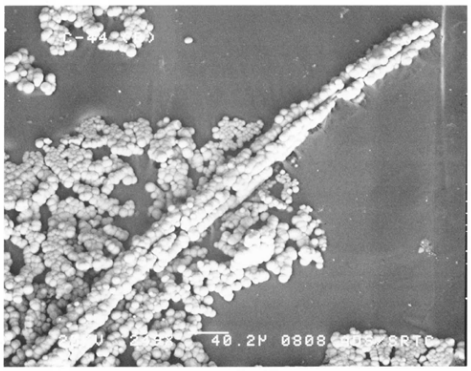
WSRC-TR-2001-00330

Results of Aluminosilicate Formation Testing



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

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Key Words: Aluminosilicate, Zeolite, Formation

Summary

The combination of silicon and aluminum in the highly caustic environment of Savannah River High Level Waste leads to the formation of sodium aluminosilicates. These solids phases have deposited in process vessels and have curtailed operation of important high-level waste evaporator operation. The Savannah River Technology Center (SRTC) along with the Oak Ridge National Laboratory and Pacific Northwest National Laboratory have been investigating the formation and deposition of aluminosilicates under high level waste conditions. The purpose of this work was to examine several experimental parameters of the formation of aluminosilicates under several tank chemistries, examine the conversion of crystalline phases, and determine inherent solubilities of certain crystal phases. Results of this work include the following.

- From a statistically designed set of experiments, we have shown that at nominal tank concentrations of aluminum the important parameters for the formation of sodium aluminosilicate are the silicon concentration and the hold time the mixture is held prior to heating to elevated temperature.
- Experiments tested the difference between frit 200 and sodium metasilicate for the source of silicon and found potentially slight differences. However, these slight differences do not outweigh the experimental difficulty of use frit.
- With respect to the conversion and solubility of crystalline phases, it was found, as classically reported in the literature, that a number of phases form during testing depending on the reaction temperature and ripening duration.
- Kinetic experiments show rapid conversion of the phases to sodalite at evaporator temperatures.
- Solubility measurements for zeolite A produced surprising results in that data indicates preferential solubilization of silicon over aluminum in simulated tank wastes.

Introduction

The 242-16H High Level Waste Evaporator processes radioactive waste from the feed tank (Tank 43H), concentrates the waste, and discharges to the concentrate receipt tank (Tank 38H). During this processing the waste typically concentrates by 30-40 vol %. However, during processing of Defense Waste Processing Facility Recycle stream, the concentration approaches 90 vol %. Included in the DWPF stream is dissolved and entrained silica. This silicon reacts with soluble aluminate ion to form an insoluble sodium aluminosilicate with a general chemical formula of $Na_8Al_6Si_6O_{24}(NO_3)_2$. This zeolilytic material has been found in the Gravity Drain Line and inside the Evaporator Pot. The accumulation of solids in the pot has prevented evaporator operation for over 1 year.

Previous testing showed the formation of aluminosilicate was rapid under evaporator conditions. These tests focused on the kinetic aspect of the aluminosilicate formation reaction and not on the precipitate characterization. Therefore, additional testing was performed to examine a wider set of chemistry conditions and examine the solid precipitate. Additionally, aspects of reaction pathways and crystal ripening were examined. These experiments complete work conducted in accordance with the Task Technical and Quality Assurance plan.

Experimental

Aluminosilicate formation tests were conducted in typical waste simulants.These tests were performed on a nominal 100-mL scale at 80 ° C for 48 hours. There are four variables (Na, Si, Al, and hold time) tested in statistically design set of experiments that includes two response variables (crystal structured produced and quantity of precipitate). The design is a three level screening factorial design. The details of the design are shown below in Table 1. Hydroxide concentration remained constant at 2 M free hydroxide. Sodium nitrate was used to balance the sodium ion concentration. After heating for 48 hours, liquid samples were removed for elemental analysis using Inductively Coupled Plasma – Emission Spectroscopy. Solids were collected, dried and weighed. Samples of the solids were sent for characterization including but not limited to X-ray Diffraction and Energy Dispersive X-ray Spectroscopy. Mathematical models were constructed using the JMP software.

Table 1. Statistical Design for Formation Tests

	Na (M)	Si (mg/L)	Al (mg/L)	Hold Time (h)
----	4	100	500	24
-+++	4	1000	15000	72
0+-0	6	1000	500	48
++0-	8	1000	1000	24
+0-+	8	500	500	72
00+-	6	500	15000	24
+-+0	8	100	15000	48

0-0+	6	100	1000	72
-000	4	500	1000	48

Another aspect of aluminosilicate formation was tested and that was path dependency. In these tests, an aliquot of either Si or Al will be added to a solution that is concentrated in the other component. For example, a caustic silicon solution was added to a salt solution containing significant concentration of aluminum. The other scenario was also tested. The solids formed in these tests were analyzed to determine differences in structure, composition and particle size.

The last tests examined crystal ripening. Scoping studies have shown that the initial precipitate has the Zeolite A structure; however, the sodalite structure is observed in the evaporator. Tests examined the conversion of Zeolite A into sodalite at elevated temperature as a function of time. Lastly, the solubility of Zeolite A in aluminum-free simulants was determined at different temperatures.

Results and Discussion

Statistically-Designed Formation Testing

Several variables have the potential to affect the amount and type of precipitate formed by the reaction of aluminate and silicate ions in highly caustic media. Therefore, using the simplified solution matrix suggested by Dworjanyn, et al., we examined the effect of four primary variables in a reduced matrix statistical design. The variables were sodium (reflective of ionic strength) aluminum, silicon, and hold time. All testing was at ambient temperature prior to heating at elevated temperature (80 ° C). As previously mentioned, Table 1 contains the statistical design. Additionally, two separate sets of experiments were conducted. The first set used sodium metasilicate as the source of silicon and the second set used Frit 200.

The results of the statistical modeling of the results from the tests containing sodium metasilicate as the source of silicon are compiled in Table 2. The linear model is capable of explaining most of the variance in the quantity of solids produced in each experiment ($R^2 = 0.9999$). Four terms incorporating the experimental variables proved to be statistically significant, i.e., have the value of Prob > | t| less than 0.05. These variables were the aluminum concentration, the time the solution was held at ambient temperature, quadratic term of silicon concentration and the quadratic term of the hold time. Interestingly, the silicon concentration was not statistically significant other than the quadratic term. However, with the limited number of experimental observations, we may not be able to discriminate between the silicon terms.

Table 2. Statistical Model of Solids Formation from Metasilicate-Containing Experiments

Solution Type A (Metasilicate)

Response Wt of Solids Produced (g)

Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.99999
RSquare Adj	0.999919
Root Mean Square Error	0.001185
Mean of Response	0.1276
Observations (or Sum Wgts)	9

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	7	0.13821321	0.019745	14051.29
Error	1	0.00000141	0.000001	**Prob > F**
C. Total	8	0.13821462		0.0065

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.1136527594	0.003577	31.78	0.0200
Si (mg/L)	-0.000014902	0.000006	-2.53	0.2399
Al (mg/L)	0.0000515556	0.000002	23.99	0.0265
Hold Time (h)	-0.007443107	0.000143	-52.03	0.0122
Si (mg/L)*Si (mg/L)	0.0000002925	5.508e-9	53.11	0.0120
Al (mg/L)*Al (mg/L)	-0.000000003	1.36e-10	-21.18	0.0300
Hold Time (h)*Al (mg/L)	-0.000000023	4.243e-9	-5.41	0.1163
Hold Time (h)*Hold Time (h)	0.0000729167	0.000001	50.11	0.0127

Table 3 contains the linear model coefficients for the results of the frit-containing experiments with regards to the amount of solids produced. The model is slightly different than the metasilicate model. One might suspect that hold time would be more significant in these tests because frit needed to dissolve to provide a source of soluble silicon to react. Indeed, two terms involving hold time were statistically significant. These variables were the cross term involving hold time and sodium concentration and the quadratic term of hold time. Lastly, silicon was also a statistically significant variable.

Table 3. Statistical Model of Solids Formation from Frit-Containing Experiments

Solution Type Frit

Response Wt of Solids Produced (g)

Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

Rsquare	0.999859
RSquare Adj	0.998876
Root Mean Square Error	0.006124
Mean of Response	0.207789
Observations (or Sum Wgts)	9

Analysis of Variance

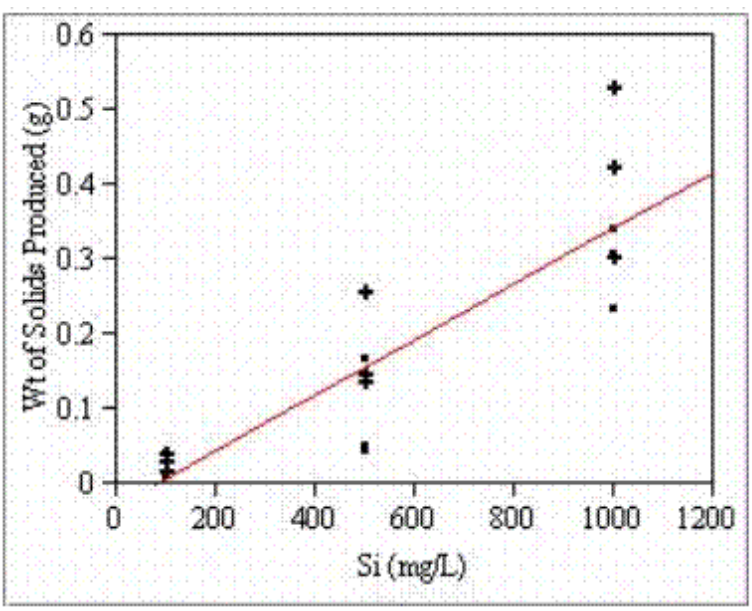
The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	7	0.26675685	0.038108	1016.217
Error	1	0.00003750	0.000038	**Prob > F**
C. Total	8	0.26679435		0.0241

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-0.111067	0.047381	-2.34	0.2567
Na (M)	0.0419417	0.01375	3.05	0.2017
Si (mg/L)	0.0004258	0.000026	16.69	0.0381
Hold Time (h)	-0.002232	0.000908	-2.46	0.2460
Na (M)*Na (M)	0.0045958	0.001083	4.25	0.1473
Si (mg/L)*Si (mg/L)	-8.167e-8	2.373e-8	-3.44	0.1801
Hold Time (h)*Na (M)	-0.001811	0.00009	-20.08	0.0317
Hold Time (h)*Hold Time (h)	0.0001211	0.000008	16.10	0.0395

We, also, examined the responses of each variable across the entire data set for the experiments conducted with both frit and sodium metasilicate. Figure 1 shows the response for the amount of solids collected versus silicon concentration. A linear model was constructed and fit to the solids formation data. The model can explain much of the variance in the data (R^2 = 0.78). Note the equation is only valid when there is sufficient aluminum for the reaction to proceed.



Wt of Solids Produced (g) =
-0.030442 + 0.0003715 Si (mg/L)

Figure 1. Relationship between Solids Formed and Silicon

Likewise, the relationship between the amount of solids collected and hold time was examined. Figure 2 shows the linear model developed for this relationship. The linear model does not fit the data (R^2 = 0.2). The effect of hold time

in the individual models showed a quadratic term that was statistically significant. Further work is need to understand the effect of hold time.

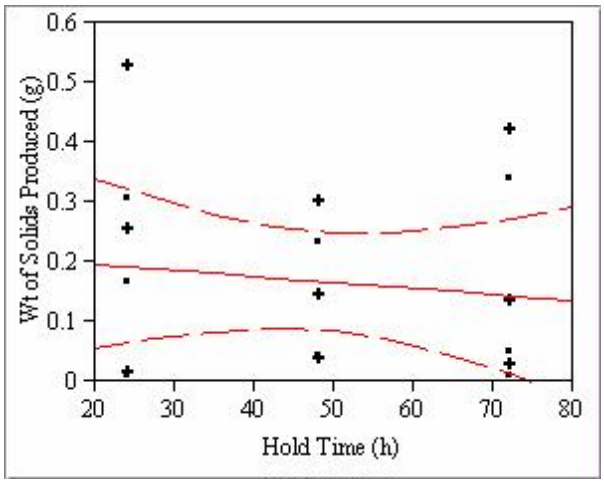


Figure 2. Relationship between Hold Time and Solids Produced

X-ray diffraction powder patterns were obtained from each sample of solids produced in these tests. Three solid phases were identified including the nitrate enclathrated sodalite and two other aluminosilicates with patterns numbered 75-2318 and 79-1159. Recognizing the limitations of X-ray diffraction analyses, we examined the patterns and assigned each phase a value between 0 and 3 with 0 being insufficient solids to analyze and 3 being a major contribution to the overall diffraction pattern. Linear models were constructed for each the crystalline phases and each of the experimental variables. Mostly, the patterns included all three phases and sodalite and the 75-2318 pattern were predominant.

The model that best fit the data for the combined frit and metasilicate experiments is shown in Figure 3. The model, however, only explains a portion in the variability of the data (R^2 = 0.46). The data suggests that with increasing starting silicon concentration there is an increase in the sodalite phase in the X-ray powder pattern. The effect may be real or the amount of solids culd provide a bias in allowing better (larger crystals) to be examined.

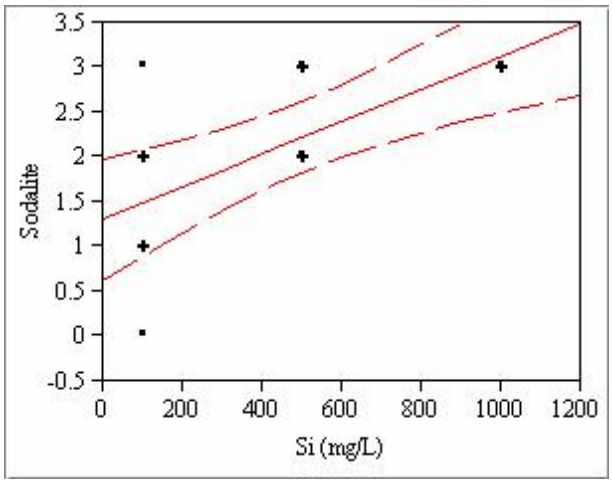


Figure 3. Relationship between Crystal Structure and Silicon Concentration

Crystal Ripening and Path Dependency

The deposits in the 242-16H Evaporator pot are predominately the sodalite polymorph of the sodium aluminosilicate with the general formula $Na_8Al_6Si_6O_{24}(NO_3)_2$-$4H_2O$. The deposits also contain approximately 10 wt % uranium. The sodium aluminosilicate with this chemical formula exists in two crystallographic phases. The sodalite phase is cubic and belongs to the P43n space group. The other polymorph is cancrinite and is hexagonal belonging to the $P6_3$ space group. Zheng, et al. observed transformation of sodalite to cancrinite in caustic media at temperatures of 90 to 160 ° C.

This caustic media was high in carbonate concentration compared to Savannah River High Level Wastes. Buhl and Löns examined the pure Na_2O-$2SiO_2$-Al_2O_3-$NaNO_3$-H_2O system under hydrothermal conditions and found the sodalite structure to be the stable phase. The previous experiments at SRTC have observed other crystalline phases such as Zeolite A and hydroxysodalite.

The number of possible crystalline phases could complicate the interpretation of experimental results. We propose that regardless of the precursor phase that sodalite was the stable phase. Therefore, we wanted to observe the kinetic of this phase change. Samples of Zeolite A, supplied by Linde, was contacted with aluminum-containing salt solution at 100 ° C for various durations. The solid phase was filtered and submitted for X-ray diffraction analysis. Please note that the material as received likely also had trace amounts of organic binders that could possibly play a role.

Figure 4 shows the results of this transformation testing. The first pattern is the baseline diffraction pattern for Zeolite A. There is a very intense peak at ~ 7° 2q from the (110) reflection in the Zeolite A structure. The next pattern is from the solids after exposure to salt solution for 1 hour at 100 ° C. One observes the same diffraction peaks from Zeolite A but another diffraction peak is detectable at 12° . This is the (110) reflection in the cubic sodalite phase. As observed in the next pattern taken after 4 hours at 100 ° C, the sodalite reflection is the dominant peak. In the final pattern taken after 24 hours, the Zeolite A diffraction pattern is no longer observable. The results strongly suggest that regardless of the initial phase formed that the thermodynamically favored sodalite phase will be ultimately produced. This is in excellent agreement with the classical literature regarding transformation of aluminosilicate phases.

In a related experiment, we examined the whether the mechanism for formation of aluminosilicate was dependent upon the limiting reagent. In most of the testing currently underway in the research and development program for the 2H Evaporator, silicon is the limiting reagent. In the actual tank chemistry, silicon was the limiting reagent when the DWPF recycle water was introduced. However, during 1998, the reaction between silicon and aluminum in Tank 43H reduced the aluminum concentration substantially. Additions of aluminum from H-canyon were resumed in late 1998. This "spike" of aluminum would react with the soluble silicon and produce an aluminosilicate.

Therefore, we produced a 6 M sodium salt solution that was 4 M sodium hydroxide and 1 M sodium nitrate and sodium nitrite. The starting silicon concentration was 1000 mg/L. To this solution we spiked a sodium aluminate solution and heated at 100 ° C for 48 hours. Afterward, we collected the solids and analyzed by X-ray diffraction analysis. Figure 5 shows the X-ray diffraction pattern obtained from the solids produced during this test. The pattern matches those produced in the set of statistically-design experiments previously discussed in this report.

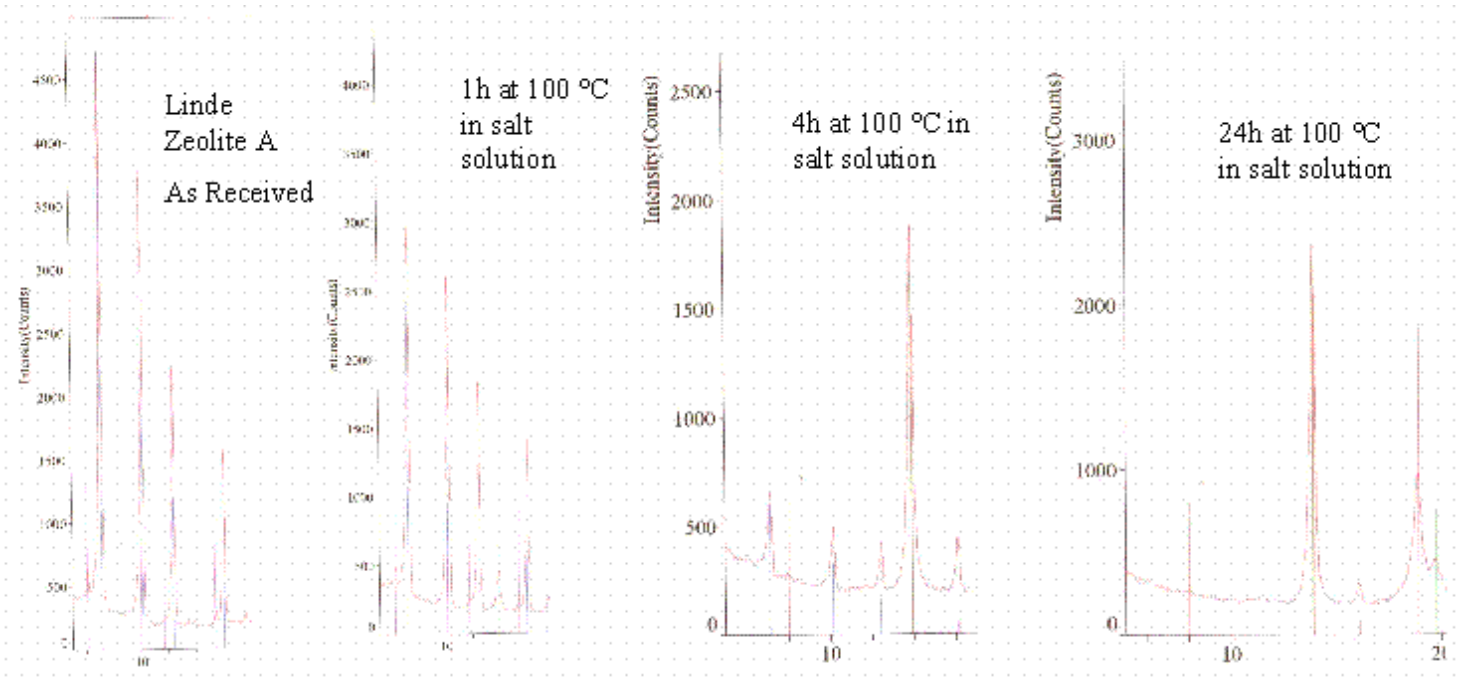


Figure 4. X-ray Diffraction Patterns from Zeolite A to Sodalite Transformation

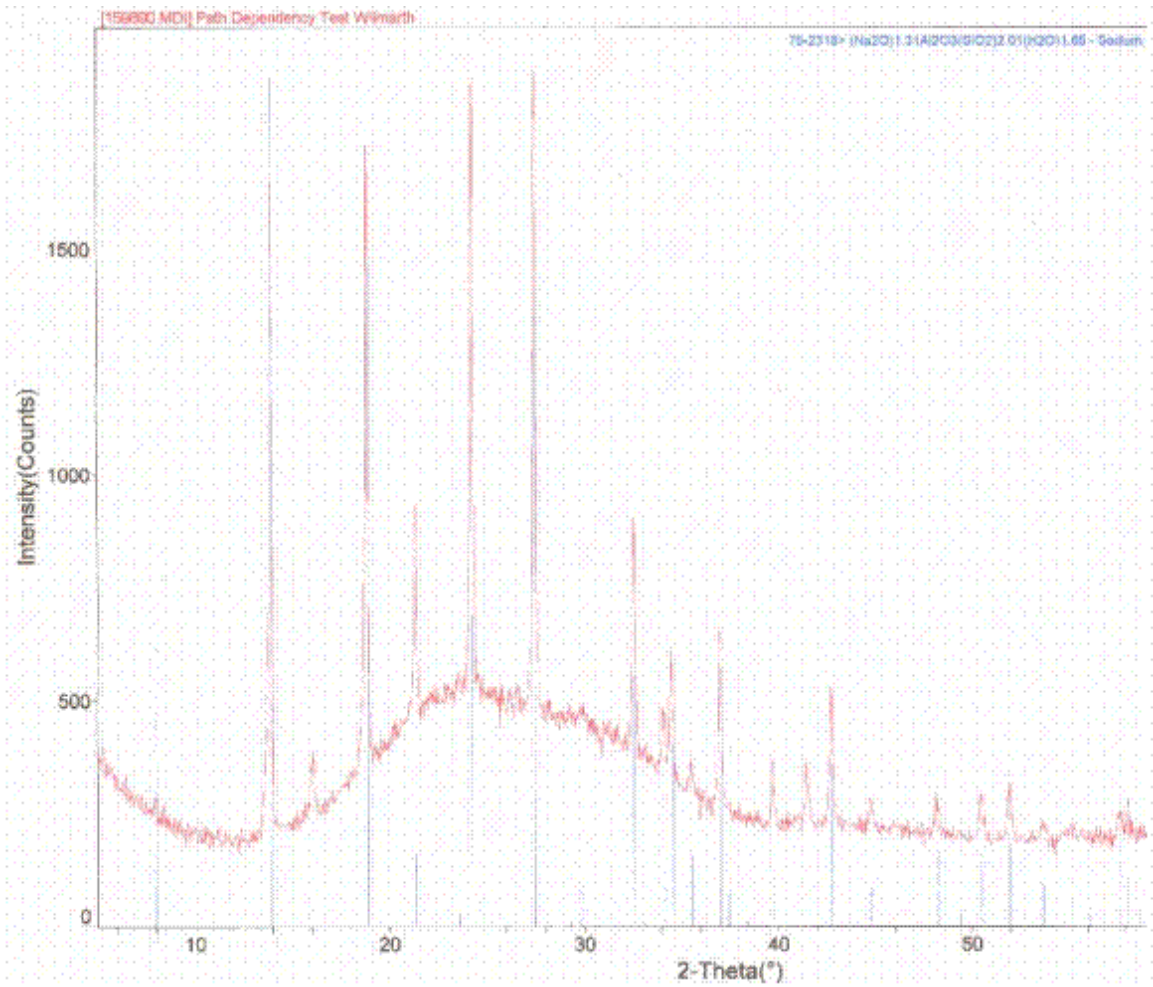


Figure 5. X-ray Powder Diffraction Pattern for Al-spiked Sample

Zeolite A Solubility

In order to thermodynamically model the chemical processes taking place in the 2H Evaporator pot, it is important to understand the solubility of the aluminosilicate at various temperatures. In these tests, 25 grams of Zeolite A was placed in a Teflon bottle with 100 mL of an aluminum-free salt solution (6 M Na^+). Figure 6 shows the measured soluble silicon and aluminum concentrations for solubility experiments at 40, 60 and 100 ° C. The data over the 120-hour test duration indicate that equilibrium was near but had not been completely reached.

One interesting aspect of this data set is that the measured aluminum concentrations are well below the silicon concentration. The highest aluminum concentration measured was 142 mg/L for the 48 hour sample at 48 ° C. In each of the tests, the aluminum concentration decreases with time while the silicon concentration increases. This behavior has been observed during the initial testing of sodalite phase removed from the 2H Gravity Drain Line. In that study, 3 M sodium hydroxide was tested for dissolution kinetic and silicon was measured to "dissolve" at a weight ratio of 17.7 compared to 150 to 200 measured in these tests.

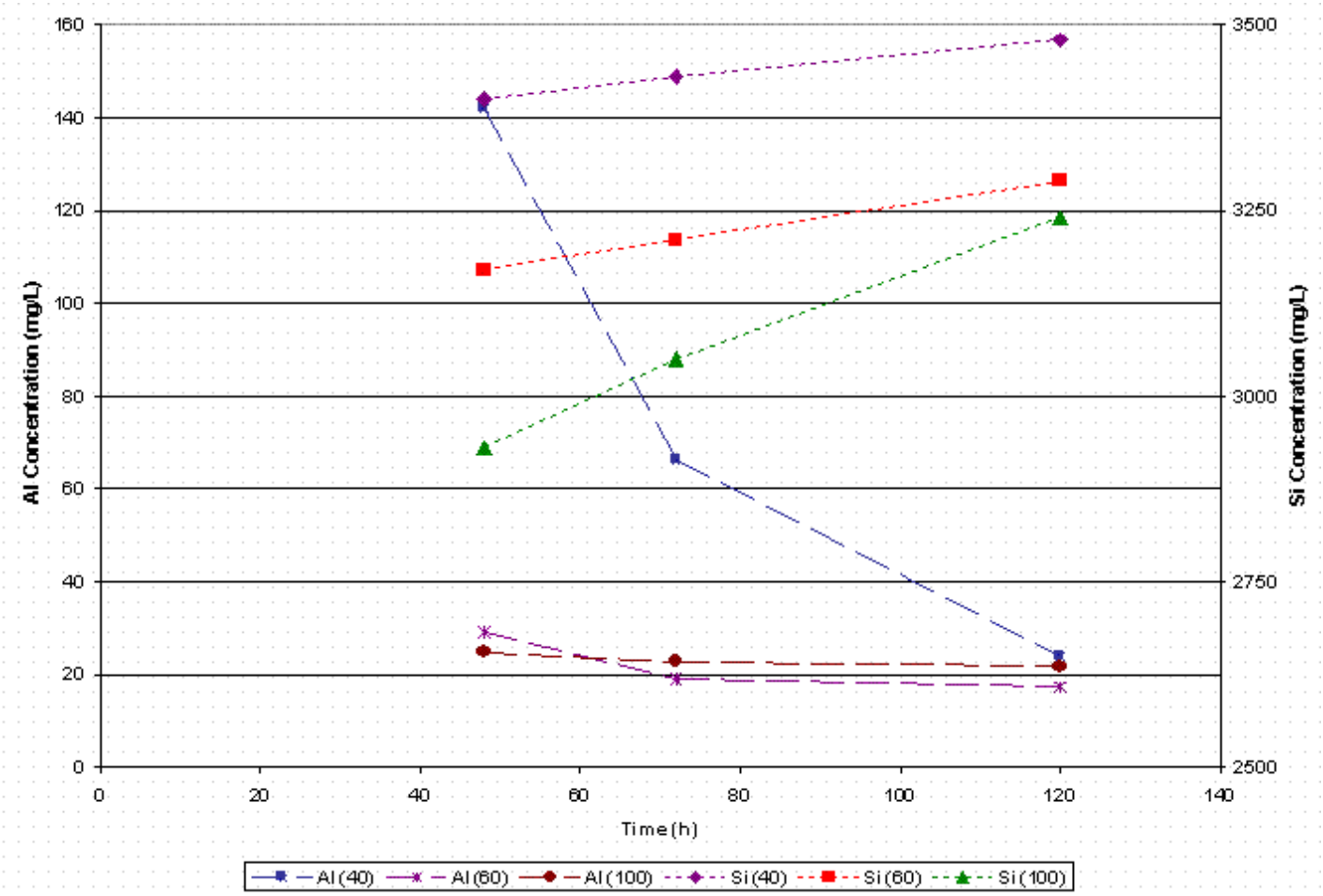


Figure 6. Al and Si Concentrations in Zeolite A Solubility Testing

Conclusions

The combination of silicon and aluminum in the highly caustic environment of Savannah River High Level Waste leads to the formation of sodium aluminosilicates. These solids phases have deposited in process vessels and have curtailed operation of critically important high-level waste evaporator operation. The purpose of this work was to examine several aspects of the formation of aluminosilicates under several tank chemistries, examine the conversion of crystalline phases, and determine inherent solubilities of certain crystal phases.

From a statistically designed set of experiments, we have shown that at nominal tank concentrations of aluminum the important parameters for the formation of sodium aluminosilicate are the silicon concentration and hold time the mixture is held prior to heating to elevated temperature. Additionally, experiments tested the difference between frit 200 and sodium metasilicate for the source of silicon and found slight differences.

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Acknowledgements

The authors wish to acknowledge the many contributions of the Analytical Development Section for their support in analyzing these many samples. Additionally, the helpful conversations with Drs. C. Jantzen and D. Hobbs were beneficial. The interest and discussion provided by the High Level Waste customers was greatly appreciated.

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