

Sodium Aluminosilicate Formation in Tank 43H Simulants

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Summary

This work studied the formation of a sodium aluminosilicate, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, at 40 °C, 95 °C, and 110 °C in simulated waste solutions with varied amounts of silicon and aluminum. The data agree well with literature solubility data for sodalite, the analogous chloride salt. The following conclusions result from this work.

- The study shows, by calculation and experiments, that evaporation of the September 1997 Tank 43H inventory will only form minor quantities of the aluminosilicate.
- The data indicate that the rate of formation of the nitrate enclathrated sodalite solid at these temperatures falls within the residence time (< 4 h) of liquid in the evaporator.
- The silicon in entrained Frit 200 transferred to the evaporator with the Tank 43H salt solution will quantitatively convert to the sodium aluminosilicate. One kilogram of Frit 200 produces 2.1 kg of the sodium aluminosilicate

Introduction

During July of 1997, operation of the 242-16H evaporator stopped due to low flow through the Gravity Drain Line (GDL) leading to Tank 38H. The Gravity Drain Line includes a 250 ft length of 304L stainless steel. Indications of flow restriction manifested as lower than expected lift rates of the concentrate from the evaporator. Video inspection of the Gravity Drain Line showed plugging of at least 90% of the inner diameter. Solid samples from the GDL showed a composition of $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.¹

Previously, Gasteiger et al. studied the equilibrium of silicon and aluminum in aqueous alkaline solutions containing chloride ion.² The results of this work showed a dependency on several variables including temperature, hydroxide ion concentration and ionic strength. The dominant product formed during these studies was sodalite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$. One would expect that the nitrate enclathrated sodalite formed in the 242-16H Evaporator would exhibit similar solubility.

After the initial discovery of solids, High Level Waste personnel expended significant manpower and expense in water blasting the GDL to remove the solid deposits. Concurrently, a research program started to determine the source of the soluble silicon and conditions for solid formation. The tests described in this report sought to determine if DWPF Frit 200 would dissolve in the aqueous alkaline waste, convert to the sodium aluminosilicate, and if the current inventory in Tank 43H would produce the nitrate enclathrated sodalite during either storage or during evaporation.

Experimental

Initial Testing

Provided in Results and Discussion section of this report.

Frit Dissolution

In these tests, Frit 200 was added to simulated salt solutions and heated at either 40 or 95 °C. The samples were prepared in steel bottles and mixed only prior to sampling. Three salt solutions were prepared: (1) simulated concentrate (11.5 M Na⁺, 8 M NaOH), (2) average salt solution (5 M Na⁺, 2 M NaOH), and (3) DWPF recycle (0.7 M Na⁺, 0.5 M NaOH). No aluminum was added to the salt solutions to prevent precipitation of the silicon. Frit 200 (2 wt %) was added to each solution. Periodically, samples were taken, filtered, and analyzed for boron and silicon.

Aluminosilicate Formation Testing

Simulated Tank 43H salt solutions were prepared and spiked with varied amounts of silicon in the form of sodium silicate, Na₂SiO₃•4H₂O. Silicon varied as a function of the aluminum concentration. The silicon/aluminum ratios studied included 1/100, which is the current Tank 43H ratio, 1/10, and 1/1. Table 1 shows the composition of the stock salt solution.

The reaction vessels were carbon-steel, 160-mL capacity containers. Solutions were added to the vessel and samples pulled periodically through a septum port using a 5-mL glass syringe. The reaction vessels were placed in pre-heated ovens at 40 °C, 95 °C, and 110 °C. Temperatures were monitored using thermometers calibrated against standards traceable to NIST.

Table 1. Simulated Tank 43H Solution

Component	Concentration (molar)
Na ⁺	6.1
OH ⁻	4.0
NO ₃ ⁻	1.5
AlO ₂ ⁻	0.4

Samples were filtered using a 0.2 micron syringe filter and submitted to the Analytical Development Section for analysis using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES). Researchers repeated the 95 °C and 110 °C testing due to erratic behavior of the silicon and aluminum concentrations in the 7.5 hour and 86 hour samples. Laboratory notebook WSRC-NB-97-62 contains data obtained during these tests along with the procedures used.

Results and Discussion

The tests studied the rate of formation of the nitrate enclathrated sodalite at elevated temperatures similar to those found in the 242-16H evaporator. At these elevated temperatures, soluble silicon, in the form of SiO₃²⁻, and aluminum in the form of AlO₂²⁻, react to form a three dimensional structure with the formula [Al₆Si₆O₂₄]⁶⁻. Figure 1 shows the cage-like structure of this anion. Previous work² measured solubilities on the order of 10⁻⁴ mol²/kg.

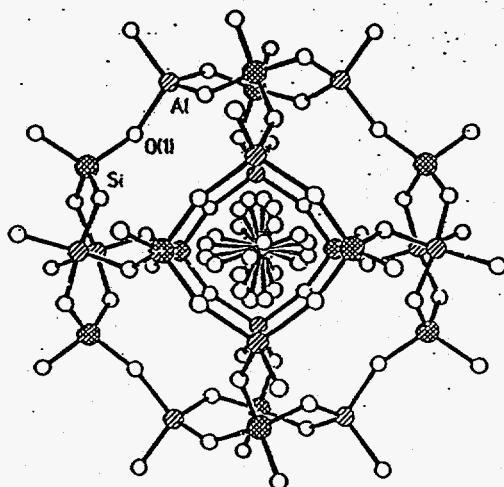


Figure 1. Structure of the Nitrate enclathrated Sodalite Anion.

Initial Tests of Frit 200

Researchers performed two experiments to examine the formation of the aluminosilicate in simulated SRS waste. These experiments showed the nitrate salt of the aluminosilicate framework as the favored product, although another compound, presumably hydroxysodalite, forms when nitrate is minimized. The yield of product was near stoichiometric based on the amount of silicon added as Frit 200. This result agrees with the solubility data for sodalite shown in Figure 2. Frit 200 is currently used in the Defense Waste Processing Facility and some of it transferred to the tank farm. Table 2 lists the composition of the frit. For most tank farm waste solutions, aluminate exists in large excess over silicon. Thus, the introduction of silicon determines the amount of precipitate that forms.

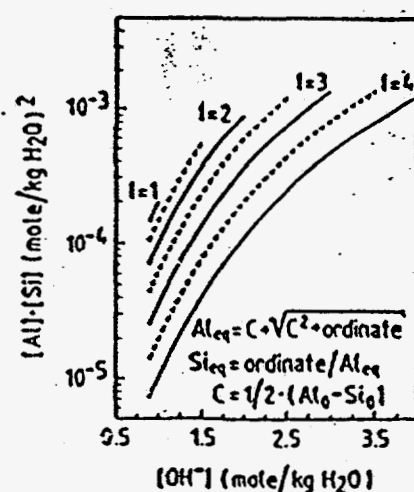


Figure 2. Solubility of Sodalite in Alkaline Solutions

Table 2. Composition of Frit 200

Component	Concentration (wt %)
SiO ₂	70
B ₂ O ₃	12
Na ₂ O	11
Li ₂ O	5
MgO	2

The first experiment used salt solution (350 mL) corresponding to the average waste composition shown in Table 1. Frit 200 (3.05 grams) was added and the solution boiled for two hours in a stainless steel beaker. During this time, solids were always present and the volume of solution was reduced by approximately 50% (175 mL). The solution cooled overnight and copious amounts of salt crystallized. On the second day, water (75 mL) was added and the slurry was boiled again for 2.5 hours without reducing the volume. After cooling, the solids were filtered, washed with water, and dried for 2 hours at 85 °C. The yield of white powder was 4.63 grams. However, approximately 1-2 grams of compact solids adhered to the bottom, heated surface of the beaker and were discarded. The dried solids were identified as $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ by X-ray diffraction (Figure 3). The yield measured 77% based on the silicon content of the Frit 200. Allowing for discarding some material, the yield approached 100%.

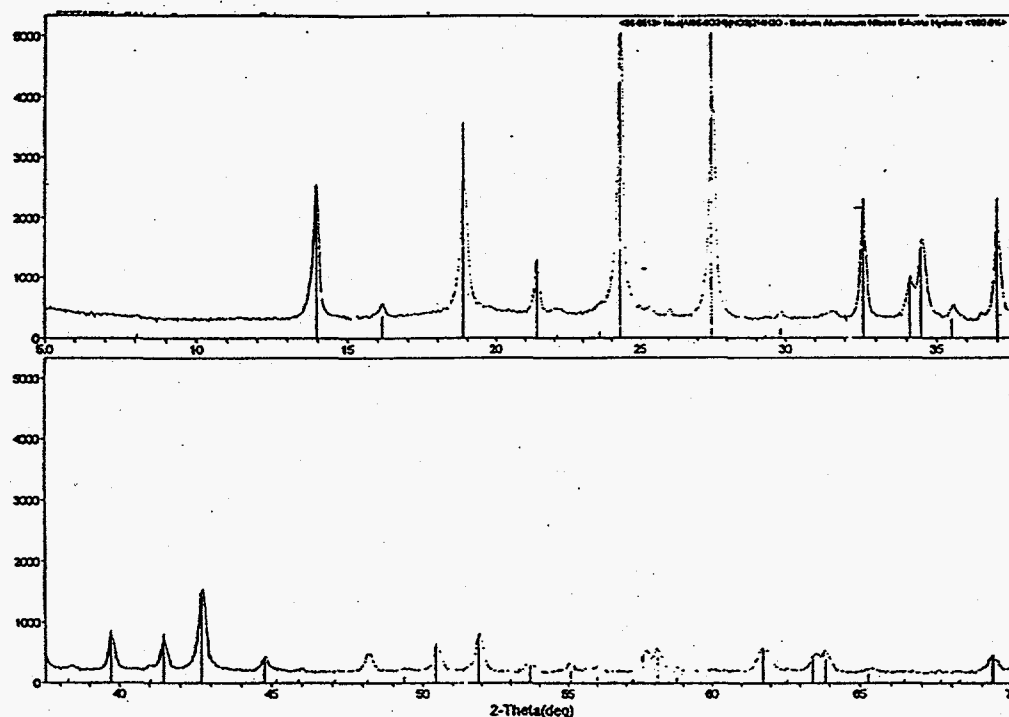


Figure 3. X-Ray Diffraction Pattern for Product of First Experiment (Reference spectrum of $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is also shown)

The second experiment boiled Frit 200 (3.04 grams) in 3.0 M NaOH solution (350 mL) for 2 hours in a stainless steel beaker. During this time, solids were always present and the volume of solution was reduced by approximately 50% (175 mL). The solution cooled overnight with no significant change in the solids. On the second day, boiling was repeated for 2.5 hours without reducing the volume, during which time the frit dissolved leaving a slightly cloudy solution. After cooling, a solution (100 mL) of aluminum nitrate nonahydrate (18.9 g) and sodium hydroxide (20.0 grams) was added. No significant precipitation occurred over a three-day period at room temperature. The solution was boiled again for 3.5 hours and a precipitate formed. The solids were filtered, washed with water, and dried for 3.5 hours at 85 °C. The yield of white powder was 5.2 grams. Figure 4 shows the X-ray diffraction pattern for the product. The peak spacings appear very similar to the nitrate salt shown in Figure 3, but with different peak intensities. This product may include hydroxysodalite or a mixed hydroxide and nitrate compound. This result is not surprising since the concentration of nitrate ion in this experiment was very low compared to the first experiment. The yield of hydroxysodalite equals 93% of theoretical based on the silicon in the frit.

Table 3. Solubility Calculations for Simulant Experiments

Component	Experiment	
	<u>First</u>	<u>Second</u>
	<u>Concentration (molar)</u>	
Na ⁺	7.7	4.5
Al(OH) ₄ ⁻	0.41	0.18
Si	0.14	0.14
OH ⁻	2.1	3.7
[Al]x[Si], mol ² /kg ²		
experiment	5.7x10 ⁻²	2.5x10 ⁻²
limit (Ref.2)	1x10 ⁻⁵	6x10 ⁻⁴
Predicted yield:	100%	100%

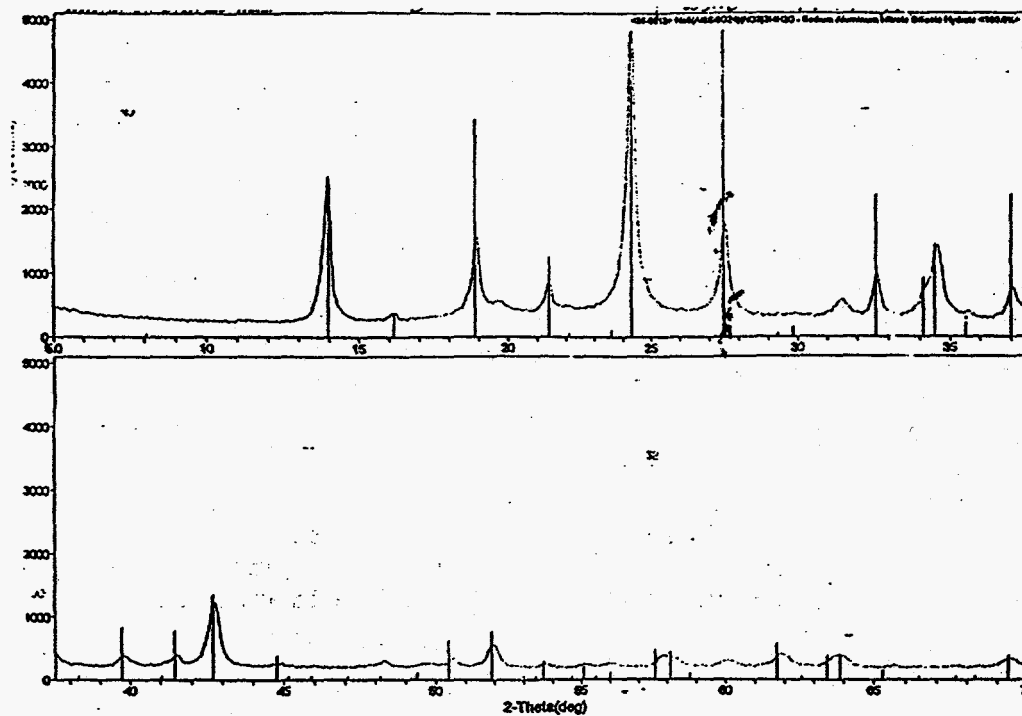


Figure 4. X-Ray Diffraction Pattern for Product of Second Experiment (Reference spectrum of $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is also shown)

Table 4. Expected Conditions for Tank 43H Salt Solution

Tank 43H salt solution composition

<u>Component</u>	<u>Concentration (molar)</u>
Na^+	6.2 ^a
OH^-	2.6 ^b
$\text{Al}(\text{OH})_4^-$	0.13 ^a
Si	0.0015 ^a

Solubility product $[\text{Al}]\text{x}[\text{Si}]$ (moles²/kg² water)

from Ref.1: 1×10^{-4}

observed: 2×10^{-4}

^a Based on analyses of samples HTF-028 and HTF-029 by W. R. Wilmarth.

^b Based on May 1997 sample reported in Reference 4.

The high product yields in these two experiments indicate the aluminosilicate compound remains insoluble under the experimental conditions. This finding agrees with the solubility data for sodalite. Table 3 summarizes experimental conditions used in the tests reported here and the expected solubility derived from the sodalite data from Gasteiger, et al.² For both experiments, the data in Figure 2 was extrapolated to estimate the limiting $[Al]x[Si]$ product. The table ignores the effect of temperature with the solubility shown at 95 °C.

One can also use the sodalite data to predict the formation of the aluminosilicate compound when processing salt solution from Tank 43H through the evaporator. Table 4 lists the composition of Tank 43H salt solution and the expected solubility product.

The observed concentrations of aluminum and silicon agree closely with the solubility limit, indicating Tank 43H salt solution appears close to saturation relative to formation of the aluminosilicate compound. When processing the Tank 43H salt solution through an evaporator, the operation will precipitate not more than 1.5 grams of aluminosilicate per liter of Tank 43H feed. This amount of aluminosilicate is calculated based on silicon being the limiting reagent and complete conversion of the silicon to aluminosilicate. Under actual operating conditions, the yield will prove less.

Since the Tank 43H salt solution nears saturation, addition of silicon will precipitate the aluminosilicate compound. The reaction will occur almost quantitatively until the aluminum concentration drops appreciably. Thus, if Frit 200 transfers to the evaporator with salt solution, as much as 140 grams of aluminosilicate could form per liter of salt solution. This upper limit corresponds to 5 wt % frit in the salt solution and assumes all of the aluminum precipitates.

Frit Dissolution Kinetics

Frit dissolution tests indicate that frit dissolves rapidly in unstirred, hot salt solutions. Under well-mixed conditions in an evaporator, all of the frit in a 1 wt % feed will dissolve. At expected storage tank temperatures (40 °C), the rate decreases to less than 2% of the high temperature rate, but remains fast enough to dissolve significant amounts of frit during storage.

In these tests, Frit 200 was added to simulated salt solutions and heated at either 40 or 95 °C. The samples were prepared in steel bottles and mixed only prior to sampling. Three salt solutions were prepared: (1) simulated concentrate (11.5 M Na⁺, 8 M NaOH), (2) average salt solution (5 M Na⁺, 2 M NaOH), and (3) DWPF recycle (0.7 M Na⁺, 0.5 M NaOH). Table 5 and 6 list the salt solution and Frit 200 compositions, respectively. No aluminum was added to the salt solutions so as to prevent precipitation of the silicon. Frit 200 (2 wt %) was added to each solution. Table 6 lists the composition of Frit 200. Periodically, samples were taken, filtered, and analyzed for boron and silicon. Figures 5 and 6 show the changes in silicon and boron concentrations at 95 °C and 40 °C respectively. Table 7 lists the data graphed in the two figures.

Table 5. Composition of Salt Solutions

Component	Concentration (molar)		DWPF Recycle
	Concentrate	Average	
Na ⁺	11.5	5.0	0.7
OH ⁻	8.0	2.5	0.5
NO ₃ ⁻	2.5	1.5	0.1
NO ₂ ⁻	0.5	0.5	0.1
SO ₄ ²⁻	0.25	0.25	-

Table 6. Composition of Frit 200

Component	Concentration (wt %)
SiO ₂	70
B ₂ O ₃	12
Na ₂ O	11
Li ₂ O	5
MgO	2

At both temperatures, silicon concentrations in filtered samples increased linearly with time (Figures 5 and 6). At 95 °C, more than 70% of the frit dissolved in 24 hours. At 40 °C, only 20% of the frit dissolved in three weeks. Table 8 gives the rates of increase in silicon. Frit dissolution as measured by soluble silicon was confirmed by corresponding increases in soluble boron. The boron yields reached between 81 to 94 % of the expected value calculated from the silicon results and frit composition. The low boron yields could reflect low boron content in this batch of frit, or biases in the analyses.

Only slight differences existed in rate between the three salt solution compositions at 95 °C, but significant differences resulted at 40 °C. At both temperatures, the fastest rates occurred in average salt solution and the slowest rates in concentrate. This order of reactivity between the three solutions may reflect to opposing factors. Dissolution of silica should increase with higher sodium hydroxide concentrations. Thus, the concentrated solution should dissolve frit fastest of the three salt compositions. However, increased mixing should also increase the rate of dissolution. Under the test conditions with mechanical mixing only prior to sampling, the major

mixing came from convection caused by temperature. Differences in viscosity may have significant impact on the convective mixing. Since the viscosity increases with hydroxide concentration, the concentrate should dissolve frit the slowest of the three. The balance between these opposing effects could produce the observed order of reactivity.

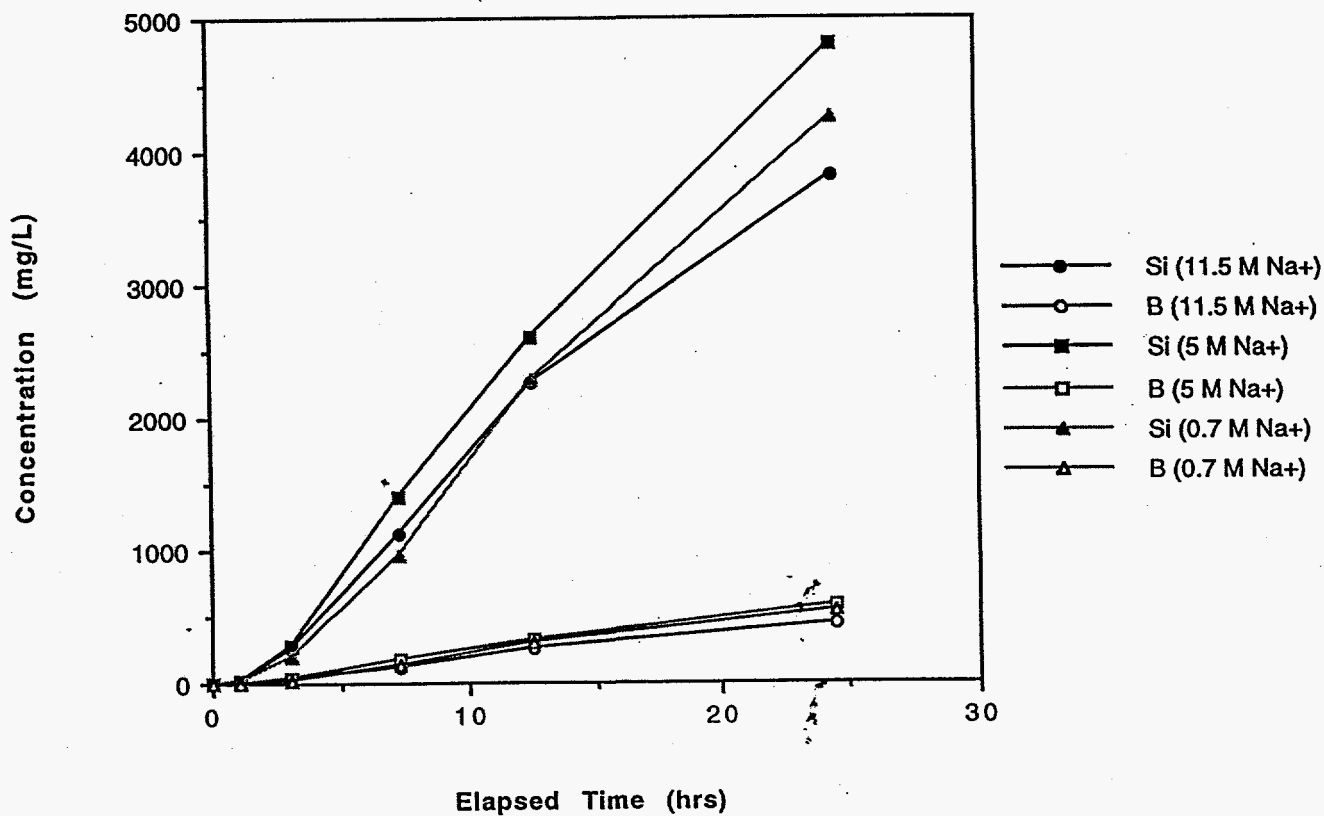


Figure 5. Silicon and Boron Behavior at 95 °C

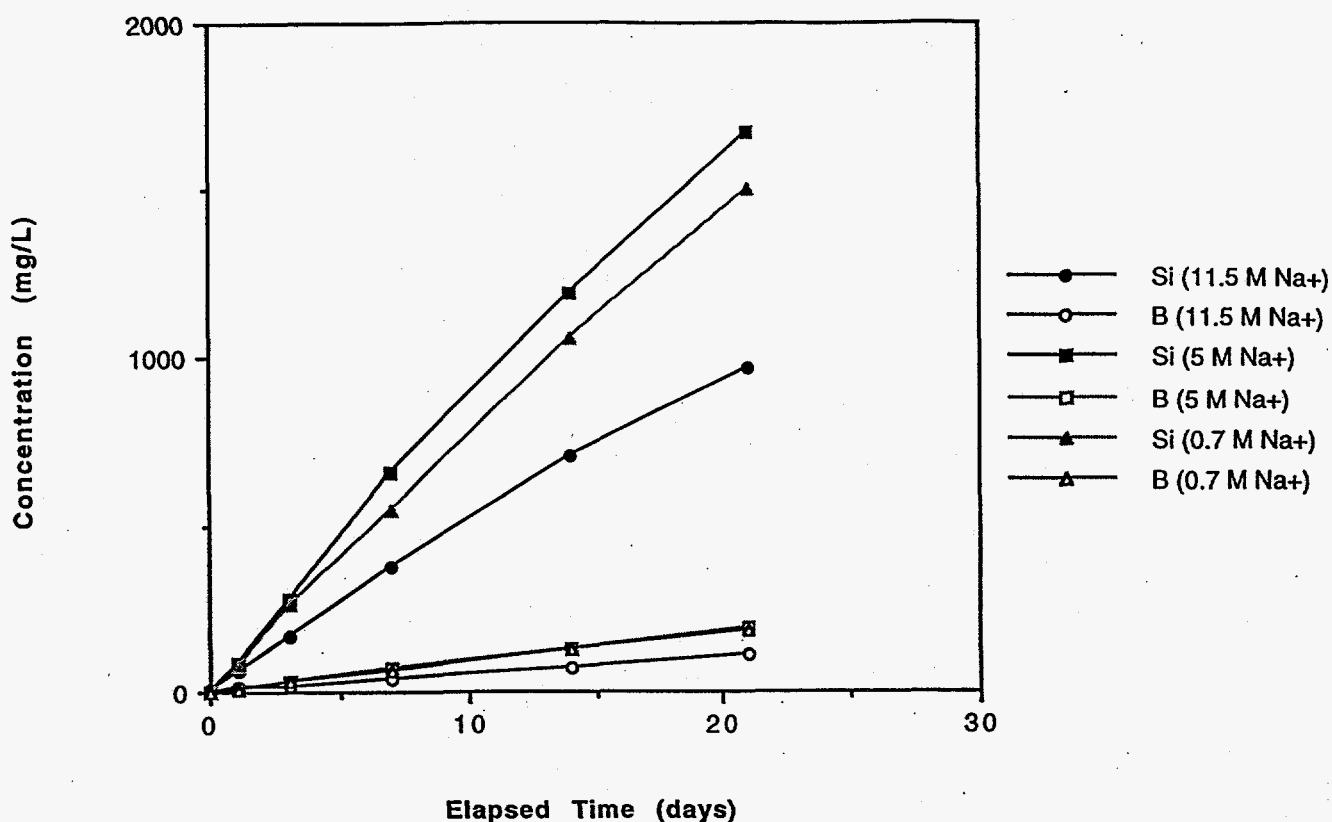


Figure 6. Silicon and Boron Behavior at 40 °C

Sodium Aluminosilicate Formation Kinetics Testing

In these experiments, soluble silicon and aluminum reacted quickly in aqueous alkaline solutions containing 3 M hydroxide ion and 6 M sodium ion. Table 9, 10, and 11 provide the data for the aluminum and silicon concentrations as a function of time for 40 °C, 95 °C and 110 °C, respectively.

40 °C Tests

In conditions similar to the September 1997 inventory Tank 43H (i.e., 100/1 Al/Si for sample Na/Al/Si-26 of Table 9), no loss of soluble silicon or aluminum occurred over a prolonged period (72 h) at 40 °C. However, this temperature was sufficient to affect a formation of the sodium aluminosilicate if excess silicon and aluminum exist in solution. Measurable loss of silicon occurred within 72 hours in sample Na/Al/Si-12 with loss of aluminum observed in sample Na/Al/Si-24. The calculated solubility product, K_{sp} , for the equilibrium silicon and aluminum concentrations ranged for $2.43 \times 10^{-4} \text{ mol}^2/\text{kg}^2$ to $8.7 \times 10^{-5} \text{ mol}^2/\text{kg}^2$. Formation of the aluminosilicate, even at this lower temperatures, occurs rapidly with an expected reaction half life of approximately 40 hours.

Table 7. Silicon and Boron Concentration in Salt Solutions

Temperature = 95 °C

Elapsed Time (h)	Si Concentration (mg/L)		
	Concentrate	Average	DWPF Recycle
0	8.1	1.9	0.6
1	24.	18.	16.
3	258.	290.	193.
7.3	1124	1397	960
12.5	2262	2609	2276
24.5	3817	4798	4266

Elapsed Time (h)	B Concentration (mg/L)		
	Concentrate	Average	DWPF Recycle
0	1.7	0.01	0.01
1	2.0	1.7	1.6
3	31	36	26
7.3	129	172	132
12.5	262	321	292
24.5	438	577	536

Temperature = 40 °C

Elapsed Time (days)	Si Concentration (mg/L)		
	Concentrate	Average	DWPF Recycle
0	8.6	1.9	0.6
1	61	89	76
3	165.	283.	266
7	377	657	542
14	708	1190	1059
21	968	1672	1500

Elapsed Time (days)	B Concentration (mg/L)		
	Concentrate	Average	DWPF Recycle
0	1.7	0.01	0.01
1	13	11	10
3	16	28	30
7	37	70	64
14	70	131	128
21	110	190	184

Table 8. Dissolution Rates

<u>Salt Solution</u>	Rate			
	95 °C (mg/L/hr)		40 °C (mg/L/day)	
	<u>Si</u>	<u>B</u>	<u>Si</u>	<u>B</u>
Concentrate	164	19	46	5.0
Average Salt	204	25	80	9.1
DWPF recycle	182	23	72	8.8

These observations, in conjunction with the dissolution rate of frit, indicate that the sodium aluminosilicate will form in Tank 43H prior to the evaporation process. Due to the specific gravity of the material, the sodium aluminosilicate will likely remain in the heel following transfer to the evaporator.

Table 9. Aluminum and Silicon Concentrations in Tank 43H Simulants at 40 °C

Sample	Time(h)	Al (mg/L)	Si (mg/L)	Al (mol/L)	Si (mol/L)
Na/Al/Si-26	1	2652	58.86	0.09830	0.00210
1:100 Si:Al	24	2649	53.86	0.09818	0.00191
Ratio	48	2511	54.4	0.09307	0.00192
	72	2658	46.41	0.09852	0.001652
Na/Al/Si-12	1	2626	493.9	0.09733	0.01758
1:10 Si:Al	24	2636	482	0.09770	0.01716
Ratio	48	2540	346.0	0.09408	0.01232
	72	2298	80	0.08517	0.00285
Na/Al/Si-24	1	161.1	1069	0.00598	0.03806
1:1 Si:Al	24	128.9	1033	0.00478	0.03678
Ratio	48	116.9	1202	0.00433	0.04279
	72	58.3	1127	0.00216	0.04012

Note: Time "zero" samples were not taken.

95 °C Tests

In conditions similar to evaporating the September 1997 inventory of Tank 43H (100/1 ratio of Al/Si similar to samples Na/Al/Si-1 and Na/Al/Si-10), no loss of soluble silicon or aluminum occurred over a prolonged period at 95 °C. This finding agrees with estimates reported in the initial testing described above. The observed solubility product constant, K_{sp} , measured 2.03 to $2.26 \times 10^{-4} \text{ mol}^2/\text{kg}^2$. Samples from the heated solutions remained clear. Subsequent filtering of the solution did not recover any measurable solids.

In tests containing silicon and aluminum above the solubility limit (i.e., tests Na/Al/Si-2, 3, 12, 13 and 14), loss of silicon or aluminum occurred. The reaction occurred within the sampling time and produced solutions depleted in silicon for test number Na/Al/Si-2, 12 and 13 and depleted in aluminum for test number Na/Al/Si-3, 14, and 15. The reaction completed within 5 to 6 hours. The observed K_{sp} measured $2.42 \times 10^{-4} \text{ mol}^2/\text{kg}^2$ to $4.27 \times 10^{-5} \text{ mol}^2/\text{kg}^2$, with an average of $1.50 \times 10^{-4} \text{ mol}^2/\text{kg}^2$. In each case, x-ray diffraction identified solids collected after filtration as the nitrate enclathrated sodium aluminosilicate.

110 °C Tests

As in the 95 °C tests, the Tank 43H simulant (Na/Al/Si-4 and Na/Al/Si-11) showed no reaction. The high aluminum and silicon values at 7.5 hours in the first run (Na/Al/Si-4) reflect a precipitation problem in the sample after sample collection. Analytical Development Section (ADS) personnel observed solids in the filtered sample. In general the 7.5-hour samples from each of the first tests showed abnormal results for all six tests. This sampling protocol apparently led to post-filtration precipitation, as observed by ADS personnel in at least one sample. However, the 86 hour sample showed similar solution values.

Reactions removing silicon and aluminum from solution occurred in the 10/1 (Na/Al/Si-5 and Na/Al/Si-13) and 1/1 (Na/Al/Si-6 and Na/Al/Si-15) samples. The solubility products calculated from the data range from $1.4 \times 10^{-3} \text{ mol}^2/\text{kg}^2$ to $3.6 \times 10^{-5} \text{ mol}^2/\text{kg}^2$. These K_{sp} values compare favorably to those obtained at 40 °C and 95 °C indicating little temperature dependence of solubility at the high ionic strength of these solutions.

Table 10. Aluminum and Silicon Concentrations in Tank 43H Simulants at 95 °C

Sample	Time (h)	Al (mg/L)	Si (mg/L)	Al (mol/L)	Si (mol/L)
Na/Al/Si-1	0	2727	55.01	0.1011	0.00196
	1	2765	60.69	0.1025	0.00216
	3	2610	56.68	0.0967	0.00202
	5	2741	59.61	0.1016	0.00212
	7.5	2731	64.52	0.1012	0.00230
	86	2638	64.82	0.0978	0.00231
Na/Al/Si-2	0	2739	486.8	0.1012	0.01733
	1	2633	453.6	0.0976	0.01615
	3	2557	393.0	0.0948	0.01400
	5	2667	377.9	0.0988	0.01345
	7.5	2200	30.1	0.0815	0.00107
	86	2159	32.8	0.0800	0.00117
Na/Al/Si-3	0	2121	3225	0.0786	0.1148
	1	915.4	1923	0.0339	0.0684
	3	402.6	1336	0.0149	0.0476
	5	268.8	1224	0.0100	0.0436
	7.5	38.41	1016	0.0014	0.0362
	86	29.79	1086	0.0011	0.0388
Na/Al/Si-10	1	2772	57.77	0.1027	0.00206
	3	2634	62.52	0.0976	0.00223
	5	2685	62.43	0.0995	0.00222
	32	2763	66.18	0.1024	0.00236
Na/Al/Si-12	1	2626	493.6	0.0973	0.01758
	3	2636	482	0.0977	0.01726
	5	2540	346	0.0941	0.01232
	32	2298	79.96	0.0852	0.00285
Na/Al/Si-14	1	430.2	1520	0.0159	0.05411
	3	346.3	1404	0.0128	0.05000
	5	178.2	1242	0.0066	0.04422
	32	38.67	1099	0.0014	0.03912

Note: Time "zero" samples were not taken.

Table 11. Aluminum and Silicon Concentrations in Tank 43H Simulants at 110 °C

Sample	Time (h)	Al (mg/L)	Si (mg/L)	Al (mol/L)	Si (mol/L)
Na/Al/Si-4	0	2721	58.95	0.1004	0.00210
	1	2707	58.57	0.1003	0.00209
	3	2816	63.30	0.1044	0.00225
	5	2983	64.90	0.1106	0.00231
	7.5	7303	138.8	0.2707	0.00494
	86	7526	144.8	0.2790	0.00515
Na/Al/Si-5	0	2751	487.7	0.1020	0.01736
	1	2214	303.0	0.0821	0.01078
	3	2406	243.0	0.0892	0.00865
	5	2438	203.6	0.0904	0.00725
	7.5	2169	28.03	0.0804	0.00100
	86	901.9	30.71	0.0334	0.00109
Na/Al/Si-6	0	780	1828	0.0289	0.0651
	1	97.38	1089	0.0036	0.0388
	3	58.29	1113	0.0022	0.0396
	5	50.22	1178	0.0019	0.0419
	7.5	29.86	1662	0.0011	0.0592
	86	30.66	1850	0.0011	0.0659
Na/Al/Si-11	1	2622	60.45	0.0972	0.00215
	3	2689	68.68	0.0997	0.00225
	5	2620	66.75	0.0971	0.00238
	32	2638	58.34	0.0978	0.00208
Na/Al/Si-13	1	2562	223	0.0946	0.00794
	3	2454	166.5	0.0910	0.00593
	5	2292	86.1	0.0850	0.00307
	32	2208	44.83	0.0818	0.00160
Na/Al/Si-15	1	361.1	1475	0.0134	0.05251
	3	161.1	1195	0.0060	0.04254
	5	72.08	1077	0.0027	0.03834
	32	38.77	1064	0.0014	0.03788

Note: Time "zero" samples were not taken.

Rate of Formation

These tests provide an estimate of the rate of formation of nitrate enclathrated sodalite in simulated evaporator. If one assumes the reaction proceeds first order in silicon, then the tests with an aluminum-to-silicon ratio of 10/1 (Na/Al/Si-2 and Na/Al/Si-4) should provide kinetic information. The data for silicon concentration, neglecting the 7.5 h data points, was regressed using Microsoft® Excel to derive pseudo-first order rate constants. These rate constants measured 0.052 h^{-1} and 0.158 h^{-1} for 95°C and 110°C , respectively. This data exhibits an activation energy for the formation of the sodalite solids of approximately $30 \pm 25 \text{ kJ/mol}$.

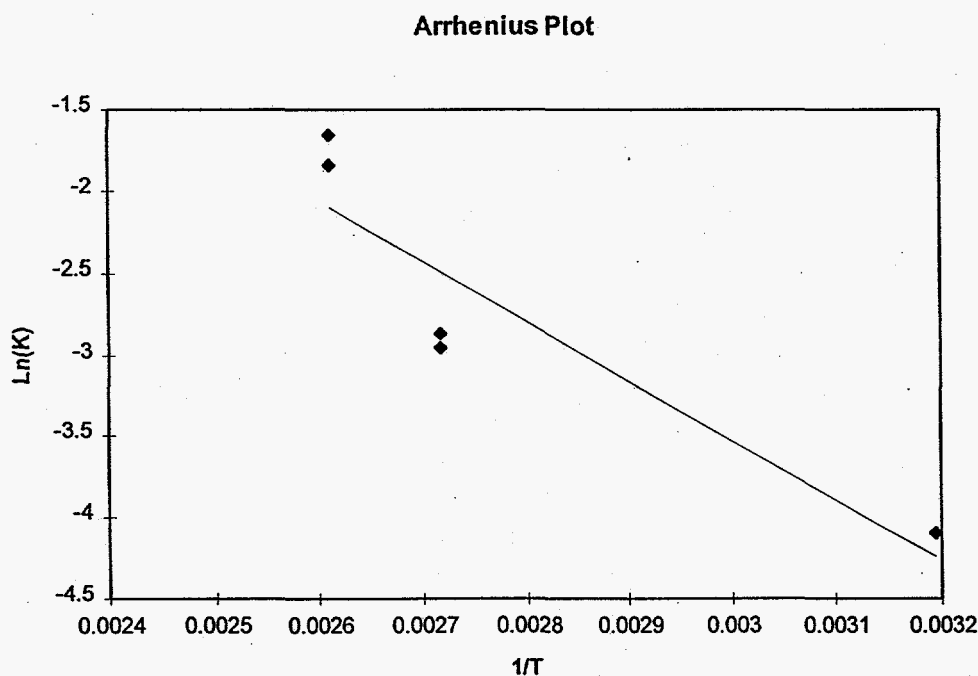


Figure 7. Arrhenius Plot of Sodium Aluminosilicate Formation

Conclusions

Researchers studied the formation of the nitrated enclathrated sodium aluminosilicate. This insoluble compound formed in the 242-16H Evaporator and plugged the Gravity Drain Line feeding Tank 38H. The results of this work indicate that Frit 200 used by the DWPF will dissolve rapidly in typical alkaline solutions at temperatures approximating the evaporator environment and will quantitatively convert to the sodium aluminosilicate. Formation, even at lower temperatures, occurs rapidly with an expected reaction half life at ambient temperatures of approximately 40 hours. Tests involving a Tank 43H simulant showed little or no solid formation. However, receipt of the DWPF Recycle stream in Tank 43H will introduce a source of silicon and renewed solid formation.

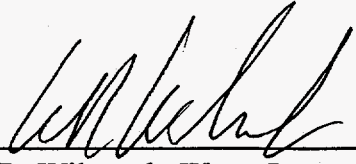
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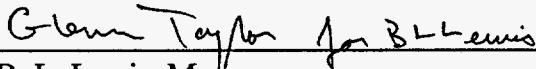
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