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THERMODYNAMIC MODELING OF THE SRS EVAPORATORS: PART V. VALIDATION

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EXECUTIVE SUMMARY

A thermodynamic model has been proposed to predict solids formation in the SRS evaporators from measured feed compositions using a commercially available software package, the Geochemist's Workbench® (GWB). In support of this work, researchers at Pacific Northwest National Laboratory (PNNL) and Oak Ridge National Laboratory (ORNL) have performed experiments to evaluate solids formation under evaporator-like conditions in the laboratory. The purpose of this report is to compare these experimental results to the calculated results from GWB.

Researchers at PNNL conducted experiments to evaluate the thermodynamic boundary between the precipitation of the deleterious sodium aluminosilicate gel (NAS_{gel}) and the field of benign potential precipitation of aluminum hydroxide formation. Several solutions were prepared and held at several temperatures to evaluate solids formation over various periods of time. Observed solids compared well to GWB calculations.

Researchers at ORNL prepared several mixtures of simulated SRS Tank 43 (high aluminum) and DWPF recycle (high silicon) solutions. These solutions were then evaporated, and precipitated solids were examined by XRD. Again, there was good agreement between observations and GWB calculations. No NAS_{gel} was identified, and none was predicted to form.

Researchers at ORNL also prepared several high caustic solutions, additional mixtures of simulated SRS Tank 43 and DWPF solutions, and simulated 3H evaporator feed. Solids deposition on stainless steel coupons with and without evaporation was examined. Because these solids were not rigorously characterized, direct comparison to GWB calculations is not appropriate. However, it should be noted that NAS_{gel} was not predicted by GWB to form, and no NAS_{gel} was identified in these experiments.

Overall, the experimental observations validate the GWB calculational results, showing that GWB is an appropriate tool for use in SRS evaporator modeling and control.

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DWPF	Defense Waste Processing Facility
GWB	Geochemist's Workbench®
log Q/K	saturation index
NAS_{gel}	sodium aluminosilicate gel
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SRTC	Savannah River Technology Center
XRD	X-ray diffraction

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1.0 INTRODUCTION

A thermodynamic model has been proposed to predict solids formation in the SRS evaporators from feed compositions (Jantzen et al., 2002a, 2002b, 2003a, 2003b). In support of this work, researchers at Pacific Northwest National Laboratory (PNNL) and Oak Ridge National Laboratory (ORNL) have done experiments to evaluate solids formation under evaporator-like conditions in the laboratory. The purpose of this report is to compare these experimental results to the calculational basis for the thermodynamic evaporator deposition model.

First, a brief overview of the commercially available software used to develop the evaporator model (Geochemist's Workbench®, GWB) is presented. Second, the experiments conducted by PNNL to evaluate the thermodynamic boundary between the deleterious sodium aluminosilicate gel (NAS_{gel}) and the field of benign potential precipitation of aluminum hydroxide formation are discussed. The evaporator deposition control model (Jantzen et al., 2003a, 2003b) is based on this boundary. Third, the ORNL evaporation experiments are compared to calculations using GWB. Finally, the solids deposition experiments performed by ORNL with and without volume reduction (evaporation) are discussed.

2.0 OVERVIEW OF THE GEOCHEMIST'S WORKBENCH

The Geochemist's Workbench® (GWB) is a set of software tools for manipulating chemical reactions, calculating stability diagrams and the equilibrium states of aqueous solutions, tracing reaction processes, and plotting the results of these calculations (Bethke, 1998). GWB consists of several programs, two of which have been used in evaporator modeling:

- **REACT** calculates the equilibrium distribution of aqueous species in a fluid and the fluid's saturation state with respect to mineral phases. Evaporation can be modeled by removing water from the system.
- **ACT2** is used to calculate and plot activity-activity diagrams (also known as stability diagrams). These diagrams show the stability of minerals and predominance of aqueous species in chemical systems.

Calculations in GWB are based on data in a thermodynamic database*. The database contains decomposition reactions for aqueous species and minerals. The reactions are written in terms of basis species (defined in the database). The base ten log of the equilibrium constant (log K) for each reaction in terms of the basis species at various temperatures is also included in the database. For application of GWB (a software package designed for geochemical modeling) to be used for evaporator modeling, the thermodynamic database had to be modified. Minerals of interest were added to the database, and the equilibrium constants for other minerals were modified to reflect the high ionic

* A detailed discussion of the calculational methods employed in GWB can be found in Bethke (1996).

strengths in the evaporators (high relative to geochemical systems), since the log K of a given reaction is typically dependant on solution ionic strength. These modifications are documented in Jantzen (2002a).

The equilibrium constants for the additions to the database (NAS_{gel}, Zeolite-A, nitrated sodalite, and nitrated cancrinite[†]) were based on limited data in the literature. Therefore, to improve the accuracy and applicability of GWB calculations, researchers at the University of South Australia were contracted to measure the solubilities of these minerals in solutions and at temperatures more relevant to SRS evaporator operation. Descriptions of these experiments and results can be found in Addai-Mensah (2002). Calculations of equilibrium constants using the Addai-Mensah results for input into the GWB database is described in Appendix A.

REACT is used to calculate the initial and final (given a change in the system such as an evaporation) equilibrium distribution of aqueous species in a fluid and the fluid's saturation state with respect to mineral phases. Mineral saturation states are determined by a saturation index or log Q/K, where Q is the reaction quotient, and K is the reaction equilibrium constant. A negative log Q/K (Q<K) indicates that a solution is predicted to be undersaturated with respect to a given mineral while a positive log Q/K (Q>K) value indicates that a solution is predicted to be supersaturated with respect to the given mineral.

The REACT module of GWB is configured by defining the bulk composition of a solution and any changes such as temperature or evaporation. Since solution composition is based on one kilogram of water, an evaporation is simulated by removing water. For example, a 20% evaporation would be simulated by removing 0.2 kilograms of water.

ACT2 is used to calculate and plot activity-activity diagrams. These diagrams are similar to phase diagrams, except instead of mass or mole fraction on the axes, activities are used as the x and y variables. They are used to show the equilibrium relationship between minerals and/or aqueous species. Because these diagrams use activities which vary as solution ionic strength changes, they are not easily transposed into molar or mass composition. They are, however, very useful in comparing solutions and graphically illustrating equilibrium between minerals and aqueous species. ACT2 is configured by defining the diagram axes, the species to be shown on the diagram, and any other constraints (e.g. temperature, pressure, bulk solution composition).

Sample input scripts for REACT and ACT2 are presented in Appendix B.

3.0 EXAMINATION OF THE NAS_{GEL} AND ALUMINUM HYDROXIDE BOUNDARY

The proposed process control model for the SRS evaporators models the chemical reaction defined by the boundary between NAS_{gel} and aluminum hydroxide (Jantzen et al., 2002a, 2003b). This boundary was examined by Mattigod, Hobbs, Parker, and McCready (2002) of PNNL/SRTC. Six solutions were prepared. The first four solutions were designed to be saturated with respect to NAS_{gel}, while the last two were designed to be undersaturated with respect to NAS_{gel}, i.e., saturated with respect to aluminum hydroxide. The solutions were heated to four different temperatures – 40°C, 80°C, 120°C, and 175°C[‡]. The solutions and precipitated solids were sampled over various periods of time to simultaneously study the thermodynamics and kinetics of this controlling reaction. Table 1 gives

[†] The chemical composition of NAS_{gel} is $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$; Zeolite-A is $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$; nitrated sodalite is $Na_8Al_6Si_6O_{24}\cdot 3.5H_2O$; and nitrated cancrinite is $Na_8Al_6Si_6O_{24}\cdot 2.5H_2O$.
[‡] Results for 120°C and 175°C have not been formally published.

each solution composition and the initial calculated log Q/K values at temperatures from 40°C to 175°C.

Table 1. Mattigod Solution Compositions and Calculated log Q/K NAS_{gel} at 40°C, 80°C, 120°C, and 175°C

						Calculated log Q/K (NAS_{gel}) from GWB			
Solution	Na (M)	OH (M)	NO_3 (M)	Si (M)	Al (M)	40°C	80°C	120°C	175°C
1	3.31	0.1	3	0.01	0.2	8.9	9.3	12.2	14.9
2	3.61	0.1	3	0.01	0.5	10.5	14.4	17.4	19.7
3	4.21	1.0	3	0.01	0.2	-3.5	-4.5	-2.3	-1.6
4	4.51	1.0	3	0.01	0.5	1.0	0.7	2.9	3.7
5	7.71	4.5	3	0.01	0.2	-11.1	-14.0	-12.3	-12.1
6	8.01	4.5	3	0.01	0.5	-5.5	-8.6	-6.9	-6.7

Bulk solution composition (sodium, hydroxide, and nitrate) and measured aluminum and silicon concentrations after each sampling were input into REACT to calculate saturation with respect to NAS_{gel}, Zeolite-A, nitrated sodalite, and nitrated cancrinite. A complete listing of sampling times, solution analyses, observed phases, and calculated log Q/K values for NAS_{gel}, Zeolite-A, nitrated sodalite, and nitrated cancrinite are given in Appendix C.

Results are shown graphically on activity diagrams. These diagrams allow one to plot solution composition onto a diagram showing predominant phases and aqueous species. The boundary of interest is defined by the equation (Jantzen et al., 2002a)[§]

$$6\text{Diaspore-M} + 6\frac{\text{Al(OH)}_4^-}{\text{H}^+} + 12\text{SiO}_2\text{(aq)} + 12\text{Na}^+ + 15\text{H}_2\text{O} \longleftrightarrow \text{NAS}_{\text{gel}} \quad [1]$$

Figure 1 shows the solutions examined by Mattigod at 120°C. Diagrams for all solutions at 40, 80, 120, and 175°C are presented in Appendix D.

The experimental observations with respect to NAS_{gel} correlate well with GWB calculations and validate the position of the NAS_{gel}/aluminum hydroxide boundary. Solutions designed to be undersaturated with respect to NAS_{gel} were calculated to be undersaturated. With the exception of Solution 3 (OH=1.0 M, Al=0.2 M), all other solutions and temperatures were accurately predicted to be saturated with respect to NAS_{gel}.

It should be noted that Zeolite-A was only observed in significant quantities in Solutions 1 to 4 at 40°C. This implies that Zeolite-A is not stable in very caustic solutions and at temperatures greater than 40°C. This is shown graphically on a time-temperature-transformation (TTT) diagram (Figure 2). In these diagrams, phases are plotted as functions of time and temperature. The diagrams in Figure 2 were generated from the Mattigod experiments.

For the solutions predicted to be unsaturated with respect to NAS_{gel}, an amorphous precursor phase was observed, but the composition of the amorphous material was not measured. It is postulated that this phase is the amorphous sodium aluminate phase, NAS_{gel}.

[§] Diaspore is the predominant phase at temperatures greater than about 120º, while gibbsite is predominant at lower temperatures.

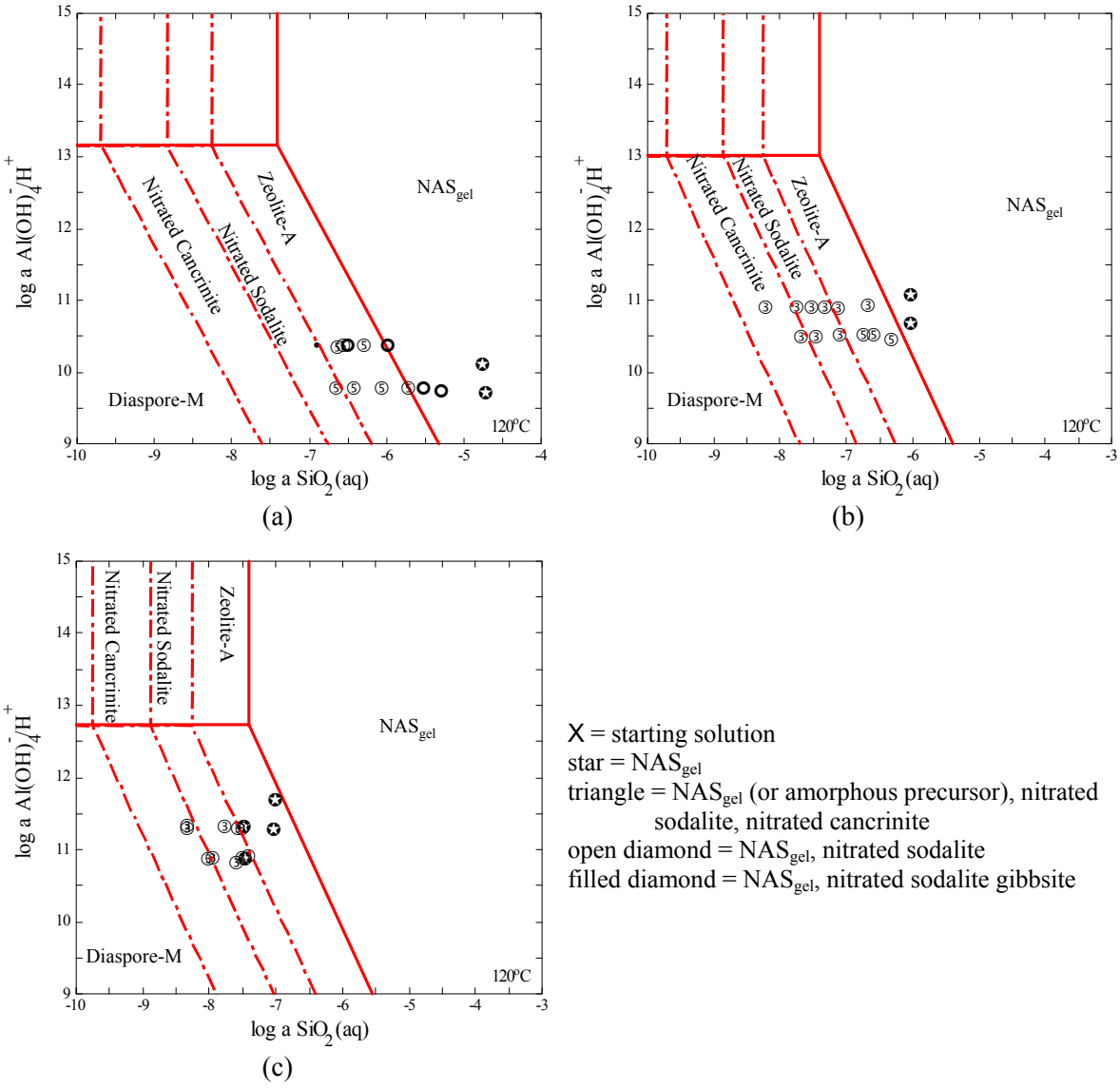
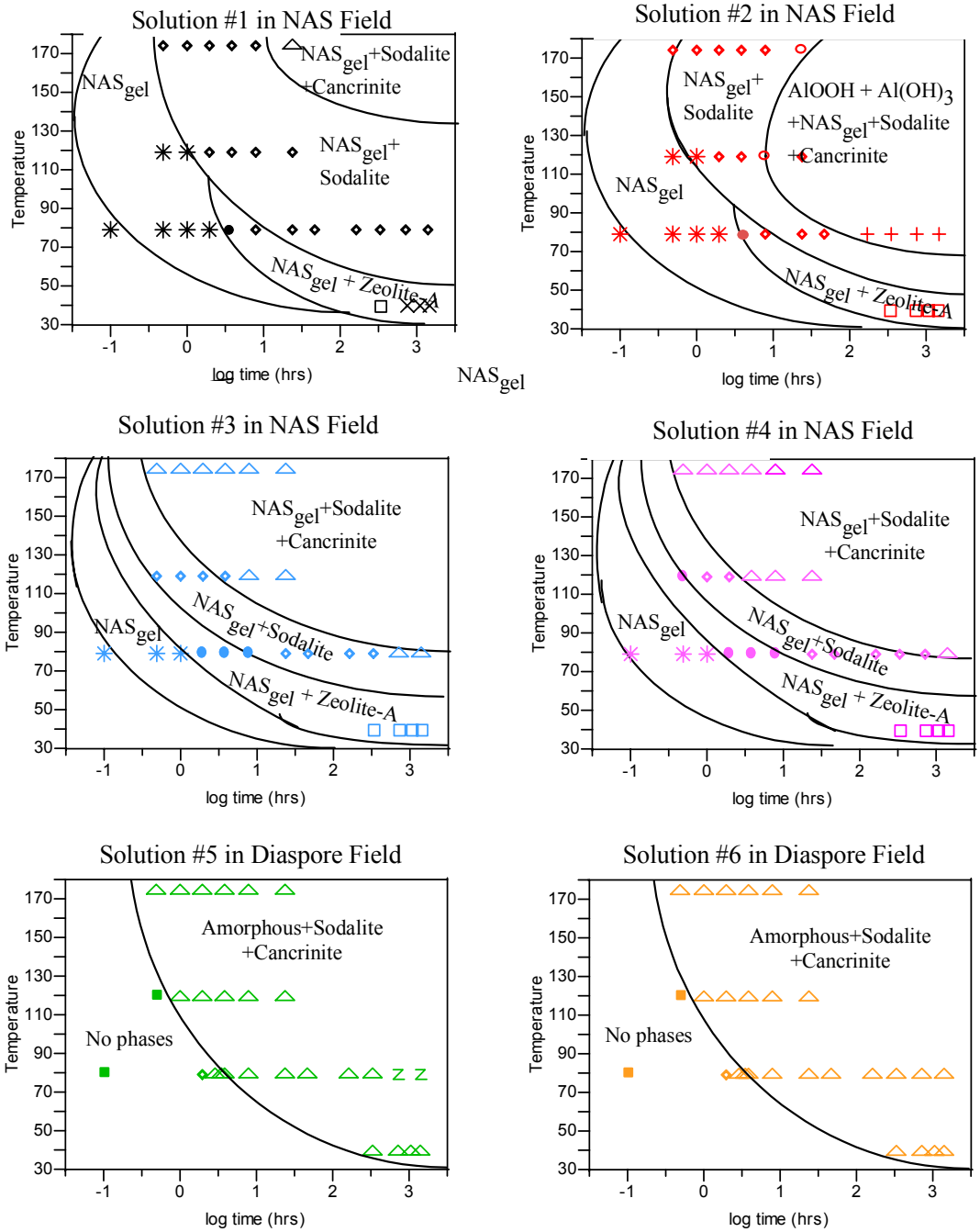


Figure 1. Activity Diagrams for the System Al-Si-Na-NO_3^- Plus H_2O at 120°C for Different Sodium and Nitrate Activities: (a) Mattigod Solutions 1 and 2, (b) Mattigod Solutions 3 and 4, and (c) Mattigod Solutions 5 and 6



Phase field designations are as follows: *=NAS_{gel}; ●=NAS_{gel}+Sodalite+Zeolite-A; ◇=NAS_{gel}+Sodalite; Δ=NAS_{gel}+Sodalite+Cancrinite; □=NAS_{gel}+Zeolite-A; +=$Al(OH)_3$, gibbsite; O=NAS_{gel}+boehmite+gibbsite

Figure 2. Time-Temperature-Transformation (TTT) diagram of the kinetic data developed by PNNL in support of SRS evaporator modeling

Figure 2 helps to illustrate the relation between thermodynamics and kinetics. For example, the diagrams show that cancrinite, the most stable mineral thermodynamically, but slowest forming

mineral kinetically, forms more quickly at higher temperatures. The diagrams also show that given the correct time, if a solution is saturated with respect to a particular mineral, that mineral will form.

4.0 EVAPORATION EXPERIMENTS

Researchers at ORNL prepared and evaporated various mixtures of Tank 43 and DWPF recycle simulants (Mattus et al., 2002). The purpose of these tests was to evaluate solids formation as a high silicon waste (DWPF recycle) is added to a relatively high aluminum waste (Tank 43). These mixtures were evaporated and evaluated for solids formation. Table 2 summarizes the calculated log Q/K values for the initial mixtures, the observations, and chemistries (calculated) after evaporations of 66%, 80%, and 90%.

There is reasonable agreement between calculated mineral saturations (log Q/K) and observations. For example, in the 50/50 mixture and 75/25 mixture, the solutions were predicted to be saturated with respect to Zeolite-A after a 90% evaporation. Compounds identified in Mattus et al. (2002) as unnamed Zeolites with similar chemical compositions to Zeolite-A were indeed observed.

Figure 3 shows the evaporation results graphically on an activity diagram. In this figure, the speciation of SiO_2(aq) is shown. With this representation, the boundary between sodium aluminosilicate minerals and aqueous Si is shown. NaH_3SiO_4 was chosen as the x-axis because it had the highest activity of all the aqueous silicate compounds in the REACT output of these evaporations. This figure does show good agreement between GWB calculations and observations. For the 75/25 and 50/50 mixtures, the figure shows the solutions should be saturated with respect to Zeolite-A, nitrated sodalite, and nitrated cancrinite. Zeolites and nitrated sodalite were indeed observed. Nitrated cancrinite was not observed in any cases. This is due to the length of time of the experiments. GWB calculates saturation based on equilibrium conditions. These solutions were likely not at equilibrium at the time of sampling. Given more time, nitrated cancrinite, the most thermodynamically stable of the minerals of interest, would inevitably have formed.

Other predominant identified phases were High Silica Zeolite ($Si_{16}O_{32}$), Zeolite Rho ($Al_{12}Si_{36}O_{90}\cdot 6H_2O$), hydroxy cancrinite, and sodium silicate. The high silica Zeolites and hydroxy cancrinite are not included in the GWB thermodynamic database. Therefore, they cannot be modeled. Sodium silicate is included in the database, and GWB calculations were consistent with observations; GWB predicted saturation with respect to sodium silicate when sodium silicate was observed.

Table 2. Compositions, Calculated log Q/K Values, and Observed Phases for Mixtures of Tank 43 and DWPF Recycle Simulants at 66, 80, and 90% Evaporation

Mix (Tk 43/ DWPF Recycle)	Percent Evaporated	Solution Composition (M)						Calculated log Q/K				Observed Phases [†]
		Na^+	OH^-	$NO_2^- + NO_3^-$	CO_3^{2-}	Al	Si	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite	
10/90	0	1.25	0.65	0.429	0.0675	0.007	0.002	-32.2	-21.9	-10.3	-5.1	N/A
	66	3.68	1.985	1.262	0.1985	0.021	0.006	-25.3	-15.0	-5.1	0.0	none
	80	6.25	3.375	2.145	0.3375	0.035	0.010	-21.3	-11.0	-2.4	2.8	none
	90	12.50	6.750	4.290	0.6750	0.070	0.020	-15.8	-5.6	1.2	6.4	HSZ, SS
50/50	0	2.25	1.25	0.91	0.0375	0.035	0.0018	-27.1	-16.8	-6.7	-1.5	N/A
	66	6.62	3.622	2.662	0.1103	0.103	0.005	-19.3	-9.0	-1.2	4.0	none
	80	11.25	6.157	4.525	0.1875	0.175	0.009	-15.2	-5.0	1.5	6.7	none
	90	22.50	12.314	9.050	0.3750	0.350	0.018	-9.7	0.6	5.2	10.3	HSZ, Z, NS, HC
75/25	0	2.88	1.63	1.20	0.0188	0.0525	0.0016	-26.5	-16.2	-5.9	-0.8	N/A
	66	8.46	4.645	3.537	0.0551	0.154	0.005	-18.5	-8.2	-0.4	4.7	none
	80	14.38	7.897	6.013	0.0938	0.263	0.008	-14.4	-4.1	2.3	7.5	none
	90	28.75	15.793	12.025	0.1875	0.525	0.016	-8.9	1.4	5.9	11.1	HSZ, Z, NS, HC

[†] HSZ = high silica Zeolite and Zeolite Rho, SS = Sodium Silicate, Z = Zeolites with ~1:1:1 Na:Al:Si ratio (similar to Zeolite-A), NS = nitrated sodalite, HC = hydroxycancrinite,

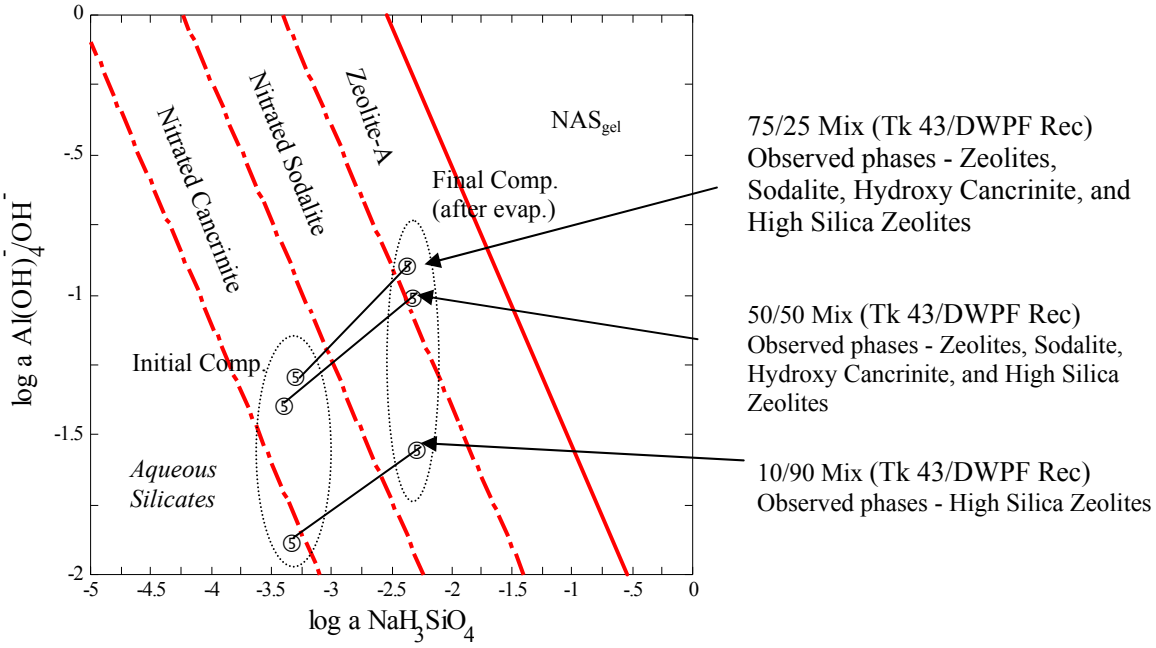


Figure 3. Activity Diagram for the System Al-Si-Na-NO_3^- Plus H_2O at 120°C with Sodium and Nitrate Activities Corresponding to the 75/25 Mixture of Tank 43 and DWPF Recycle at 90% Evaporation

To illustrate the effect of silicon and aluminum concentrations on the formation of sodium aluminosilicates, Figure 3 was redrawn with an expanded y-axis to show lower aluminum concentration (Figure 4). As can be seen from the figure, as aluminum concentration drops and silicon concentration rises, sodium silicates are predicted to be the predominant solid phases. Based on experimental results, high silica Zeolites will also likely form, but, as stated above, these minerals are not present in the GWB database.

Figure 4 is intended to be illustrative, not exact. The boundary between aqueous silicates and sodium silicate is dependent on pH - higher pH shifts this boundary to the left. The impact of silicates other than aluminosilicates on SRS evaporator operations is not fully understood. This impact is being evaluated in future SRTC research*.

It should be noted that while these experiments confirm GWB calculations, they are not directly applicable to the SRS evaporator model as presented by Jantzen et al. (2002a, 2002b, 2003a, 2003b). The evaporator model is based on an average residence time in the evaporator of eight hours and an average evaporation of 40%, while these experiments lasted between eight and sixteen hours with 90% evaporation.

* Research to evaluate the impact of uranium silicates on SRS evaporator operations has been requested by SRS High Level Waste (HLW-TTR-2003-086).

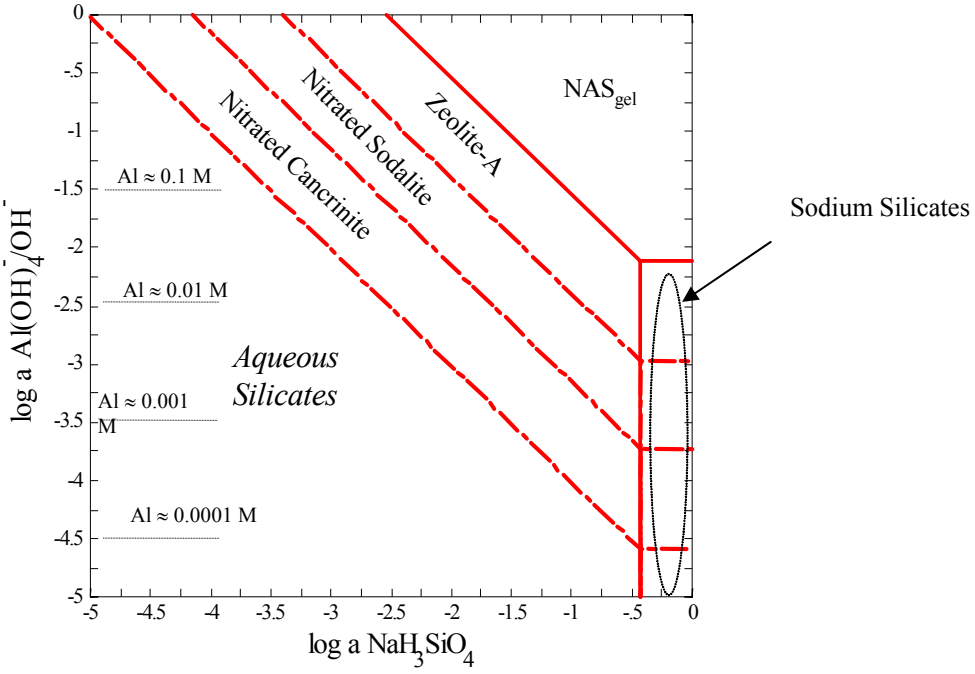


Figure 4. Activity Diagram for the System Al-Si-Na-NO_3^- Plus H_2O at 120°C with Sodium and Nitrate Activities Corresponding to the 10/90 Mixture of Tank 43 and DWPF Recycle and a pH of 11

5.0 DEPOSITION EXPERIMENTS

Researchers at ORNL evaluated solids deposition on stainless steel coupons with (1) high sodium concentration solutions, (2) mixtures of Tank 43 and DWPF recycle simulants (SRS 2H Evaporator feed), and (3) simulated SRS 3H Evaporator feed (Hu et al., 2002). With the high sodium solutions, there was no volume reduction - the solutions were heated and allowed to reflux. For the evaporator feeds, the solutions were volume reduced and coupons were examined at various stages of volume reduction.

Table 3 and Figure 5 summarize the results and calculations for the deposition experiments. As in Section 4.0, the figure was drawn with NaH_3SiO_4 as the x-axis since it had the highest activity of all the aqueous silicate compounds in the REACT output of these evaporations and solutions.

The observed solids were not rigorously identified, except as sodium aluminosilicate compounds. Without better characterization of these solids, it is difficult to compare observations and calculations. GWB does predict saturation with respect to nitrated cancrinite. With experimental times between four and eight hours and temperatures at approximately 120°C, the observed particles could be cancrinite (see Solutions 5 and six of the TTT diagrams in Figure 2).

Table 3. Summary of ORNL Deposition Experiments

No vol. reduction	Solution Composition (M)						Calculated log Q/K				
	Na^+	OH^-	$NO_2^- + NO_3^-$	CO_3^{2-}	Al	Si	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite	Observation[†]
	9.0	6.0	3.0	0	0.04	0.04	-16.0	-5.8	0.9	6.0	V
	9.0	6.0	3.0	0	0.03	0.03	-19.1	-8.9	-0.7	4.5	M
	9.0	6.0	3.0	0	0.025	0.025	-21.0	-10.8	-1.6	3.5	M
	9.0	6.0	3.0	0	0.02	0.02	-23.4	-13.2	-2.8	2.3	None
2H Feed (Tk 43/ DWPF Recycle											
26/74	1.65	0.898	0.619	0.0555	0.018	0.002	-28.8	-18.5	-8.1	-2.9	N/A
66%	4.85	2.640	1.822	0.1632	0.054	0.006	-21.5	-11.2	-2.8	2.4	M
80%	8.25	4.488	3.097	0.2775	0.091	0.010	-17.4	-7.2	0.0	5.1	M
90%	16.50	8.976	6.194	0.5550	0.182	0.019	-12.0	-1.7	3.6	8.8	M
39/61	1.98	1.079	0.774	0.0458	0.027	0.002	-27.8	-17.5	-7.3	-2.1	N/A
66%	5.81	3.172	2.277	0.1346	0.080	0.005	-20.2	-9.9	-1.8	3.3	M
80%	9.88	5.393	3.871	0.2288	0.137	0.009	-16.2	-5.9	0.9	6.1	M
90%	19.75	10.785	7.741	0.4575	0.273	0.018	-10.6	-0.4	4.5	9.7	M
63/37	2.58	1.412	1.060	0.0278	0.044	0.002	-26.7	-16.4	-6.2	-1.1	N/A
66%	7.57	4.154	3.117	0.0816	0.130	0.005	-18.8	-8.5	-0.7	4.4	M
80%	12.88	7.062	5.299	0.1388	0.221	0.009	-14.7	-4.4	2.0	7.2	M
90%	25.75	14.123	10.597	0.2775	0.441	0.017	-9.2	1.1	5.6	10.8	M
3H Feed [‡]											
-14%	12.0	8.49	2.71	0	0.8	0.0021	-16.1	-5.8	1.0	6.1	N/A
0%	13.6	9.64	3.08	0	0.9	0.0024	-15.1	-4.8	1.6	6.8	M
32%	20.0	14.14	4.52	0	1.3	0.0035	-12.0	-1.7	3.6	8.8	V
42%	23.5	16.64	5.31	0	1.6	0.0041	-10.7	-0.4	4.5	9.6	M

[†] V = particles visible on stainless steel coupon with the naked eye, M = particles visible on stainless steel coupon via SEM.

[‡] These experiments began with a solution more dilute than an average 3H feed. The percent reduction is relative to an average 3H feed.

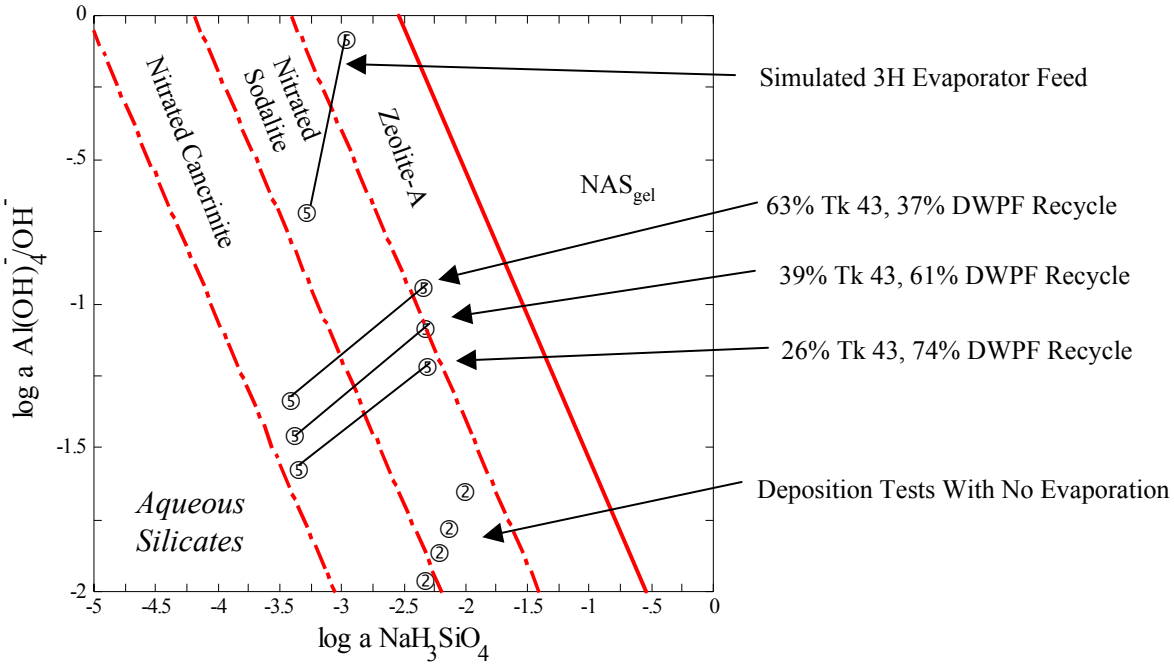


Figure 5. Activity Diagram for the System Al-Si-Na-NO_3^- Plus H_2O at 120°C with Sodium and Nitrate Activities Corresponding to the 42% Evaporation of Simulated 3H Evaporator Feed

6.0 SUMMARY

- PNNL experiments to evaluate the thermodynamic boundary between the deleterious NAS_{gel} and the field of benign aluminum hydroxide formation compared well to GWB calculations. These experiments also validate the boundary between NAS_{gel} and aluminum hydroxide.

- There is good agreement between observations from ORNL evaporation experiments using mixtures of simulated Tank 43 and DWPF recycle solutions and GWB calculations. No NAS_{gel} was identified, and none was predicted to form.

- ORNL deposition experiments, although not directly comparable to GWB calculations, showed NAS_{gel} was neither observed or predicted.

- Overall, GWB calculational results correlated well with experimental observations, showing that GWB is an appropriate tool for use in SRS evaporator modeling.

7.0 ACKNOWLEDGEMENTS

Thomas B. Caldwell is especially thanked for the database that he provided with >1800 data points spanning 29 years of operating history in the tank farm that related tank composition to density. This data was used to develop a relationship to relate sodium concentration to solution density for the conversion from molar to molal concentrations.

The authors would like to thank Jonas Addai-Mensah and his research team at the University of South Australia for providing sodium aluminosilicate solubilities in SRS-like solutions.

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8.0 REFERENCES

Addai-Mensah, A. J., J. Li, and M. Zbik, 2002, *The Chemistry, Crystallization, Physicochemical Properties, and Behavior of Sodium Aluminosilicate Solid Phases: Final Report*, WSRC-MS-2002-00907, Savannah River Site, Aiken, SC.

Bethke, C. M., 1996, *Geochemical Reaction Modeling*, Oxford Press, New York.

Bethke, C. M., 1998, *The Geochemist's Workbench® Release 3.0, A User's Guide to Rxn, Act2, Tact, React, and Gtplot*, University of Illinois Hydrology Program, Urbana, IL .

Hu, M. Z., D. W. DePaoli, and A. J. Mattus, 2002, *Results of Deposition Scoping Tests***.** SMR/SR/EVAP-006, Rev.1, Oak Ridge National Laboratory, Oak Ridge, TN.

Jantzen, C. M., J.E. Laurinat, and K.G. Brown, 2002a, *Thermodynamic Modeling of the SRS Evaporators: Part I. The 2H and 2F Systems (U)***,** WSRC-TR-2000-00293, Rev. 1, Savannah River Site, Aiken, SC.

Jantzen,, C. M. J. E. Laurinat, and K. G. Brown, 2002b, *Thermodynamic Modeling of the SRS Evaporators: Part II. The 3H System (U)*, WSRC-TR-2001-00155, Rev. 1, Savannah River Site, Aiken, SC.

Jantzen, C. M., K. G. Brown, T. B. Edwards, and J. M. Pareizs, 2003a, *Thermodynamic Modeling of the SRS Evaporators: Part III. Temperature, Evaporation, and Composition Effects on Process Control Strategy*, WSRC-TR-2002-00318, Rev. 0, Savannah River Site, Aiken, SC.

Jantzen, C. M., and J. M. Pareizs, 2003b, *Thermodynamic Modeling of the SRS Evaporators: Part IV. Incorporation of High Caustic Aluminosilicate Solubility Data (U)*, WSRC-TR-2002-00319, Rev. 0, Savannah River Site, Aiken, SC.

Mattigod, S. V., D. T. Hobbs, K. E. Parker, and D. E. McCready, 2002, *Precipitation of Aluminum Containing Species in Tank Wastes*, PNNL-13881, Pacific Northwest Laboratory, Richland, WA.

Mattus, A. J., C. H. Mattus, and R. D. Hunt, 2002, *Letter Report on Phase I Evaporation Investigations Utilizing Tank 43 and DWPF Recycle Waste Solution Mixtures***.** PC/SR/EVAP/LTR/RPT-008, Oak Ridge National Laboratory, Oak Ridge, TN.

APPENDIX A - MODIFICATION OF GEOCHEMIST'S WORKBENCH® THERMODYNAMIC DATABASE

The Geochemist's Workbench® (GWB) software package uses equilibrium constants to predict mineral saturation. For the SRS evaporators, minerals of interest are sodium aluminosilicate gel (NAS_{gel}), Zeolite-A, nitrated sodalite, and nitrated cancrinite. Solubility data for these minerals is either not readily available, or the available data is at much lower sodium concentrations than the SRS evaporators (nominally 8.5 molal sodium). Therefore, Jonas Addai-Mensah of the University of South Australia† was contracted to measure solubilities of these minerals at varying solution compositions. These solubilities were then used to calculate equilibrium constants for the GWB thermodynamic database. An outline of the methodology follows.

1. Add the mineral to the database (if it does not already exist). An entry in the database includes the mineral name, molecular weight, molecular formula, decomposition reaction using GWB basis species, and the log of the equilibrium constant at 0, 25, 60, 100, 150, 200, 250, and 300°C. At this step all log K values are set to zero.
2. Run the react.exe module of GWB with the experimentally determined solution compositions and temperatures. Output will be a log Q/K for each composition and temperature. Since log K is set to zero in the database, the calculated log Q/K is equivalent to a calculated log K.
3. Fit a model of log K as a function of composition and temperature.
4. Using the model, calculate log K for the composition 8.5 m Na, 3 m NO_2^-+ NO_3^-, and 0.2 m $Al(OH)_4^-$ at the following temperatures: 0, 25, 60, 100, 150, 200, 250, and 300°C.
5. Enter the log K values in the database

In GWB, the basis species that make up each mineral are H^+, Na^+, Al^{3+}, $SiO_2(aq)$, and H_2O‡. Each mineral formation reaction and molecular weight, as used by GWB, is given in Table A-1. The mineral compositions were determined experimentally†.

Table A-1. Mineral Decomposition Reactions and Molecular Weights

Mineral	Reaction	Molecular Weight
NAS_{gel}	$Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O + 48H^+ \longleftrightarrow 12Na^+ + 12Al^{3+} + 12SiO_2(aq) + 51H_2O$	2191
Zeolite-A	$Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O + 48H^+ \longleftrightarrow 12Na^+ + 12Al^{3+} + 12SiO_2(aq) + 51H_2O$	2191
Nitrated Sodalite	$Na_8Al_6Si_6O_{24} \cdot 3.5H_2O + 24H^+ \longleftrightarrow 8Na^+ + 6Al^{3+} + 6SiO_2(aq) + 2NO_3^- + 15.5H_2O$	1085
Nitrated Cancrinite	$Na_8Al_6Si_6O_{24} \cdot 2.5H_2O + 24H^+ \longleftrightarrow 8Na^+ + 6Al^{3+} + 6SiO_2(aq) + 2NO_3^- + 14.5H_2O$	1067

† Addai-Mensah, A. J., J. Li, and M. Zbik, *The Chemistry, Crystallization, Physicochemical Properties, and Behavior of Sodium Aluminosilicate Solid Phases*, SRT-LWP-2002-00060, Savannah River Site, Aiken, SC.

‡ The actual species that are involved in the reaction (e.g., $Al(OH)_4^-$) are swapped for basis species when running the REACT.exe application.

To calculate solubility concentrations of silicon and aluminum, each mineral was dissolved in a variety of solutions at several temperatures. After equilibrium was reached, the silicon and aluminum concentrations were measured. For input into REACT, the solution composition at equilibrium was calculated. Based on measured silicon concentration, sodium, nitrate, and nitrite concentrations were adjusted using the stoichiometry in Table A-1. For example, one mole of sodium is formed per mole of silicon as the mineral Zeolite-A dissolves. Also, aluminum is shown in the form $Al(OH)_4^-$, silicon in the form $H_2SiO_4^{2-}$, and hydroxide is calculated from a charge balance. Table A-2 through Table A-5 list the equilibrium solution compositions for the Addai-Mensah solubility experiments.

Table A-2. NAS_{gel} Equilibrium Compositions (Moles/L solution)

Solution ID	Na^+	OH^-	NO_3^-	NO_2^-	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C						
NAS-1	3.0702	2.8507	0	0	0.0702	0.0791
NAS-2	6.1013	5.7998	0	0	0.1013	0.0989
NAS-3	6.0861	3.8348	1	1	0.0861	0.0791
NAS-4	6.0558	3.7501	1	1	0.0558	0.1941
NAS-5	6.0398	3.4899	1	1	0.0398	0.4703
NAS-6	12.1088	7.7821	2	2	0.1088	0.1091
NAS-7	12.0852	7.6947	2	2	0.0852	0.2201
NAS-8	12.0564	7.4332	2	2	0.0564	0.5104
T = 65°C						
NAS-9	3.0881	2.807	0	0	0.0881	0.1049
NAS-10	6.2074	5.5865	0	0	0.2074	0.2061
NAS-11	6.1163	3.7587	1	1	0.1163	0.125
NAS-12	6.0705	3.7243	1	1	0.0705	0.2052
NAS-13	6.0454	3.4463	1	1	0.0454	0.5083
NAS-14	12.2578	7.458	2	2	0.2578	0.2842
NAS-15	12.1937	7.4555	2	2	0.1937	0.3508
NAS-16	12.1447	7.2757	2	2	0.1447	0.5796
T = 130°C						
NAS-17	3.1119	2.7749	0	0	0.1119	0.1132
NAS-18	6.2934	5.4114	0	0	0.2934	0.2952
NAS-19	6.1565	3.6846	1	1	0.1565	0.1589
NAS-20	6.0892	3.6826	1	1	0.0892	0.2282
NAS-21	6.0576	3.4316	1	1	0.0576	0.5108

Table A-3. Zeolite-A Equilibrium Compositions (Moles/L solution)

Solution ID	Na^+	OH^-	NO_3^-	NO_2^-	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C						
ZEO-1	3.0118	2.9681	0	0	0.0118	0.0201
ZEO-2	6.0314	5.9187	0	0	0.0314	0.0499
ZEO-3	6.0151	3.9535	1	1	0.0151	0.0314
ZEO-4	6.0059	3.8456	1	1	0.0059	0.1485
ZEO-5	6.0042	3.5558	1	1	0.0042	0.44
ZEO-6	12.039	7.9002	2	2	0.039	0.0608
ZEO-7	12.0221	7.8122	2	2	0.0221	0.1657
ZEO-8	12.0172	7.5225	2	2	0.0172	0.4603
T = 65°C						
ZEO-9	3.0199	2.9532	0	0	0.0199	0.0269
ZEO-10	6.044	5.8824	0	0	0.044	0.0736
ZEO-11	6.0201	3.9516	1	1	0.0201	0.0283
ZEO-12	6.008	3.8154	1	1	0.008	0.1766
ZEO-13	6.0053	3.5386	1	1	0.0053	0.4561
ZEO-14	12.0681	7.8358	2	2	0.0681	0.0961
ZEO-15	12.0363	7.6828	2	2	0.0363	0.2809
ZEO-16	12.0249	7.4914	2	2	0.0249	0.4837
T = 130°C						
ZEO-17	3.0309	2.9349	0	0	0.0309	0.0342
ZEO-18	6.0618	5.8667	0	0	0.0618	0.0715
ZEO-19	6.0306	3.9343	1	1	0.0306	0.0351
ZEO-20	6.0105	3.8247	1	1	0.0105	0.1648
ZEO-21	6.0074	3.5282	1	1	0.0074	0.4644
ZEO-22	12.1007	7.7991	2	2	0.1007	0.1002
ZEO-23	12.054	7.7406	2	2	0.054	0.2054
ZEO-24	12.0354	7.4766	2	2	0.0354	0.488

Table A-4. Nitrated Sodalite Equilibrium Compositions (Moles/L solution)

	Na^+	OH^-	NO_3^-	NO_2^-	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C						
SOD-1	3.0104	2.9817	0.0013	0.0013	0.0078	0.0105
Sod-2	6.0236	5.9624	0.0029	0.0029	0.0177	0.0199
SOD-3	6.0077	3.9880	1.0010	1.0010	0.0058	0.0062
SOD-4	6.0032	3.8448	1.0004	1.0004	0.0024	0.1528
SOD-5	6.0011	3.5596	1.0001	1.0001	0.00081	0.4396
SOD-6	12.0105	7.9725	2.0013	2.0013	0.0079	0.0196
SOD-7	12.0043	7.8463	2.0005	2.0005	0.0032	0.1505
SOD-8	12.0028	7.5477	2.0004	2.0004	0.0021	0.4502
T = 65°C						
SOD-9	3.0191	2.9705	0.0024	0.0024	0.0143	0.0152
SOD-10	6.0432	5.9277	0.0054	0.0054	0.0324	0.0399
SOD-11	6.0167	3.9703	1.0021	1.0021	0.0125	0.0172
SOD-12	6.0036	3.8384	1.0005	1.0005	0.0027	0.1589
SOD-13	6.0021	3.5517	1.0003	1.0003	0.0016	0.4467
SOD-14	12.0241	7.9588	2.0030	2.0030	0.0181	0.0231
SOD-15	12.0071	7.8390	2.0009	2.0009	0.0053	0.1557
SOD-16	12.0043	7.5377	2.0005	2.0005	0.0032	0.4591
T = 130°C						
SOD-17	3.0301	2.9478	0.0038	0.0038	0.0226	0.0296
SOD-18	6.0579	5.9081	0.0072	0.0072	0.0434	0.0485
SOD-19	6.0233	3.9616	1.0029	1.0029	0.0175	0.0209
SOD-20	6.0049	3.8403	1.0006	1.0006	0.0037	0.156
SOD-21	6.0033	3.5465	1.0004	1.0004	0.0025	0.451
SOD-22	12.0397	7.9397	2.0050	2.0050	0.0298	0.0305
SOD-23	12.0125	7.8307	2.0016	2.0016	0.0094	0.1599
SOD-24	12.0083	7.5334	2.0010	2.0010	0.0062	0.4604

Table A-5. Nitrated Cancrinite Compositions (Moles/L solution)

Solution ID	Na^+	OH^-	NO_3^-	NO_2^-	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C						
CAN-1	3.0061	2.9875	0.0008	0.0008	0.0046	0.0079
CAN-2	6.0121	5.9792	0.0015	0.0015	0.0091	0.0117
CAN-3	6.0025	3.9948	1.0003	1.0003	0.0019	0.0033
CAN-4	6.0004	3.8532	1.0001	1.0001	0.0003	0.1465
CAN-5	6.0003	3.5596	1.0000	1.0000	0.0002	0.4402
CAN-6	12.0027	7.9903	2.0003	2.0003	0.0020	0.0077
CAN-7	12.0005	7.8497	2.0001	2.0001	0.0004	0.1499
CAN-8	12.0004	7.5538	2.0000	2.0000	0.0003	0.4459
T = 65°C						
CAN-9	3.0095	2.9828	0.0012	0.0012	0.0071	0.0101
CAN-10	6.0187	5.9712	0.0023	0.0023	0.0140	0.0148
CAN-11	6.0033	3.9918	1.0004	1.0004	0.0025	0.0057
CAN-12	6.0007	3.8496	1.0001	1.0001	0.0005	0.1499
CAN-13	6.0004	3.5571	1.0001	1.0001	0.0003	0.4426
CAN-14	12.0043	7.9855	2.0005	2.0005	0.0032	0.0113
CAN-15	12.0008	7.8507	2.0001	2.0001	0.0006	0.1487
CAN-16	12.0005	7.5474	2.0001	2.0001	0.0004	0.4522
T = 130°C						
CAN-17	3.0137	2.9762	0.0017	0.0017	0.0103	0.0135
CAN-18	6.0249	5.9591	0.0031	0.0031	0.0187	0.0222
CAN-19	6.0068	3.9868	1.0009	1.0009	0.0051	0.0081
CAN-20	6.0009	3.8396	1.0001	1.0001	0.0007	0.1597
CAN-21	6.0007	3.5480	1.0001	1.0001	0.0005	0.4515
CAN-22	12.0105	7.9827	2.0013	2.0013	0.0079	0.0094
CAN-23	12.0011	7.8501	2.0001	2.0001	0.0008	0.1491
CAN-24	12.0008	7.5507	2.0001	2.0001	0.0006	0.4487

For input into REACT.exe of GWB, the molarities must now be converted to molalities.

$$[X] = (X)\left(\frac{1}{density - solute\ mass}\right) \qquad \text{A-1}$$

where

[X] = molality of component X
(X) = molarity of component X
density = solution density in kg/L
solute mass = mass in kg of solute in 1 L of solution

Density measurements from Tank Farm sampling were used to develop a correlation between sodium concentration and density (see Appendix B of Jantzen and Pareizs[§])

$$density = 1.013 + 5.701 \cdot 10^{-2} \cdot \left(Na^+\right) - 1.725 \cdot 10^{-3} \cdot \left(Na^+\right)^2 \qquad \text{A-2}$$

[§] Jantzen, C. M., and J. M. Pareizs, *Thermodynamic Modeling of the SSRS Evaporators: Part IV. Incorporation of High Caustic Aluminosilicate Solubility Data (U)*, WSRC-TR-2002-00319, Rev. 0, Savannah River Site, Aiken, SC.

The solute mass is then calculated:

$$solute\ mass = \frac{1}{1000}\sum (X_i) MW_i \qquad \text{A-3}$$

Table A-6 through Table A-9 show the results of the conversion of equilibrium molar concentrations to equilibrium molal concentrations.

Table A-6. Calculated Solution Density, Solute Mass, and Composition in Mol /kg Water for NAS_{gel} Solutions

Solution ID	Solution Density (kg/L)	Solute Mass (kg/L)	Na^+	OH^-	$NO_2^-+NO_3^-$	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C							
NAS-1	1.117	0.133	3.121	2.898	0.000	0.0714	0.0804
NAS-2	1.219	0.258	6.350	6.036	0.000	0.1054	0.1029
NAS-3	1.246	0.329	6.634	4.180	2.180	0.0939	0.0862
NAS-4	1.246	0.335	6.646	4.115	2.195	0.0612	0.2130
NAS-5	1.249	0.355	6.754	3.903	2.236	0.0445	0.5259
NAS-6	1.476	0.647	14.618	9.395	4.829	0.1313	0.1317
NAS-7	1.476	0.654	14.699	9.359	4.865	0.1036	0.2677
NAS-8	1.478	0.673	14.981	9.236	4.970	0.0701	0.6342
T = 65°C							
NAS-9	1.118	0.137	3.146	2.860	0.000	0.0898	0.1069
NAS-10	1.227	0.277	6.534	5.880	0.000	0.2183	0.2169
NAS-11	1.249	0.335	6.697	4.115	2.190	0.1273	0.1369
NAS-12	1.247	0.337	6.671	4.093	2.198	0.0775	0.2255
NAS-13	1.250	0.358	6.780	3.865	2.243	0.0509	0.5701
NAS-14	1.487	0.676	15.105	9.190	4.929	0.3177	0.3502
NAS-15	1.484	0.675	15.059	9.208	4.940	0.2392	0.4332
NAS-16	1.485	0.688	15.238	9.129	5.019	0.1816	0.7272
T = 130°C							
NAS-17	1.120	0.140	3.175	2.831	0.000	0.1142	0.1155
NAS-18	1.233	0.292	6.688	5.750	0.000	0.3118	0.3137
NAS-19	1.252	0.342	6.768	4.051	2.199	0.1720	0.1747
NAS-20	1.249	0.341	6.708	4.057	2.203	0.0983	0.2514
NAS-21	1.251	0.360	6.799	3.851	2.245	0.0646	0.5733

Table A-7. Calculated Solution Density, Solute Mass, and Composition in Mol /kg Water for Zeolite-A Solutions

Solution ID	Solution Density (kg/L)	Solute Mass (kg/L)	Na^+	OH^-	$NO_2^-+NO_3^-$	$H_2SiO4_2^-$	$Al(OH)_4^-$
T = 30°C							
ZEO-1	1.169	0.123	2.879	2.837	0.000	0.0113	0.0192
ZEO-2	1.294	0.247	5.761	5.653	0.000	0.0300	0.0477
ZEO-3	1.293	0.318	6.166	4.053	2.050	0.0155	0.0322
ZEO-4	1.293	0.326	6.211	3.977	2.068	0.0061	0.1536
ZEO-5	1.293	0.349	6.358	3.765	2.118	0.0044	0.4659
ZEO-6	1.449	0.637	14.815	9.722	4.922	0.0480	0.0748
ZEO-7	1.449	0.643	14.918	9.694	4.964	0.0274	0.2056
ZEO-8	1.449	0.666	15.342	9.604	5.107	0.0220	0.5876
T = 65°C							
ZEO-9	1.169	0.124	2.889	2.825	0.000	0.0190	0.0257
ZEO-10	1.294	0.250	5.787	5.633	0.000	0.0421	0.0705
ZEO-11	1.294	0.318	6.172	4.051	2.050	0.0206	0.0290
ZEO-12	1.293	0.329	6.228	3.955	2.073	0.0083	0.1831
ZEO-13	1.293	0.350	6.368	3.753	2.121	0.0056	0.4837
ZEO-14	1.450	0.642	14.947	9.705	4.954	0.0843	0.1190
ZEO-15	1.449	0.654	15.127	9.656	5.027	0.0456	0.3530
ZEO-16	1.449	0.668	15.400	9.594	5.123	0.0319	0.6195
T = 130°C							
ZEO-17	1.170	0.126	2.903	2.811	0.000	0.0296	0.0328
ZEO-18	1.295	0.252	5.810	5.623	0.000	0.0592	0.0685
ZEO-19	1.294	0.320	6.190	4.038	2.053	0.0314	0.0360
ZEO-20	1.293	0.328	6.226	3.962	2.072	0.0109	0.1707
ZEO-21	1.293	0.351	6.376	3.745	2.123	0.0079	0.4929
ZEO-22	1.450	0.646	15.045	9.697	4.973	0.1252	0.1246
ZEO-23	1.449	0.649	15.066	9.675	5.000	0.0675	0.2567
ZEO-24	1.449	0.670	15.438	9.590	5.131	0.0454	0.6260

Table A-8. Calculated Solution Density, Solute Mass, and Composition in Mol /kg Water for Nitrated Sodalite Solutions

Solution ID	Solution Density (kg/L)	Solute Mass (kg/L)	Na^+	OH^-	$NO_2^-+NO_3^-$	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C							
SOD-1	1.169	0.122	2.875	2.847	0.002	0.0074	0.0100
Sod-2	1.294	0.244	5.737	5.679	0.006	0.0169	0.0190
SOD-3	1.293	0.315	6.143	4.078	2.047	0.0059	0.0063
SOD-4	1.293	0.326	6.209	3.977	2.070	0.0025	0.1580
SOD-5	1.293	0.348	6.353	3.769	2.118	0.0009	0.4654
SOD-6	1.449	0.631	14.678	9.743	4.891	0.0097	0.0240
SOD-7	1.449	0.640	14.846	9.704	4.948	0.0040	0.1861
SOD-8	1.449	0.663	15.284	9.611	5.094	0.0027	0.5733
T = 65°C							
SOD-9	1.169	0.123	2.885	2.839	0.005	0.0137	0.0145
SOD-10	1.294	0.247	5.770	5.660	0.010	0.0309	0.0381
SOD-11	1.294	0.317	6.161	4.065	2.052	0.0128	0.0176
SOD-12	1.293	0.327	6.213	3.972	2.071	0.0028	0.1644
SOD-13	1.293	0.349	6.359	3.763	2.119	0.0017	0.4732
SOD-14	1.449	0.632	14.718	9.742	4.904	0.0222	0.0283
SOD-15	1.449	0.641	14.861	9.702	4.953	0.0066	0.1927
SOD-16	1.449	0.664	15.302	9.608	5.100	0.0041	0.5852
T = 130°C							
SOD-17	1.170	0.125	2.900	2.822	0.007	0.0216	0.0283
SOD-18	1.295	0.249	5.793	5.650	0.014	0.0415	0.0464
SOD-19	1.294	0.318	6.172	4.059	2.055	0.0179	0.0214
SOD-20	1.293	0.327	6.213	3.974	2.071	0.0038	0.1614
SOD-21	1.293	0.349	6.363	3.759	2.121	0.0026	0.4780
SOD-22	1.449	0.634	14.770	9.740	4.919	0.0366	0.0374
SOD-23	1.449	0.642	14.882	9.701	4.959	0.0116	0.1981
SOD-24	1.449	0.665	15.315	9.608	5.104	0.0079	0.5872

Table A-9. Calculated Solution Density, Solute Mass, and Composition in Mol /kg Water for Nitrated Cancrinite Solutions

Solution ID	Solution Density (kg/L)	Solute Mass (kg/L)	Na^+	OH^-	$NO_2^-+NO_3^-$	$H_2SiO_4^{2-}$	$Al(OH)_4^-$
T = 30°C							
CAN-1	1.169	0.121	2.870	2.852	0.001	0.0044	0.0075
CAN-2	1.293	0.242	5.719	5.688	0.003	0.0087	0.0111
CAN-3	1.293	0.314	6.134	4.083	2.045	0.0019	0.0034
CAN-4	1.293	0.325	6.202	3.983	2.067	0.0003	0.1514
CAN-5	1.293	0.348	6.353	3.769	2.117	0.0002	0.4660
CAN-6	1.449	0.629	14.640	9.746	4.880	0.0024	0.0094
CAN-7	1.449	0.640	14.835	9.704	4.945	0.0005	0.1853
CAN-8	1.449	0.663	15.271	9.612	5.090	0.0004	0.5674
T = 65°C							
CAN-9	1.169	0.122	2.874	2.848	0.002	0.0068	0.0096
CAN-10	1.294	0.243	5.728	5.683	0.004	0.0133	0.0141
CAN-11	1.293	0.315	6.137	4.080	2.045	0.0026	0.0058
CAN-12	1.293	0.326	6.204	3.980	2.068	0.0005	0.1550
CAN-13	1.293	0.349	6.354	3.767	2.118	0.0003	0.4687
CAN-14	1.449	0.629	14.650	9.745	4.883	0.0039	0.0138
CAN-15	1.449	0.640	14.834	9.704	4.945	0.0007	0.1838
CAN-16	1.449	0.663	15.281	9.610	5.094	0.0005	0.5758
T = 130°C							
CAN-17	1.169	0.122	2.879	2.843	0.003	0.0098	0.0129
CAN-18	1.294	0.244	5.740	5.677	0.006	0.0178	0.0211
CAN-19	1.293	0.315	6.143	4.077	2.047	0.0052	0.0083
CAN-20	1.293	0.327	6.210	3.973	2.070	0.0007	0.1653
CAN-21	1.293	0.349	6.359	3.760	2.120	0.0005	0.4785
CAN-22	1.449	0.630	14.663	9.746	4.887	0.0096	0.0115
CAN-23	1.449	0.640	14.836	9.704	4.945	0.0010	0.1843
CAN-24	1.449	0.663	15.276	9.612	5.092	0.0008	0.5712

The above compositions and temperatures were then input into REACT to calculate log K values. These calculated values are given in Table A-10.

Table A-10. Calculated log K Values

Solution ID	log K	Solution ID	log K	Solution ID	log K	Solution ID	log K
NAS-1	157.7136	ZEO-1	140.7047	SOD-1	61.8369	CAN-1	59.115
NAS-2	158.0517	ZEO-2	147.9692	Sod-2	65.753	CAN-2	61.9907
NAS-3	161.6694	ZEO-3	147.3376	SOD-3	67.7964	CAN-3	63.224
NAS-4	164.4053	ZEO-4	150.9353	SOD-4	74.1933	CAN-4	68.5399
NAS-5	168.2868	ZEO-5	155.9014	SOD-5	74.8389	CAN-5	70.9204
NAS-6	164.4158	ZEO-6	155.6909	SOD-6	72.833	CAN-6	66.7312
NAS-7	167.0295	ZEO-7	158.1857	SOD-7	75.9904	CAN-7	70.5563
NAS-8	169.9796	ZEO-8	163.0089	SOD-8	78.2103	CAN-8	73.2006
NAS-9	135.4874	ZEO-9	119.8969	SOD-9	52.6631	CAN-9	48.9316
NAS-10	141.3506	ZEO-10	126.8731	SOD-10	57.115	CAN-10	51.4624
NAS-11	140.6694	ZEO-11	123.0464	SOD-11	59.8513	CAN-11	52.7639
NAS-12	140.7778	ZEO-12	128.3081	SOD-12	61.9254	CAN-12	57.2625
NAS-13	144.2983	ZEO-13	132.1605	SOD-13	63.8669	CAN-13	59.313
NAS-14	149.3309	ZEO-14	135.6953	SOD-14	62.5986	CAN-14	56.1631
NAS-15	148.9351	ZEO-15	138.4095	SOD-15	64.5511	CAN-15	58.568
NAS-16	150.5189	ZEO-16	139.8008	SOD-16	66.5107	CAN-16	60.9753
NAS-17	114.779	ZEO-17	101.0238	SOD-17	44.4752	CAN-17	39.5604
NAS-18	122.9535	ZEO-18	105.844	SOD-18	47.1319	CAN-18	42.0537
NAS-19	120.7002	ZEO-19	103.3125	SOD-19	49.3984	CAN-19	43.659
NAS-20	119.6384	ZEO-20	106.2153	SOD-20	50.8114	CAN-20	46.4637
NAS-21	122.5377	ZEO-21	110.9678	SOD-21	53.1471	CAN-21	48.85
		ZEO-22	114.5211	SOD-22	52.5035	CAN-22	45.8914
		ZEO-23	115.1417	SOD-23	53.9479	CAN-23	47.3501
		ZEO-24	118.1511	SOD-24	56.07	CAN-24	50.011

The statistical software JMP® was used to fit a model of log K as a function of composition. For NAS_{gel} and Zeolite-A, $[Na^+]$, $[Al(OH)_4^-]$, and the inverse of the temperature in Kelvin were the components of the model. For nitrated sodalite and nitrated cancrinite, $[NO_3^-]$ was also included.

Sodium was chosen because it is the major component of the solutions. Aluminate was chosen because, when added to a starting solution, it had a major impact on solubility. The inverse temperature was chosen because the log of an equilibrium constant is typically proportional to the inverse temperature. Nitrate and nitrite were not used for NAS_{gel} and Zeolite-A because they had little direct impact on solubility. Hydroxide was not chosen because it is calculated from a charge balance, and highly correlated to the sodium concentration.

The resulting models are given in Table A-11.

Table A-11. Relationships Between log K and Solution Compositions and Temperatures

NAS_{gel}	$\log K = 9.125 \cdot \log\left[Na^+\right] + 7.003 \cdot \log\left[Al(OH)_4^-\right] + \frac{5.277 \cdot 10^4}{T} - 14.54$
Zeolite-A	$\log K = 16.582 \cdot \log\left[Na^+\right] + 5.883 \cdot \log\left[Al(OH)_4^-\right] + \frac{5.285 \cdot 10^4}{T} - 32.72$
Nitrated Sodalite	$\log K = 5.367 \cdot \log\left[Na^+\right] + 3.224 \cdot \log\left[Al(OH)_4^-\right] + 1.524 \cdot \log\left[NO_3^-\right] + \frac{2.578 \cdot 10^4}{T} - 14.94$
Nitrated Cancrinite	$\log K = 3.529 \cdot \log\left[Na^+\right] + 3.049 \cdot \log\left[Al(OH)_4^-\right] + 1.102 \cdot \log\left[NO_3^-\right] + \frac{2.631 \cdot 10^4}{T} - 19.66$

Using the models in Table A-11, log K values were calculated at 8.5 m Na^+, 0.2 m $Al(OH)_4^-$, and the following temperatures: 0, 25, 60, 100, 150, 200, 250, and 300°C. Table A-12 lists the log K values calculated using the equations in Table A-11. These values were then input into the GWB thermodynamic database.

Table A-12. log K Values for Input into GWB Thermodynamic Database

Temperature (°C)	NAS_{gel} log K	Zeolite-A log K	Nitrated Sodalite log K	Nitrated Cancrinite log K
0	182.3431	172.1567	82.9577	78.3746
25	166.1269	155.9171	75.0350	70.2907
60	147.5148	137.2781	65.9417	61.0123
100	130.5209	120.2596	57.6390	52.5407
150	113.7981	103.5127	49.4687	44.2042
200	100.6108	90.3063	43.0258	37.6301
250	89.9449	79.6250	37.8148	32.3131
300	81.1405	70.8079	33.5133	27.9240

APPENDIX B - SAMPLE REACT AND ACT2 INPUT SCRIPTS

Sample REACT input Script Commands	Description of Command
`T = 120`	Temperature of system

`swap O2(g) for O2(aq)`
`swap Al(OH)4- for Al+++`
`swap CO3-- for HCO3-`
`swap OH- for H+`
`swap H2SiO4-- for SiO2(aq)`
	Calculations are based on a set of basis species. Species not in the basis must be swapped into the basis.

`f O2(g) = 0.2`
`Al(OH)4- = 0.006893165 molal`
`CO3-- = 0.06646981 molal`
`Na+ = 1.230922404 molal`
`OH- = 0.664698098 molal`
`NO3- = 0.422452569 molal`
`H2SiO4-- = 0.001969476 molal`
	The initial system conditions must be defined. The preferred units for REACT input is molal (moles per kg water). The fugacity of oxygen is set at that of air to ensure that oxidizing solution conditions are modeled.

`balance on OH-`	This command tells REACT what species to adjust to balance the charge.
`react -0.66 kg H2O`	This command simulates evaporation by removing water from the system.
`suppress all`	This command prevents REACT from precipitating minerals, resulting in positive log Q/K values for saturated minerals.

`print species long`
`print minerals long`
`dxprint = 1`
	These commands control the content and size of the REACT output file.

`go`	

Sample ACT2 input Script Commands	Description of Command
`T = 120 C`	Temperature of system

`swap Al(OH)4-/H+ for Al+++`
`swap CO3-- for HCO3-`
`swap O2(g) for O2(aq)`
`swap NAS for H+`
	Calculations are based on a set of basis species. Species not in the basis must be swapped into the basis.

`diagram Na+ on Al(OH)4-/H+ vs SiO2(aq)`	This command specifies the species to diagram and the species on the y- and x-axes.

`log a Na+ = 0.7666`
`log a NO3- = 0.3792`
`log a CO3-- = -1.4638`
	These commands define the system.

`suppress Gibbsite Zeolite-A Diaspore Beidellit-Na Nepheline Analcime Albite Sodalite-OH "Albite low" Paragonite "Albite high" Boehmite Dawsonite Corundum Mordenite-Na Jadeite Cancrinite Sodalite-NO3 Kalsilite Muscovite`	The suppress command prevents these minerals from being considered in the construction of the activity diagram so that the field of NAS_{gel} can be visualized.

`x-axis from -10 to -6 increment .5`
`y-axis from 9 to 14 increment .5`
`line bounds med-fine`
`font = times`
	These commands control the display of the activity diagram.

APPENDIX C - MATTIGOD EXPERIMENTS AND REACT OUTPUT

Temperature = 40°C

	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 1										
0	0.0104	0.1712	3.81	0.12	3.45	--	8.9	19.2	13.7	18.5
336	0.0005	0.1498	NM	NM	NM	NAS/ZA	-8.5	1.7	5.0	9.8
720	0.0002	0.1515	NM	NM	NM	NAS/ZA	-13.2	-3.0	2.6	7.5
1080	0.0001	0.1537	NM	NM	NM	NAS/ZA	-16.7	-6.5	0.9	5.7
1440	0.0001	0.1568	NM	NM	NM	NAS/ZA	-16.5	-6.3	1.0	5.8
Solution 2										
0	0.0088	0.4241	4.18	0.12	3.47	--	10.5	20.8	14.6	19.4
336	0.0011	0.4115	NM	NM	NM	NAS/ZA	-0.9	9.3	8.9	13.7
720	0.0003	0.4038	NM	NM	NM	NAS/ZA	-8.0	2.3	5.3	10.2
1080	0.0002	0.4110	NM	NM	NM	NAS/ZA	-9.8	0.4	4.4	9.2
1440	0.0002	0.4037	NM	NM	NM	NAS/ZA	-10.1	0.2	4.3	9.1
Solution 3										
0	0.0096	0.1623	4.91	1.17	3.50	--	-3.5	6.7	7.6	12.4
336	0.0010	0.1632	NM	NM	NM	NAS/ZA	-15.4	-5.1	1.7	6.5
720	0.0005	0.1422	NM	NM	NM	NAS/ZA	-19.8	-9.6	-0.6	4.3
1080	0.0005	0.1639	NM	NM	NM	NAS/ZA	-18.9	-8.7	-0.1	4.7
1440	0.0006	0.1732	NM	NM	NM	NAS/SOD/ZA	-17.6	-7.4	0.5	5.4
Solution 4										
0	0.0086	0.4376	5.24	1.16	3.48	--	1.0	11.2	9.9	14.7
336	0.0017	0.4568	NM	NM	NM	NAS/ZA	-7.2	3.1	5.8	10.7
720	0.0007	0.4259	NM	NM	NM	NAS/ZA	-12.3	-2.1	3.2	8.1
1080	0.0006	0.4176	NM	NM	NM	NAS/ZA	-13.3	-3.1	2.7	7.6
1440	0.0006	0.4492	NM	NM	NM	NAS/ZA	-12.7	-2.5	3.0	7.9
Solution 5										
0	0.0115	0.1874	9.23	5.39	3.59	--	-11.1	-0.9	4.1	8.9
336	0.0050	0.1841	NM	NM	NM	NAS/SOD/CAN	-15.6	-5.4	1.8	6.6
720	0.0033	0.1753	NM	NM	NM	NAS/SOD/CAN	-18.0	-7.8	0.6	5.4

‡ NAS = NAS_{gel}; ZA = Zeolite-A; SOD = Sodalite-NO_3; CAN = Cancrinite; GIB = Gibbsite; BOE = Boehmite

Time (hrs)	Solution Composition (molal) Si	Al	Na	OH	NO3	Observed Phases ‡	log Q/K NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
1080	0.0025	0.1791	NM	NM	NM	NAS/SOD/CAN	-19.4	-9.2	-0.1	4.8
1440	0.0026	0.1934	NM	NM	NM	NAS/SOD/CAN	-18.7	-8.5	0.3	5.1
Solution 6										
0	0.0121	0.4987	9.83	5.52	3.68	--	-5.5	4.7	6.9	11.7
336	0.0015	0.4695	NM	NM	NM	NAS/SOD/CAN	-16.8	-6.6	1.3	6.1
720	0.0023	0.4712	NM	NM	NM	NAS/SOD/CAN	-14.6	-4.4	2.4	7.2
1080	0.0022	0.4873	NM	NM	NM	NAS/SOD/CAN	-14.6	-4.4	2.4	7.2
1440	0.0017	0.5118	NM	NM	NM	NAS/SOD/CAN	-15.6	-5.4	1.9	6.7

Temperature = 80°C

	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 1										
0	0.01149	0.2298	3.81	0.12	3.45		9.3	19.5	13.5	18.5
0.1	0.00067	0.1533	NM	NM	NM	NAS	-10.9	-0.7	3.4	8.5
0.5	0.00093	0.1616	NM	NM	NM	NAS	-8.7	1.6	4.6	9.6
1	0.00093	0.1462	NM	NM	NM	NAS	-9.6	0.6	4.1	9.1
2	0.00094	0.1611	NM	NM	NM	NAS	-8.6	1.6	4.6	9.6
4	0.00063	0.1493	NM	NM	NM	NAS	-11.5	-1.2	3.1	8.2
8	0.00067	0.1474	NM	NM	NM	NAS/SOD	-11.3	-1.0	3.2	8.3
24	0.00021	0.1488	NM	NM	NM	NAS/SOD	-17.3	-7.0	0.3	5.3
48	0.00011	0.1487	NM	NM	NM	NAS/SOD	-20.6	-10.4	-1.4	3.6
168	0.00004	0.1555	NM	NM	NM	NAS/SOD	-25.5	-15.2	-3.9	1.2
336	0.00004	0.1588	NM	NM	NM	NAS/SOD	-25.3	-15.0	-3.7	1.3
720	0.00007	0.1573	NM	NM	NM	NAS/SOD	-22.4	-12.2	-2.3	2.7
1440	0.00004	0.1594	NM	NM	NM	NAS/SOD	-25.2	-15.0	-3.7	1.3
Solution 2										
0	0.01157	0.5786	4.18	0.12	3.47		14.4	24.6	16.2	21.2
0.1	0.00193	0.4388	NM	NM	NM	NAS	-1.2	9.1	8.4	13.4
0.5	0.00175	0.4419	NM	NM	NM	NAS	-1.6	8.7	8.2	13.2
1	0.00176	0.4452	NM	NM	NM	NAS	-1.4	8.8	8.2	13.3
2	0.00197	0.4599	NM	NM	NM	NAS	-0.3	9.9	8.8	13.8
4	0.00129	0.4099	NM	NM	NM	NAS	-4.3	6.0	6.8	11.8
8	0.00125	0.4069	NM	NM	NM	NAS/SOD	-4.5	5.7	6.7	11.7
24	0.00035	0.4004	NM	NM	NM	NAS/SOD	-11.4	-1.2	3.2	8.3
48	0.00018	0.4176	NM	NM	NM	NAS/SOD	-14.3	-4.1	1.8	6.8
168	0.00007	0.3212	NM	NM	NM	NAS/GIB	-22.4	-12.2	-2.3	2.8
336	0.00006	0.2711	NM	NM	NM	GIB	-24.9	-14.7	-3.5	1.5
720	0.00007	0.2681	NM	NM	NM	GIB	-24.2	-14.0	-3.2	1.9
1440	0.00006	0.2527	NM	NM	NM	GIB	-25.5	-15.3	-3.8	1.2

‡ NAS = NAS_{gel}; ZA = Zeolite-A; SOD = Sodalite-NO_3; CAN = Cancrinite; GIB = Gibbsite; BOE = Boehmite

Time (hrs)	Solution Composition (molal) Si	Al	Na	OH	NO3	Observed Phases ‡	log Q/K NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 3										
0	0.01165	0.2331	4.91	1.17	3.50		-4.5	5.8	6.8	11.8
0.1	0.01043	0.1793	NM	NM	NM	NAS	-6.8	3.4	5.6	10.6
0.5	0.00852	0.1799	NM	NM	NM	NAS	-7.9	2.4	5.1	10.1
1	0.00828	0.1795	NM	NM	NM	NAS	-8.0	2.2	5.0	10.0
2	0.00813	0.1754	NM	NM	NM	NAS/SOD	-8.3	2.0	4.9	9.9
4	0.00527	0.1662	NM	NM	NM	NAS/SOD	-10.9	-0.7	3.5	8.6
8	0.00187	0.1665	NM	NM	NM	NAS/SOD	-16.3	-6.1	0.8	5.9
24	0.00068	0.1640	NM	NM	NM	NAS/SOD/CAN	-21.7	-11.5	-1.9	3.2
48	0.00032	0.1574	NM	NM	NM	NAS/SOD/CAN	-25.9	-15.6	-3.9	1.1
168	0.00017	0.1618	NM	NM	NM	NAS/SOD/CAN	-29.0	-18.8	-5.5	-0.5
336	0.00022	0.1616	NM	NM	NM	NAS/SOD/CAN	-27.7	-17.4	-4.8	0.2
720	0.00011	0.1683	NM	NM	NM	NAS/SOD/CAN	-31.0	-20.8	-6.5	-1.5
1440	0.00012	0.1786	NM	NM	NM	NAS/SOD/CAN	-30.2	-20.0	-6.1	-1.1
Solution 4										
0	0.01161	0.5806	5.24	1.16	3.48	--	0.7	10.9	9.4	14.4
0.1	0.01110	0.4648	NM	NM	NM	NAS	-1.5	8.7	8.3	13.3
0.5	0.00939	0.4531	NM	NM	NM	NAS	-2.6	7.6	7.7	12.8
1	0.00290	0.4908	NM	NM	NM	NAS	-8.1	2.1	5.0	10.0
2	0.00207	0.4748	NM	NM	NM	NAS/SOD	-10.2	0.1	4.0	9.0
4	--	0.4512	NM	NM	NM	NAS/SOD	N/A	N/A	N/A	N/A
8	0.00249	0.3993	NM	NM	NM	NAS/SOD/CAN	-10.6	-0.3	3.7	8.8
24	0.00084	0.4206	NM	NM	NM	NAS/SOD/CAN	-15.8	-5.6	1.1	6.1
48	0.00032	0.4324	NM	NM	NM	NAS/SOD/CAN	-20.7	-10.4	-1.3	3.7
168	0.00019	0.4305	NM	NM	NM	NAS/SOD/CAN	-23.4	-13.2	-2.7	2.3
336	0.00017	0.4303	NM	NM	NM	NAS/SOD/CAN	-24.0	-13.8	-3.0	2.1
720	0.00014	0.4165	NM	NM	NM	NAS/SOD/CAN	-25.3	-15.0	-3.6	1.4
1440	0.00014	0.4093	NM	NM	NM	NAS/SOD/CAN	-25.4	-15.2	-3.7	1.4

Time (hrs)	Solution Composition (molal) Si	Al	Na	OH	NO3	Observed Phases ‡	log Q/K NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 5										
0	0.01197	0.2394	9.23	5.39	3.59	--	-14.0	-3.8	2.2	7.3
0.1	0.01360	0.1762	NM	NM	NM	NAS/SOD/CAN	-15.1	-4.9	1.7	6.7
2	0.01371	0.1830	NM	NM	NM	NAS/SOD/CAN	-14.9	-4.6	1.8	6.9
3	0.01280	0.1775	NM	NM	NM	NAS/SOD/CAN	-15.4	-5.1	1.6	6.6
3.5	0.01331	0.1776	NM	NM	NM	NAS/SOD/CAN	-15.2	-4.9	1.7	6.7
4	--	0.1960	NM	NM	NM	NAS/SOD/CAN	N/A	N/A	N/A	N/A
8	0.00111	0.1848	NM	NM	NM	NAS/SOD/CAN	-27.9	-17.7	-4.7	0.3
24	0.00127	0.1801	NM	NM	NM	NAS/SOD/CAN	-27.4	-17.1	-4.4	0.6
48	0.00210	0.1965	NM	NM	NM	NAS/SOD/CAN	-24.3	-14.0	-2.9	2.1
168	0.00111	0.1939	NM	NM	NM	NAS/SOD/CAN	-27.7	-17.4	-4.6	0.4
336	0.00046	0.1845	NM	NM	NM	NAS/SOD/CAN	-32.5	-22.3	-7.0	-2.0
720	0.00044	0.1914	NM	NM	NM	SOD/CAN	-32.6	-22.3	-7.0	-2.0
1440	0.00041	0.1973	NM	NM	NM	SOD/CAN	-32.8	-22.5	-7.1	-2.1
Solution 6										
0	0.01227	0.6133	9.83	5.52	3.68	--	-8.6	1.6	5.0	10.0
0.1	0.01019	0.4568	NM	NM	NM	NAS/SOD	-11.5	-1.2	3.6	8.6
2	0.01385	0.4730	NM	NM	NM	NAS/SOD/CAN	-9.7	0.6	4.5	9.5
3	0.01388	0.4725	NM	NM	NM	NAS/SOD/CAN	-9.7	0.6	4.5	9.5
3.5	0.01267	0.4673	NM	NM	NM	NAS/SOD/CAN	-10.2	0.0	4.2	9.2
4	0.00064	0.4840	NM	NM	NM	NAS/SOD/CAN	-25.6	-15.3	-3.5	1.5
8	0.00165	0.4864	NM	NM	NM	NAS/SOD/CAN	-20.6	-10.4	-1.0	4.0
24	0.00165	0.5017	NM	NM	NM	NAS/SOD/CAN	-20.4	-10.2	-0.9	4.1
48	0.00167	0.4879	NM	NM	NM	NAS/SOD/CAN	-20.5	-10.3	-0.9	4.1
168	0.00096	--	NM	NM	NM	NAS/SOD/CAN	N/A	N/A	N/A	N/A
336	0.00061	0.4526	NM	NM	NM	NAS/SOD/CAN	-26.3	-16.0	-3.8	1.2
720	0.00035	0.4925	NM	NM	NM	NAS/SOD/CAN	-28.6	-18.4	-5.0	0.0
1440	0.00040	0.4966	NM	NM	NM	NAS/SOD/CAN	-27.9	-17.6	-4.6	0.4

Temperature = 120°C

	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 1										
0	0.0115	0.2298	3.81	0.11	3.45	--	12.2	22.5	14.6	19.8
0.5	0.0068	0.1247	N/M	N/M	N/M	NAS	2.3	12.5	9.6	14.8
1	0.0036	0.1438	N/M	N/M	N/M	NAS	0.1	10.4	8.6	13.7
2	0.0025	0.14	N/M	N/M	N/M	NAS/SOD	-2.1	8.2	7.5	12.6
4	0.0011	0.1396	N/M	N/M	N/M	NAS/SOD	-6.4	3.9	5.3	10.5
8	0.0005	0.1368	N/M	N/M	N/M	NAS/SOD	-10.7	-0.5	3.1	8.3
24	0.0003	0.1343	N/M	N/M	N/M	NAS/SOD	-13.6	-3.3	1.7	6.9
Solution 2										
0	0.0116	0.5786	4.18	0.12	3.47	--	17.4	27.6	17.2	22.4
0.5	0.0007	0.3692	N/M	N/M	N/M	NAS	-6.2	4.1	5.5	10.6
1	0.0025	0.3422	N/M	N/M	N/M	NAS	-0.4	9.9	8.3	13.5
2	0.0013	0.3281	N/M	N/M	N/M	NAS/SOD	-4.3	5.9	6.4	11.6
4	0.0007	0.3357	N/M	N/M	N/M	NAS/SOD	-7.3	3.0	4.9	10.1
8	0.0004	0.3041	N/M	N/M	N/M	NAS/SOD/GIB	-11.3	-1.0	2.9	8.1
24	0.0007	0.2875	N/M	N/M	N/M	NAS/SOD	-9.0	1.3	4.1	9.2
Solution 3										
0	0.0117	0.2331	4.91	1.17	3.5	--	-2.3	8.0	7.5	12.6
0.5	0.0068	0.1247	N/M	N/M	N/M	NAS/SOD	-9.2	1.0	4.0	9.2
1	0.0036	0.1438	N/M	N/M	N/M	NAS/SOD	-11.7	-1.4	2.8	7.9
2	0.0025	0.14	N/M	N/M	N/M	NAS/SOD	-13.8	-3.5	1.7	6.9
4	0.0011	0.1396	N/M	N/M	N/M	NAS/SOD/CAN	-18.1	-7.8	-0.4	4.7
8	0.0005	0.1368	N/M	N/M	N/M	NAS/SOD/CAN	-22.3	-12.1	-2.6	2.6
24	0.0003	0.1343	N/M	N/M	N/M	NAS/SOD/CAN	-25.1	-14.8	-3.9	1.2
Solution 4										
0	0.0116	0.5806	5.24	1.16	3.48	--	2.9	13.1	10.1	15.3
0.5	0.0034	0.3488	N/M	N/M	N/M	NAS/SOD/CAN	-7.9	2.4	4.7	9.9
1	0.0013	0.3053	N/M	N/M	N/M	NAS/SOD/CAN	-13.9	-3.6	1.7	6.9
2	0.0008	0.3184	N/M	N/M	N/M	NAS/SOD/CAN	-16.1	-5.8	0.6	5.8
4	0.0005	0.333	N/M	N/M	N/M	NAS/SOD/CAN	-18.2	-8.0	-0.5	4.7
8	0.0003	0.3181	N/M	N/M	N/M	NAS/SOD/CAN	-21.2	-11.0	-2.0	3.2

‡ NAS = NAS_{gel}; ZA = Zeolite-A; SOD = Sodalite-NO_3; CAN = Cancrinite; GIB = Gibbsite; BOE = Boehmite

	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
24	0.0001	0.3317	N/M	N/M	N/M	NAS/SOD/CAN	-26.7	-16.4	-4.7	0.5
Solution 5										
0	0.012	0.2394	9.23	5.39	3.59	--	-12.3	-2.0	2.7	7.9
0.5	0.0048	0.0886	N/M	N/M	N/M	No obs.	-22.6	-12.3	-2.4	2.7
1	0.0051	0.0986	N/M	N/M	N/M	NAS/SOD/CAN	-21.7	-11.4	-2.0	3.2
2	0.0043	0.0922	N/M	N/M	N/M	NAS/SOD/CAN	-23.0	-12.7	-2.6	2.6
4	0.0035	0.081	N/M	N/M	N/M	NAS/SOD/CAN	-24.7	-14.5	-3.5	1.7
8	0.0015	0.0913	N/M	N/M	N/M	NAS/SOD/CAN	-28.5	-18.2	-5.4	-0.2
24	0.0013	0.0886	N/M	N/M	N/M	NAS/SOD/CAN	-29.4	-19.1	-5.8	-0.7
Solution 6										
0	0.01227	0.6132	9.83	5.52	3.68	--	-6.9	3.4	5.5	10.7
0.5	0.0047	0.2398	N/M	N/M	N/M	No observation	-17.6	-7.4	0.1	5.3
1	0.0046	0.2342	N/M	N/M	N/M	NAS/SOD/CAN	-17.9	-7.6	0.0	5.1
2	0.004	0.2287	N/M	N/M	N/M	NAS/SOD/CAN	-18.7	-8.5	-0.5	4.7
4	0.0025	0.2404	N/M	N/M	N/M	NAS/SOD/CAN	-20.9	-10.6	-1.5	3.6
8	0.0007	0.2342	N/M	N/M	N/M	NAS/SOD/CAN	-27.7	-17.4	-4.9	0.2
24	0.0007	0.2622	N/M	N/M	N/M	NAS/SOD/CAN	-27.1	-16.8	-4.6	0.6

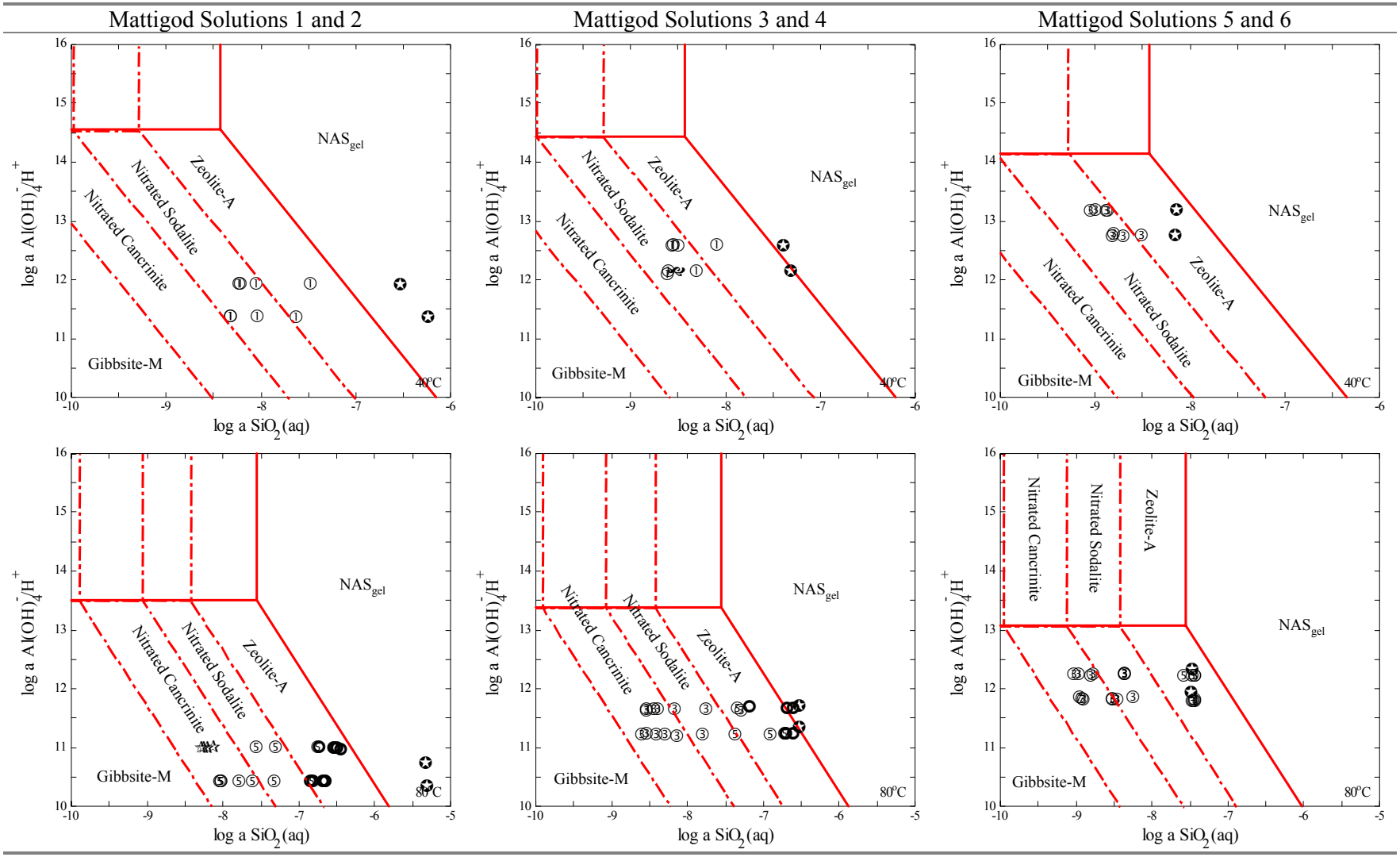
Temperature = 175°C

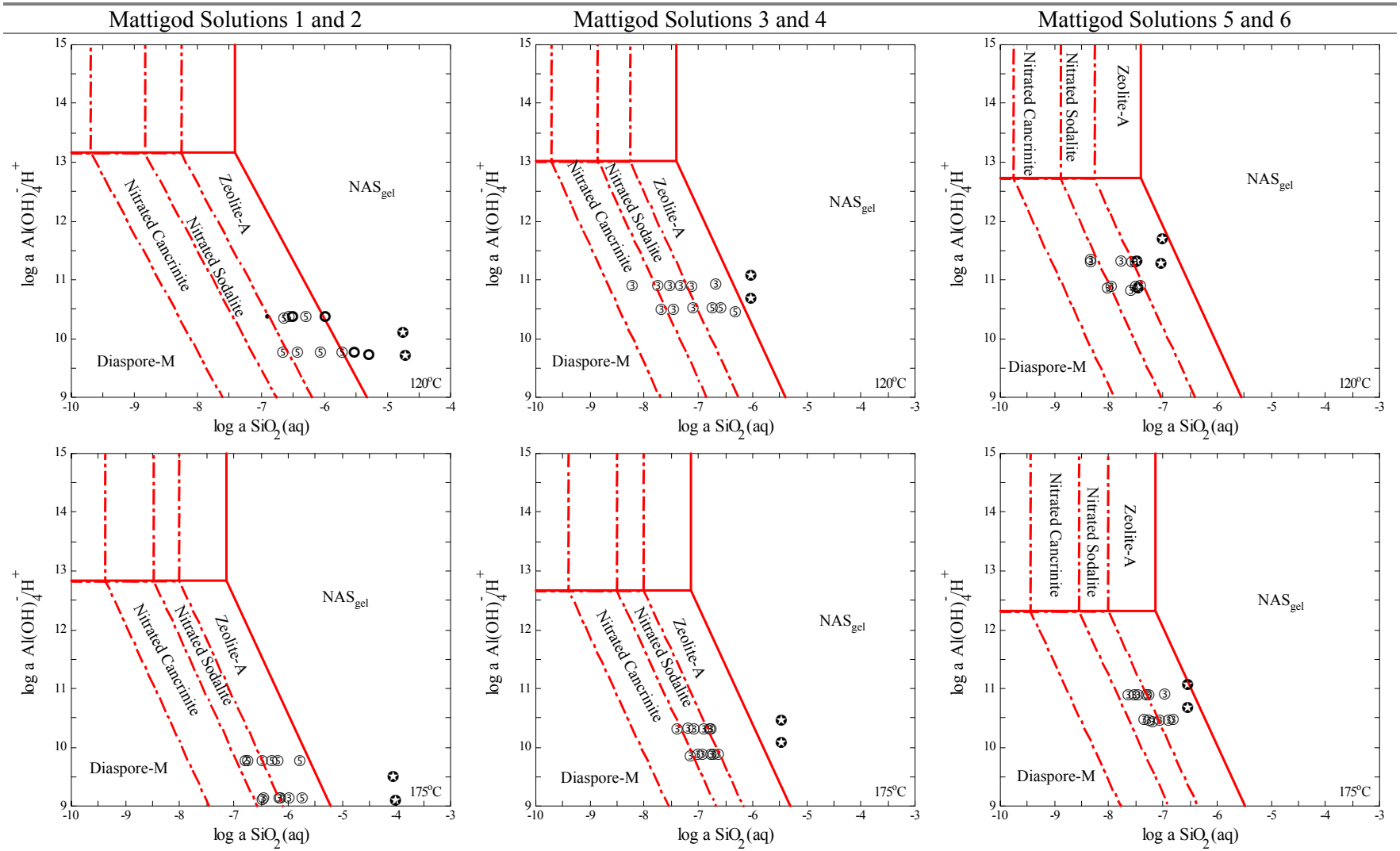
	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
Solution 1										
0	0.0115	0.23	3.81	0.12	3.45		14.9	25.2	15.4	20.8
0.5	0.0005	0.1336	N/M	N/M	N/M	NAS/SOD	-8.8	1.5	3.6	8.9
1	0.0003	0.1302	N/M	N/M	N/M	NAS/SOD/CAN	-11.7	-1.4	2.1	7.4
2	0.0002	0.1321	N/M	N/M	N/M	NAS/SOD/CAN	-13.7	-3.4	1.1	6.4
4	0.0002	0.1362	N/M	N/M	N/M	NAS/SOD/CAN	-13.4	-3.1	1.2	6.6
8	0.0001	0.1282	N/M	N/M	N/M	NAS/SOD/CAN	-17.6	-7.3	-0.8	4.5
24	0.0001	0.1211	N/M	N/M	N/M	NAS/SOD/CAN	-18.1	-7.8	-1.1	4.2
Solution 2										
0	0.0116	0.5791	4.19	0.12	3.47		19.7	30.0	17.9	23.2
0.5	0.001	0.3409	N/M	N/M	N/M	NAS/SOD	-3.7	6.6	6.2	11.5
1	0.0004	0.3336	N/M	N/M	N/M	NAS/SOD	-8.7	1.6	3.7	9.0
2	0.0003	0.3386	N/M	N/M	N/M	NAS/SOD	-10.0	0.3	3.0	8.3
4	0.0002	0.343	N/M	N/M	N/M	NAS/SOD	-12.0	-1.7	2.0	7.4
8	0.0001	0.3549	N/M	N/M	N/M	NAS/SOD	-15.2	-4.9	0.4	5.8
24	0.0001	0.3343	N/M	N/M	N/M	NAS/SOD/CAN/ BOE	-15.9	-5.6	0.1	5.4
Solution 3										
0	0.0117	0.2333	4.92	1.17	3.5		-1.6	8.7	7.3	12.6
0.5	0.0008	0.1332	N/M	N/M	N/M	NAS/SOD/CAN	-19.4	-9.1	-1.6	3.7
1	0.001	0.1336	N/M	N/M	N/M	NAS/SOD/CAN	-18.2	-7.9	-1.0	4.3
2	0.0007	0.1317	N/M	N/M	N/M	NAS/SOD/CAN	-20.2	-9.9	-2.0	3.3
4	0.0005	0.1336	N/M	N/M	N/M	NAS/SOD/CAN	-21.8	-11.6	-2.8	2.5
8	0.0004	0.1347	N/M	N/M	N/M	NAS/SOD/CAN	-23.0	-12.7	-3.4	1.9
24	0.0003	0.1299	N/M	N/M	N/M	NAS/SOD/CAN	-24.7	-14.4	-4.3	1.1
Solution 4										
0	0.0116	0.581	5.25	1.16	3.49		3.7	14.0	10.0	15.3
0.5	0.0008	0.3264	N/M	N/M	N/M	NAS/SOD/CAN	-15.3	-5.0	0.5	5.8
1	0.0008	0.3444	N/M	N/M	N/M	NAS/SOD/CAN	-14.9	-4.6	0.7	6.0
2	0.0006	0.3367	N/M	N/M	N/M	NAS/SOD/CAN	-16.5	-6.2	-0.1	5.2
4	0.0004	0.3374	N/M	N/M	N/M	NAS/SOD/CAN	-18.6	-8.3	-1.2	4.1

‡ NAS = NAS_{gel}; ZA = Zeolite-A; SOD = Sodalite-NO_3; CAN = Cancrinite; GIB = Gibbsite; BOE = Boehmite

	Solution Composition (molal)						log Q/K			
Time (hrs)	Si	Al	Na	OH	NO3	Observed Phases ‡	NAS_{gel}	Zeolite-A	Nitrated Sodalite	Nitrated Cancrinite
8	0.0003	0.3555	N/M	N/M	N/M	NAS/SOD/CAN	-19.7	-9.4	-1.7	3.6
24	0.0002	0.3423	N/M	N/M	N/M	NAS/SOD/CAN	-22.1	-11.8	-2.9	2.4
Solution 5										
0	0.012	0.2396	9.24	5.39	3.59		-12.1	-1.8	2.3	7.6
0.5	0.0071	0.146	N/M	N/M	N/M	NAS/SOD/CAN	-17.7	-7.4	-0.5	4.8
1	0.0058	0.1417	N/M	N/M	N/M	NAS/SOD/CAN	-18.9	-8.6	-1.1	4.2
2	0.004	0.1409	N/M	N/M	N/M	NAS/SOD/CAN	-20.9	-10.6	-2.1	3.2
4	0.0028	0.135	N/M	N/M	N/M	NAS/SOD/CAN	-23.0	-12.7	-3.2	2.2
8	0.0025	0.1385	N/M	N/M	N/M	NAS/SOD/CAN	-23.4	-13.2	-3.4	2.0
24	0.002	0.1441	N/M	N/M	N/M	NAS/SOD/CAN	-24.4	-14.1	-3.8	1.5
Solution 6										
0	0.0123	0.6138	9.84	5.52	3.68		-6.7	3.6	5.0	10.4
0.5	0.005	0.3886	N/M	N/M	N/M	NAS/SOD/CAN	-14.4	-4.1	1.2	6.6
1	0.0026	0.382	N/M	N/M	N/M	NAS/SOD/CAN	-17.9	-7.6	-0.5	4.8
2	0.0023	0.3783	N/M	N/M	N/M	NAS/SOD/CAN	-18.6	-8.3	-0.9	4.4
4	0.0016	0.386	N/M	N/M	N/M	NAS/SOD/CAN	-20.4	-10.1	-1.8	3.6
8	0.0014	0.3772	N/M	N/M	N/M	NAS/SOD/CAN	-21.2	-10.9	-2.2	3.1
24	0.0011	0.372	N/M	N/M	N/M	NAS/SOD/CAN	-22.5	-12.2	-2.9	2.5

APPENDIX D - ACTIVITY DIAGRAMS OF MATTIGOD SOLUTIONS


Mattigod Solutions 1 and 2
Mattigod Solutions 3 and 4
Mattigod Solutions 5 and 6
log a Al(OH)4-/H+
log a SiO2(aq)
NASgel
Zeolite-A
Nitrated Sodalite
Nitrated Cancrinite
Gibbsite-M
40°C
80°C



*=NAS_{gel}; ●=NAS_{gel}+Sodalite+Zeolite-A; ◇=NAS_{gel}+Sodalite; Δ=NAS_{gel}+Sodalite+Cancrinite; □=NAS_{gel}+Zeolite-A; +=$Al(OH)_3$, gibbsite; O=NAS_{gel}+boehmite+gibbsite