high pH condition of 10 and above and temperatures ranging from 90 to 150 ºC. Sodium weeksite ($Na_2(UO_2)_2(Si_2O_5)_3 \cdot 7H_2O$) is also synthesized at moderate pH conditions at temperatures ranging from 100 to 150 ºC.[5] Uranophane($Ca(H_3O)_2 (UO_2)_2(SiO_4)_2 \cdot H_2O$) is the only uranyl silicate mineral that can be synthesized at a wide range of pH conditions ranging from pH 1 to 13. Synthesis temperatures for uranophane[6] are between 100 and 150 ºC. Thus, sodium boltwoodite, sodium weeksite and uranophanes are some of the main uranyl silicates produced under conditions, which are similar to the oxidizing environments of the evaporators and hence are considered as possible uranyl silicate minerals which could be produced in the evaporators.

This investigation was undertaken to verify whether selected uranium silicate minerals (sodium weeksite, sodium boltwoodite and uranophane) which are naturally made under conditions similar to that of an evaporator could be synthesized under laboratory conditions like those of a nuclear waste evaporator, in particularly high sodium ion concentration. If the synthesis of these minerals is possible under the high caustic evaporator conditions, one would expect that these evaporator fouling minerals would pose a serious problem to the continuous operation of a nuclear waste evaporator as has been observed with NAS at the Savannah River Site (SRS)[1,2].

II. EXPERIMENTAL

The standard laboratory reflux vessel used for the first part of the mixing and reflux reactions in the uranium silicate synthesis consisted of a one-liter stainless steel reaction vessel equipped 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 up to 200 rpm, was used to keep the reactor contents well mixed. The reaction precipitates, recovered after mixing and reflux reactions in the reflux unit was fed together with ultra pure water into the pressure reactor for enhanced crystallization of the silicates. The pressure reaction unit used for the long crystallization reaction phase for the uranyl silicates was a fixed-head high pressure Parr reactor rated for use at up to 3000 psi at 350 ºC. The Parr reactor was equipped with a variable-speed, explosion-proof, 1/4 hp motor, an electrical barrier box for thermocouples, pressure, and rpm signals, and a model 4843 controller. The reaction vessel itself was made of inconel-600 and designed and equipped with a removable 600-mL Teflon® insert liner for holding reagents during synthesis. The maximum pressure recorded during a typical synthesis, at 150 ºC with 300 mL of reagent solution charged into the reaction vessel, was 51 psi with an average pressure read out of 48 ± 2 psi over 96 hours of operation.

The reagent grade chemicals and precursors used as starting materials for the silicate synthesis were uranium acetate (Alpha Aesar), sodium metasilicate nonahydrate (Sigma) and calcium acetate (Alpha Aesar). Stock solution was made up with compositions of 0.1 M solutions of the above chemical reagents. Two approaches were used in the making of the reagent solutions for the synthesis:

(1) all reagents prepared in water by dissolving each of the starting reagent materials in distilled water with the synthetic mixture containing less than 0.02 moles of Na^+ (sodium coming only from the reagent precursors) (low Na^+ synthesis) and

(2) dissolving of the reagents in 20-25 mL of distilled water with the addition of sufficient amount of a typical evaporator feed simulant salt solution (see Table 2) to bring the Na^+ concentration in the combined reaction mixture to 5.6 M.

The last approach, referred to as high Na^+ synthesis, is one of the most important evaporator conditions. The final volume of each reaction mixture for every synthesis was 300 mL. This volume was chosen because of safety limitations on the Parr reactor used for the final phase of the synthesis.

In general, in the synthesis of sodium boltwoodite and sodium weeksite, stoichiometric amounts of uranium and silicate precursors (uranium acetate and sodium silicate nonahydrate) were mixed for a given length of time depending on which of the silicates was being synthesized as summarized in **Table 3**. After pH adjustment, the mixture was refluxed for a length of time. Following this step, the decision was made whether to perform a solid liquid separation and wash the resulting precipitate in ultrapure water several times before introducing the precipitate with ultrapure water into the Parr reactor at a given temperature (first synthesis) or to send the unwashed synthetic product and the reaction liquor directly into the Parr reactor (second synthesis). In the first synthesis, a solid liquid separation of the reaction mixtures with a 0.2 micron Teflon filter disc was performed and the solid was washed several times with distilled water until the conductivity of the wash-filtrate was approximately that of the distilled waster. After washing, the solid fraction together with distilled water was introduced into the Parr reactor for a given length of time and temperature. After thermal treatment in the Parr reactor, the solids are recovered through filtration using a 0.2 micron Teflon filter disc and vacuum dried overnight. The resulting uranium mineral solid was then characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopic techniques. The FTIR spectra were based on transmission of IR signals through self-supporting discs made out of a mixture of KBr and the uranium silicate minerals.

The second synthesis step above was designed to mimic an evaporator condition that does not involve the separation of the mineral solids from the mother synthesis liquor. Here the refluxed mixture/solid minerals are introduced directly into the Parr reactor for thermal treatment without washing of any kind. Following the thermal treatment and solid liquid separation, the solid fraction is vacuum dried and characterized by XRD and FTIR techniques.

In the synthesis of uranophane, an additional ingredient, calcium as calcium acetate, was added into the mixture also in stoichiometric amounts and the procedures repeated as above.

II A. Synthesis of sodium weeksite and sodium boltwoodite

The laboratory synthesis of the uranyl silicates typically requires a minimum of 10-11 days, with seven of these days for crystallizations only at an average temperature of 150ºC (**see reference 10**). We chose to limit the synthesis time to at most half the time or less as detailed in the references above. A typical low Na^+ synthesis reactant solution for sodium weeksite and sodium boltwoodite was a mixture of 100 mL solution of uranium acetate (0.1 M), 50 mL of sodium silicate nonahydrate (0.1 M) and 150 mL of ultrapure water. The pH of the reaction mixtures was raised with either ammonium hydroxide or carbonate free sodium hydroxide and lowered with acetic acid. The desired pH values were 8.5 for sodium weeksite and 10.5 for sodium boltwoodite.

In the first few trial syntheses for sodium weeksite, using low Na^+ concentration (less than 0.02 M Na^+ in the 100 mL of 0.1 M solution of sodium silicate nanohydrate reagent) the total synthesis time was reduced to about 40 hours, with test sample (aliquot) taken out of the Parr reactor after 8 hours. This 8-hour sample was washed and vacuum dried for several days before XRD and FTIR characterizations (**see Figure 1 and inserts)** The remaining sample in the Parr reactor was left at the 150 ºC crystallization temperature for a total of 40 hours. This 40-hour sample was washed and vacuum dried as before prior to XRD and IR characterizations (**Figure 1).** The same synthesis was repeated. This time, the total Na^+ concentration in the reaction mixture was adjusted to

5.6 M Na^+ with the simulant salt solution (see Table 2). Sodium weeksite products were synthesized in stoichiometric amounts ($2UO_2(C_2H_2O_2)_2 \cdot 2H_2O + Na_2SiO_3 \cdot 9H_2O$).

The washing and solid/liquid separation of the crystallized silicate solids from the reagent liquor was slow because of the colloidal dimensions (<5 μm) of the uranium solid particles. On those occasions when the uranium solids formed needed to be washed and fast recovery of washed particles was essential, a series of decanting and washing steps was performed. In these steps, ultrapure water was re-introduced into the solids decanted fraction and stirred for 15 minutes and allowed to settle for about two hours. After the settling time, the decanting process was repeated several times to ensure that most of the reagent liquor had been removed in the washing process. The final solid fractions were then vacuum dried over night and air dried to constant weight. The samples which did not require washing at the end of synthesis were simply vacuum dried over night and air dried to constant weight.

In the synthesis of sodium boltwoodite at a pH of 10.5 the crystallization time in the Parr reactor was increased from 40 to 96 hours to minimize poor crystallization results as observed in the 8-hour synthesis of sodium weeksite described above. Again, the synthesis was performed at two Na^+ concentration levels; a low level Na^+ concentration of less than 0.02 M to a high of 5.6 M Na^+. Three synthesis products were produced: synthesis of sodium boltwoodite at low Na^+ levels with the final product washed several times with ultrapure water before introduction into the Parr reactor to enhance crystallization for 96 hours at 150 ºC, a second synthesis at low Na^+ levels, the washing step above was left out and a third synthesis, which was performed at high Na^+ level of 5.6 M, the washing step was also left out, too. All three sodium boltwoodite products were synthesized in stoichiometric amounts ($2\ UO_2(C_2H_2O_2)_2{\cdot}2H_2O$ + $Na_2SiO_3{\cdot}9H_2O$).

II B. Synthesis of uranophane

The reagent mixtures used for the synthesis of uranophane were similar to the mixtures used for the synthesis of both sodium weeksite and sodium boltwoodite with the addition of calcium acetate. It consisted of 50 mL of sodium silicate nonahydrate (0.1 M), 100 mL of uranium acetate (0.1 M), 50 mL of calcium acetate (0.1 M) and 100 mL of ultrapure water. In reactions involving 5.6 M Na^+ concentration, the 100 mL of ultrapure water was replaced with 100 mL of a typical SRS simulant salt solution (11.2 M Na^+), see Table 2. The simulant salt solution was used to increase the Na^+ concentration in the reaction mixture from < 0.02 M Na^+ solution to about 5.6 M Na^+. In the high salt synthesis, the reagent solutions were first mixed to enhance the formation of the desired products thereby minimizing precipitation reactions due to changes in solution pH. The higher sodium salt solution was added after mixing the reagents for about 15 minutes.

Uranophane was synthesized in stoichiometric amounts ($2UO_2(C_2H_2O_2)_2{\cdot}2H_2O$ + $Na_2SiO_3{\cdot}9H_2O$ + $Ca(C_2H_3O_2)_2{\cdot}H_2O$).

III . RESULTS AND DISCUSSION

III A. Sodium weeksite

The FTIR and XRD[*] spectra of the sodium weeksite produced are shown, respectively, in Figure 1 (overlay of FTIR spectra) and Figure 2, inserts A-C. This FTIR

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[*] Question marks,?, on XRD spectra indicate the existence of unmatched and unidentified peaks.

spectrum for the (low Na^+) synthetic sodium weeksite, Figure 1, (40-hour sample), is almost identical to the published infrared spectrum for synthetic weeksite.[5]

XRD characterization of the 8-hour weeksite sample shows that the material produced after 8 hours of synthesis is not crystalline (Figure 2 insert A.), while the 40-hour sample is fairly crystalline (Figure 2, insert B). The overlay of FTIR spectra, Figure 1, for both the 8 and 40-hour samples also shows that the 40-hoursample has more infrared spectra features, meaning distinct peaks after 1200 cm^{-1}, compared to the 8-hour sample, which showed broad absorptions, characteristic of amorphous phases. Figure **1** shows the overlay FTIR spectra for the high and low Na^+ synthesis products made using the sodium weeksite synthesis method. The color of the low Na^+ synthesis crystals was yellowish-green and that of the high Na^+ synthesis was brownish. The brownish color of the crystals is characteristic of clarkeite mineral.

The XRD characterization of the solids made at low and high Na^+ concentrations using the sodium weeksite synthesis method shows that they are, respectively, a mixture of sodium weeksite and other minor uranium oxide products[3] and either pure clarkeite ($Na(UO_2)O(OH)$) or a mixture of clarkeite and sodium nitrate (nitratine) and uranium oxide hydrate for the unwashed solids. The failure to make 100 % sodium weeksite even after washing several times may be attributed to the significant reduction in synthesis time from an average of 240 hours to just less than 40 hours and difficulty encountered in washing the crystals.

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[3] Minor products from low Na^+ synthesis included questionable XRD assignments matching studtite ($UO_4 \cdot 4H_2O$) mineral.

The synthesis of this particular uranyl silicate (sodium weeksite) was only used as a test case in the synthesis, because the evaporator pH is by far greater than 8.5, which is the synthesis pH for sodium weeksite.

III B. Sodium boltwoodite

The FTIR and XRD characterizations of the first two sodium boltwoodite products (Figure 3 and Figure 4A) show that a crystalline yellow-green material was made. Both the washed and unwashed low level Na^+ synthesis produced sodium boltwoodite with impurities of uranium oxide. The third synthesis, a high sodium synthesis product, was a brownish precipitate instead of the golden yellow products as observed in the low Na^+ synthesis. XRD pattern matching showed that this high Na^+ synthesis product was clarkeite with uranium oxide impurities and not sodium boltwoodite.

Figure 3 shows the overlay FTIR spectra for all three products (low Na^+ washed, low and high Na^+ unwashed products). This clearly shows that the high Na^+ unwashed product does not resemble the first two products. The following IR bands, characteristic of the products consisting of mostly sodium boltwoodite, are either completely missing or significantly reduced in intensity: 1637, 1303, 1019, 944, 765, 725 and 628 cm^{-1}. These IR spectra for the low Na^+ synthetic sodium boltwoodites are almost identical to the published IR spectra for synthetic boltwoodite.[5]

III C. Uranophane

Figure 4B show the XRD spectra for the products formed using the uranophane synthesis method at low Na^+ concentration (uranophane). The high Na^+

concentration synthesis product matched the XRD spectra for clarkeite. The low Na^+ crystal product is pale yellow-green while the high Na^+ product is brownish in color. The overlay of FTIR spectra for the two products is shown in Figure 5. The IR spectra for the synthetic uranophane made at low Na^+ is identical to the published IR spectra for synthetic uranophane.[5, 10] The FTIR spectrum of the high Na^+ product (clarkeite) is almost devoid of any pronounced IR peaks or features at the characteristic IR "finger print" section for uranophane, below 1200 cm^{-1}.

IV . Summary of synthesis products

Table 4 shows a summary of the target uranium silicate minerals, the uranium solids produced and the synthesis conditions. In all cases, the target uranium mineral was produced except under conditions which involved high Na^+ concentration, which is a typical evaporator condition. In all high Na^+ concentrations synthesis the end products, irrespective of pH and reaction temperature factors, were always clarkeite.

The laboratory conditions (temperature range of 80-150º C, hydrothermal and oxidizing environment, soluble uranium and silica, atmospheric and pH conditions) under which synthetic uranyl silicates are made are almost identical to SRS evaporator conditions, with the exception of differences in Na^+ concentration. Synthetic crystalline uranyl silicates have been made only under low Na^+ concentration, while attempts to synthesize crystalline uranyl silicates in the presence of high Na^+ concentration, typical of SRS evaporators proved unfruitful.

Looking at all the uranium products synthesized in this study, there appears to be a relationship between the amount or relative amount of sodium-to-uranium concentration that determines whether uranyl silicate or the sodium-uranium mineral, in this case clarkeite, is produced. At relatively low Na^+ concentration in the reaction mixture, with the source of Na^+ coming from mostly the silicate precursor (sodium metasilicate nonahydrate), the predominant synthetic products are uranyl silicates. In this low sodium synthesis condition, only the reaction conditions (reagent mixing time and temperature, reflux time and temperature, and crystallization temperature and duration) and reaction solution pH determine the nature of the uranyl silicates produced. Alternatively, when the Na^+ concentration in the reaction mixture is raised above yet undefined Na^+ concentration, the end product, irrespective of synthesis conditions and pH, is always a sodium uranate compound (clarkeite) and not the uranyl silicate.

The Na^+ concentration at SRS evaporators and evaporator feed tanks averages about 5.6 M. Based on the important roles played by Na^+ concentration in determining whether uranium silicate or clarkeite is produced during synthesis described so far, this will seem to suggest that the potential for the formation of any type of uranyl silicate minerals at SRS evaporators is relatively small. Based on the synthesis results in this study, one can simply conclude that clarkeite ($Na[(UO_2)O(OH)](H_2O)$) is the predominant uranium mineral in the evaporators. This fact is supported by a recent characterization of evaporator scales[11, 12], where the principal uranium mineral identified was sodium uranates, which is dehydrated clarkeite ($Na_2U_2O_7$). Therefore, this leads one to conclude that the recent observations. indicating the presence of possible uranyl silicate solid phases occluded in bulk aluminosilicate may be due to the presence of amorphous uranyl silicate mineral. Thus, crystalline uranyl silicates may be precluded from forming at high Na^+ concentrations but amorphous uranyl silicates may form at high sodium concentrations.

V . CONCLUSIONS

Therefore, based on the synthesis information presented in this study the following conclusions are made:

- Crystalline uranyl silicates are readily formed in the presence of dissolved uranium and silica.
- The presence of high Na^+ in a reaction mixture of dissolved uranium and silica inhibits the formation of uranyl silicates.
- The reaction path way favors the formation of sodium hydroxyl uranates over uranyl silicates in a reaction mixture with high Na^+ concentration.
- Crystalline uranyl silicate minerals are not easily produced under SRS evaporator conditions because of high Na^+ concentration in the evaporators and in the evaporator feed tanks.
- The principal uranium minerals which could be produced under evaporator conditions are sodium uranate minerals or clarkeite, which could also exist in the dehydrated forms called sodium uranates.

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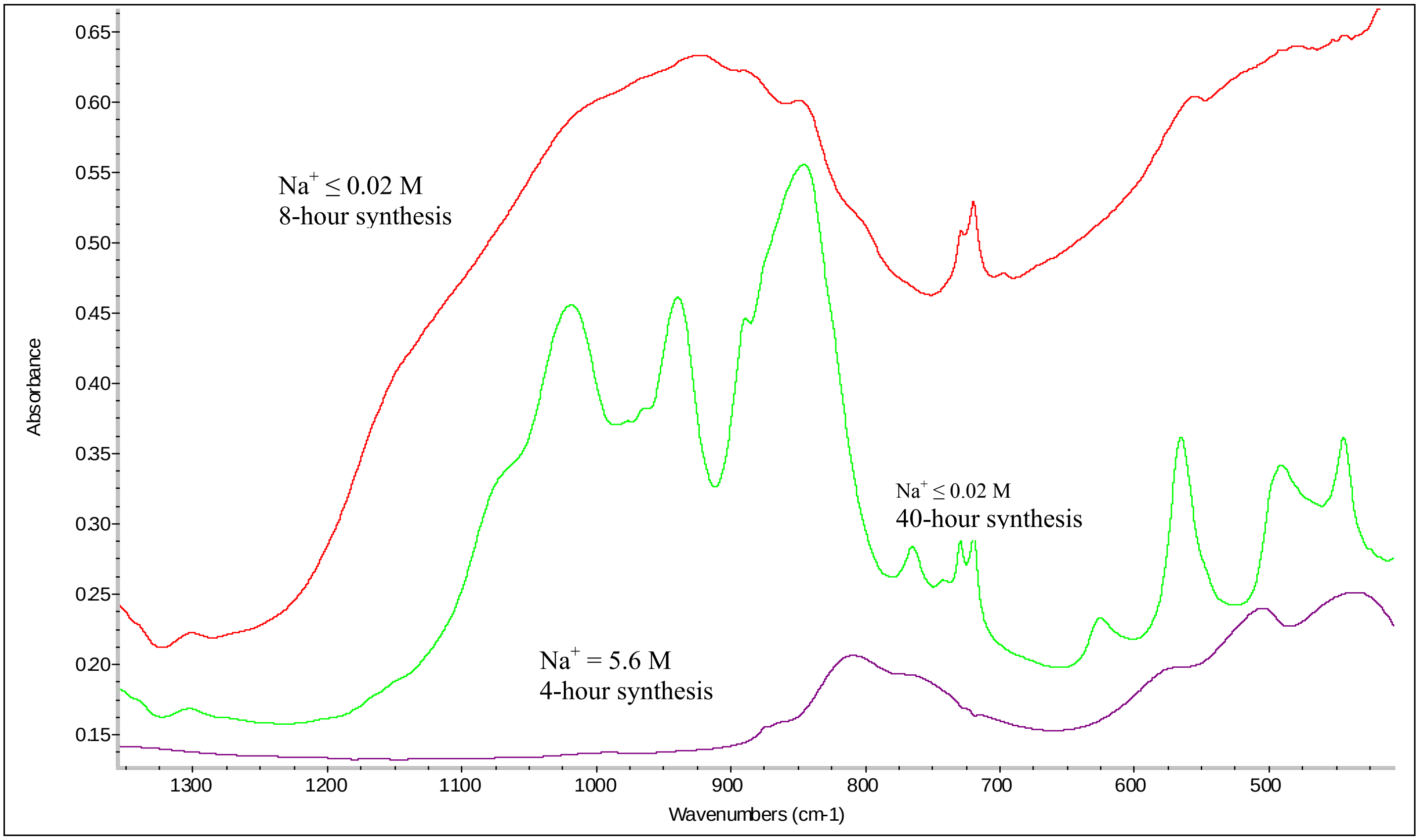
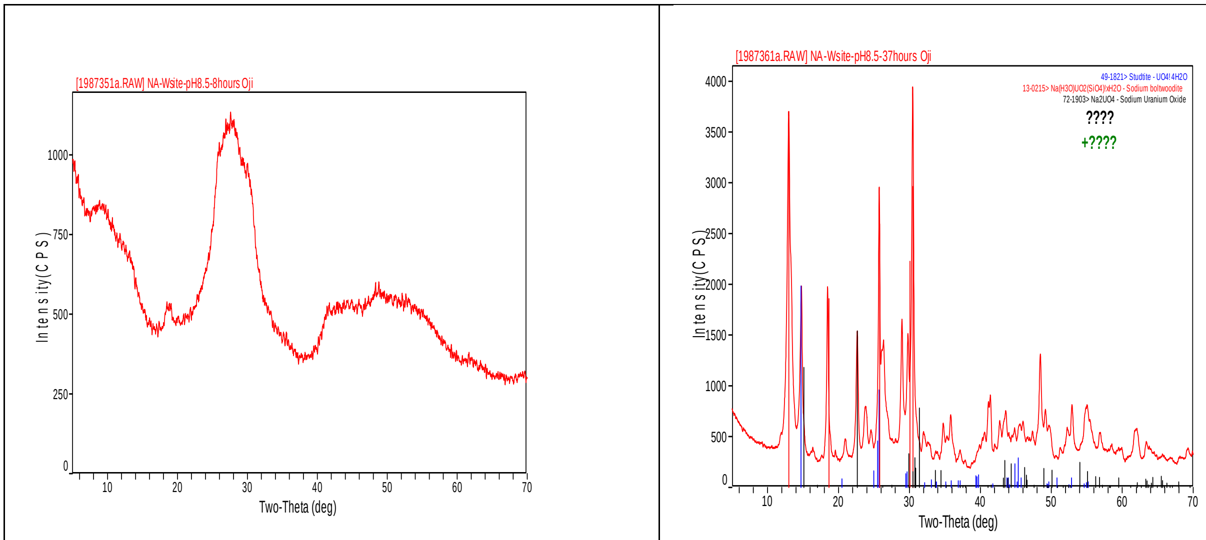
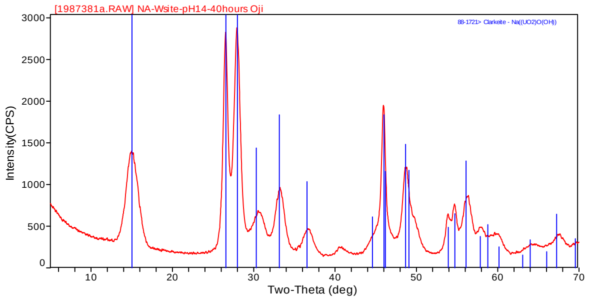


Figure1. Overlay of IR spectra for synthesis products after 8, 37 and 40 hours, respectively, at pH 8.5, low Na$^+$; pH 8.5, low Na$^+$; and 5.6 M Na$^+$ and pH > 13.



A: XRD spectra at pH 8.5, low Na+ (≤ 0.2M) and 8 hour synthesis. No crystalline solids formed.

B: XRD spectra at pH 8.5, low Na^+ (≤ 0.2M) and 40-hour synthesis. Crystalline solids are formed.



C: XRD spectra results at pH 14 and 5.6 M [Na^+], 40 hour reaction time (evaporator conditions). Clarkeite is the only product.

Figure 2. XRD spectra of uranium minerals synthesized with the sodium weeksite method.

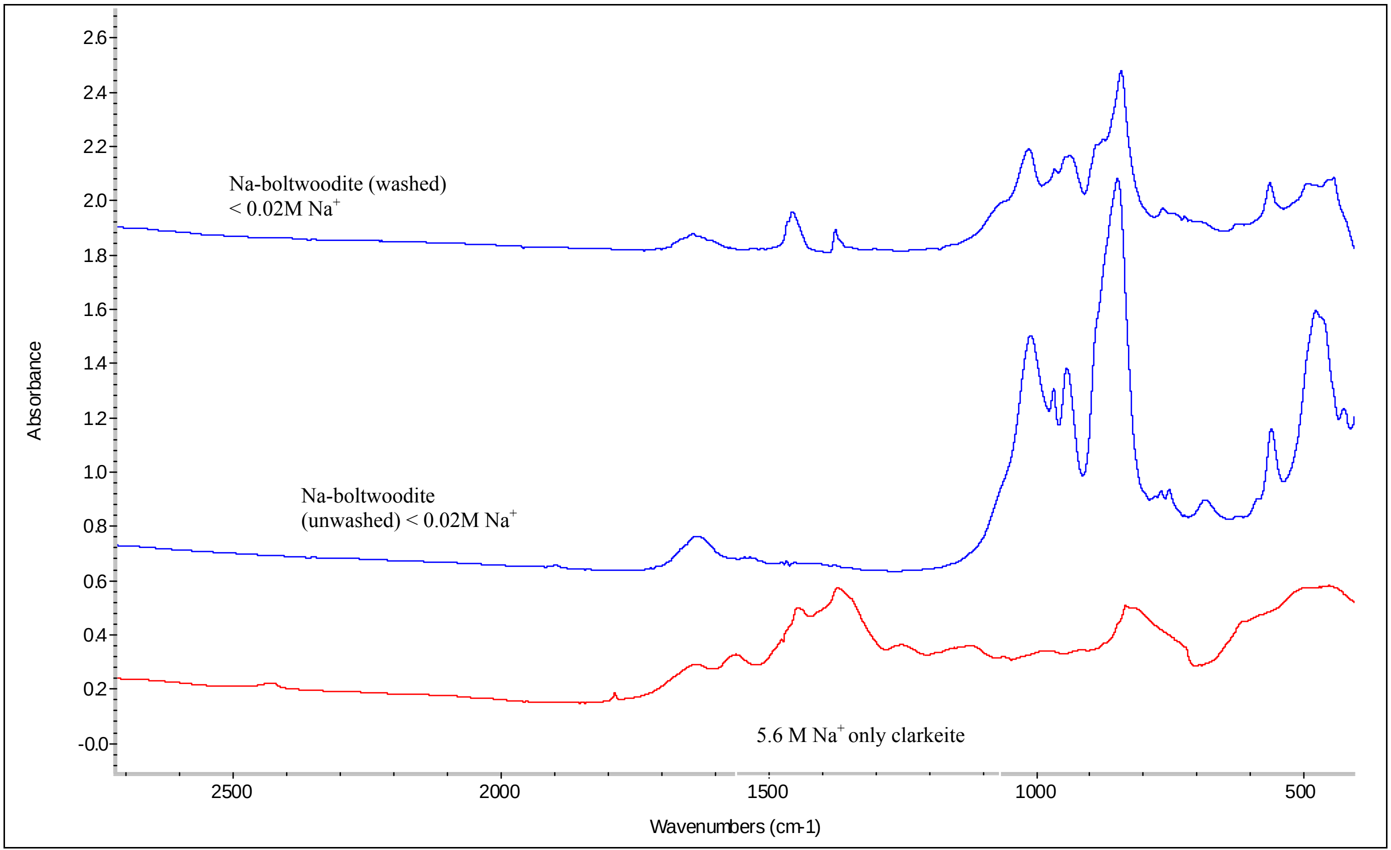


Figure 3. Infrared characterization (Overlay spectra) of solids made using the sodium boltwoodite synthesis method in the presence of low Na^+ (< 0.02 M) and high Na^+ (5.6 M).

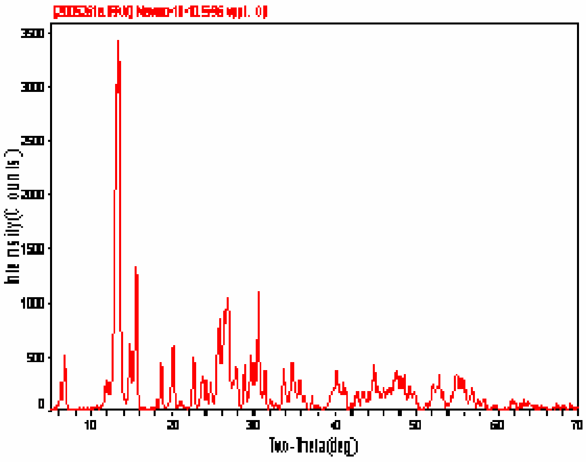
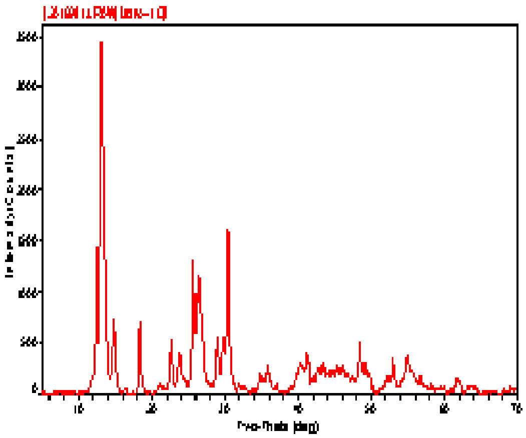
	
A: Sodium boltwoodite: Synthesis at < 0.02 M Na^+ with traces of impurities.	**B:** Uranophane: Synthesis at < 0.02 M Na^+ produced uranophane with traces of impurities.

Figure 4 (A, B). A typical XRD spectra for Sodium boltwoodite and Uranophane with traces of impurities.

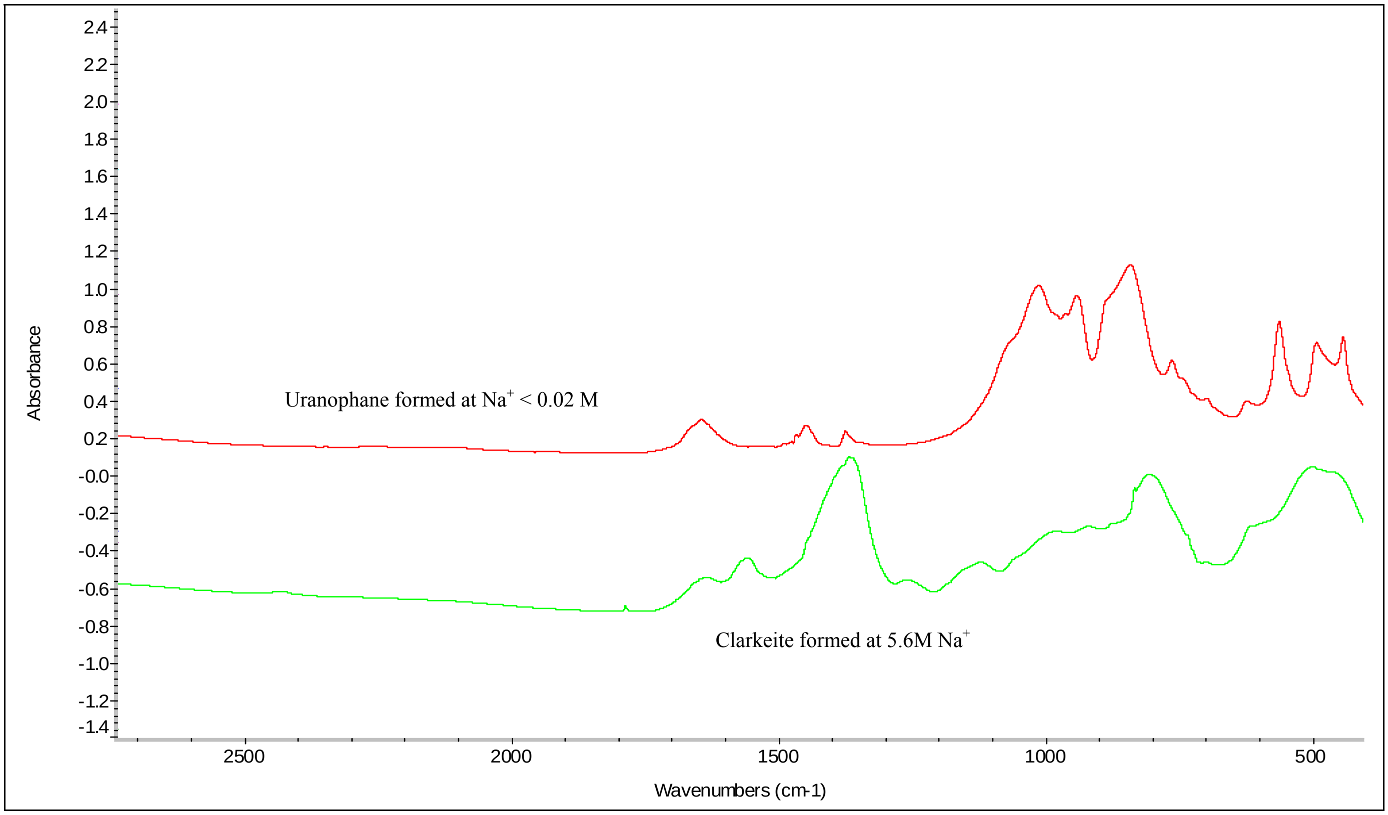


Figure 5. Infrared characterization (Overlay spectra) of solids made using the uranophane synthesis method in the presence of low Na$^+$ (< 0.02 M) and high Na$^+$ (5.6 M).

Table 1. Laboratory synthesis condition for the uranyl silicates versus evaporator operating conditions.

Condition	Evaporator operation	Uranyl silicate synthesis
Temperature, ºC	120-150	80-150
pH	>12	8.5-13
Uranium oxidation state	U^{+6}	UO_2^{2+}, uranyl silicate species
Pressure	Atmospheric	Atmospheric
Dissolved ions	U, Si, Na, Ca, K, etc.	U, Si, Na, Ca
Specific gravity	1.37-1.62	>1.30
Na^+ concentration	5.6 M	< 0.020 M

Table 2. A typical simulant salt composition.

Component		Sodium wt., g	Moles of component
Sodium nitrate	$NaNO_3$	118	5.13
Sodium nitrite	$NaNO_2$	20	0.87
Sodium sulfate	Na_2SO_4	40	0.87
Sodium carbonate monohydrate	$Na_2CO_3 \cdot H_2O$	10	0.218
Sodium hydroxide	NaOH	70	3.044
$[Na^+]$, M =11.22			

Table 3. Synthesis conditions for the uranyl silicates.

Target Uranyl Silicate	Mixing Time, h	pH	Reflux Temp. ºC	Reflux Time, h	Parr Reactor Temperature, ºC	Parr Reactor Synthesis Duration, (Days)
Sodium Weeksite	2	8.5, > 13	100	72	150	4
Sodium Boltwoodite	2	10.5, > 13	90	24	150	4
Uranophane	4	8, >13	90	24	118	4

Table 4 Summary of synthesized uranium silicate minerals.

Target mineral	**Sodium concentration, M**	**Synthesis temperature, ºC**	**pH**	**Synthesis Duration, h.**	**Primary mineral obtained**
Sodium weeksite	< 0.02	150	8.5	8	Undefined amorphous uranium silicate
Sodium weeksite	< 0.02	150	8.5	40	Sodium weeksite
Sodium weeksite	< 0.02 (washed)	150	8.5	40	Sodium weeksite
Sodium weeksite	< 0.02 (unwashed)	150	8.5	40	Sodium weeksite
Sodium weeksite	5.6	150	>13	40	**Clarkeite**
Sodium boltwoodite	< 0.02 (Washed)	150	10.5	96	Sodium boltwoodite
Sodium boltwoodite	< 0.02 (unwashed)	150	10.5	96	Sodium boltwoodite
Sodium boltwoodite	5.6	150	>13	96	**Clarkeite**
Uranophane	< 0.02	118	8	96	Uranophane
Uranophane	5.6	118	>13	96	**Clarkeite**

REFERENCES

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[1] W. R. Wilmarth, S. D. Fink, D. T. Hobbs, and M. S. Hay, “Characterization and Dissolution Studies of Samples from the 242-16H Gravity Line,” WSRC-TR-97-03326, October 16, 1997.

[2] W. R. Wilmarth, D. D. Walker, and S. D. Fink, “Sodium Aluminosilicate Formation in Tank 43H Simulant,” WSRC-TR-97-00389, Nov. 15, 1997.

[3] D. T. Hobbs and T. B. Edwards, “Solubility of Uranium in Alkaline Salt Solutions,” WSRC-TR-94-453, March 29, 1994.

[4] Reviews in Mineralogy, Volume 38: Uranium Mineralogy, Geochemistry and the Environment, 1999; P. C. Burns and R. Finch (eds.) Chapter 3: R. Finch and T. Murakami “Systematics and Paragenesis of Uranium Minerals,” pg. 91-179.

[5] S. N. Nguyen et al., “Standard Gibbs free energies of formation at the temperature of 303.15 K of four uranyl silicates: soddyite, uranophane, sodium bolwoodite and sodium weeksite,” *J. Chemical Thermodynamics, Vol. 24,* 359-376, 1992.

[6] F. Cesbron, P. Ildefonse, and M. Sichere, “New mineralogy data on uranophane and beta-uranophane; synthesis of uranophane,” *Mineralogical Magazine, Vol. 57,* 301-308 (1993).

[7] I. Perez, et al., “The thermodynamics and kinetics of uranophane dissolution in bicarbonate test solutions,” *Geochimica et Cosmochimica Acta. Vol. 64,* 603-608, (2000).

[8] P. C. Burns, R. A. Olson, R. J. Finch, J. M. Hanchar, and Y. Thibault, “$KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$ a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass,” *Journal of Nuclear Materials, Vol.* 278, 290-300 (2000).

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[9] R. Vochten, N. Blaton, and O. Peeters, “Synthesis of sodium weeksite and its transformation into weeksite,” *Neus Jb Miner Mh, Vol. 12*, 569-576 (1997).

[10] Reviews in Mineralogy Volume 38: Uranium Mineralogy, Geochemistry and the Environment, 1999; P. C. Burns and R. Finch (eds.) Chapter 12: J. Cejka, “Infrared spectroscopy and thermal analysis of the uranyl minerals,” pg. 521-622.

[11] W. R. Wilmarth, C. J. Coleman, A. R. Jurgensen, W. M. Smith, J. C. Hart, W. T. Boyce, D. Messimer, and C. M. Conley, “Characterization and Dissolution Studies of Samples from the 242-16H Evaporator,” WSRC-TR-2000-00038, Jan. 16, 2000.

[12] 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.