

DOE FINAL REPORT

A Comprehensive Study of the Solubility, Thermochemistry, Ion Exchange and Precipitation Kinetics of NO₃ Cancrinite and No₃ Sodalite

Award Number: DE-FG07-01ER63298

Work Done at Davis: 9/15/01 -- 9/14/04

Introduction

The precipitation of aluminosilicate phases from caustic nuclear wastes has proven to be problematic in a number of processes including radionuclide separations (cementation of columns by aluminosilicate phases), tank emptying (aluminosilicate tank heels), and condensation of wastes in evaporators (aluminosilicate precipitates in the evaporators, providing nucleation sites for growth of critical masses of radioactive actinide salts). In a collaboration between SNL and UCD, we have investigated why and how these phases form, and which conditions favor the formation of which phases. These studies have involved synthesis and characterization of aluminosilicate phases formed using a variety of synthesis techniques, kinetics of precipitation, structural investigations of aluminosilicate phases, thermodynamic calculations of aluminosilicate solubility, calorimetric studies of aluminosilicate precipitation, and a limited investigation of radionuclide partitioning and ion exchange processes (involving typical tank fluid chemistries and these materials).

The predominant phases that are observed in the aluminosilicate precipitates from basic tanks wastes (i.e. Hanford, Savannah River Site "SRS" wastes) are the salt enclathrated zeolites: sodium nitrate, sodium carbonate and sodium hydroxide sodalite and cancrinite. These phases precipitate readily from the high ionic strength, highly basic solutions at ambient temperatures as well as at elevated temperatures, with or without the presence of an external Al and Si source (both are contained in the waste solutions), and upon interactions with reactive soil components such as clays.

This report focuses on the portion of the work performed at UC Davis by Professor Navrotsky's group.

Synthesis of high purity materials

The objectives of current research at UC Davis are the acquisition of thermodynamic data, such as heats and free energies of formation and heat capacities, for NO₃ cancrinite and NO₃ sodalite, and investigating the formation of these phases using techniques such as X-ray diffraction and *in situ* calorimetry. Dr. Qingyuan Liu, a postdoctoral researcher fully supported by this EMSP grant, did most of the work reported in this section. After investigating several cancrinite and sodalite samples from Sandia National Laboratory (all of which contained substantial carbonate) we undertook a program to synthesize purer materials. This task describes our successes in this area.

Composition Analysis and Formula Calculation:

Composition has a significant impact on the thermodynamic properties of materials. It has an even larger effect on the thermochemical cycles used to calculate heats of formation, since mass balance must be conserved in each step. Therefore, it is imperative to know the exact composition of the compounds of interest before proceeding with calorimetric measurements.

Thorough analyses were performed using a variety of techniques such as the electron microprobe, thermogravimetry, commercial carbon and nitrogen analysis, and evolved gas analysis. Table 1.1 is a summary of data for the Sandia samples. Cancrinite and sodalite samples have been denoted as NC and NS series, respectively. NC_{ideal} and NS_{ideal} stand for the ideal stoichiometric compounds.

Table 1.1 Composition and formulae of Sandia (SNL) samples

Sample ID	Na:Al:Si	N (wt%)	C (wt%)	H ₂ O (wt%)	Formula	FW (g/mol)
NC _{ideal}	8 : 6 : 6	2.65	0	3.40	Na ₈ Al ₆ Si ₆ O ₂₄ (NO ₃) ₂ ·2H ₂ O	1058.17
NC#1	7.032 : 5.570 : 6.000	2.02	0.84	3.06	Na _{8.893} [Al _{5.777} Si _{6.223} O ₂₄](NO ₃) _{1.582} (CO ₃) _{0.767} ·1.863(H ₂ O)	1096.73
NC#2	7.960 : 6.007 : 6.000	2.00	0.17	3.04	Na _{7.754} [Al _{6.003} Si _{5.997} O ₂₄](NO ₃) _{1.461} (CO ₃) _{0.145} ·1.726(H ₂ O)	1023.00
NS _{ideal}	8 : 6 : 6	2.74	0	0	Na ₈ Al ₆ Si ₆ O ₂₄ (NO ₃) ₂	1022.15
NS#1	8.023 : 5.823 : 6.000	1.10	1.85	0	Na _{10.179} [Al _{5.910} Si _{6.090} O ₂₄](NO ₃) _{0.867} (CO ₃) _{1.701}	1104.36
NS#2	7.459 : 5.974 : 6.000	0.56	1.85	0	Na _{9.681} [Al _{5.987} Si _{6.013} O ₂₄](NO ₃) _{0.424} (CO ₃) _{1.635}	1061.38

Synthesis of Cancrinite and Sodalite

Synthesis at UC Davis has several goals. For the measurements of heats of formation and heat capacity, it is desirable that we have pure samples. Therefore, one of the goals of our synthesis is to obtain stoichiometric NO₃ cancrinite and NO₃ sodalite samples. Both oven and *in situ* calorimetric syntheses (using our Setaram C-80 calorimeter) have been performed. The latter has the advantage of far better temperature control and homogeneity. Table 1.2 shows detailed synthesis conditions for different series of samples.

Table 1.2 Synthesis conditions of different sample series

Series	Amount of Material (g)					
	Zeolite A	NaNO ₃	NaOH	Na ₂ SiO ₃ ·9H ₂ O	Al ₂ O ₃ ·Na ₂ O	H ₂ O
1	/	2.55	0.55	2.86	0.82	20 ~ 40*
2	/	40.76	8.72	11.44	3.28	80
Zeolite A conversion	1	6	2	/	/	40

* See text for explanation.

Oven and in situ Synthesis of Series 1 Samples

For the synthesis of this series of samples, the following solutions were prepared: 6 M NaNO₃ (10.19 g in 20 ml H₂O), 2.7 M NaOH (2.18 g in 20 ml H₂O), 2 M Na₂SiO₃·9H₂O (11.44 g in 20 ml H₂O), 1 M Al₂O₃·Na₂O (3.28 g in 20 ml H₂O). Then 5 ml of each solution was mixed together in a plastic bottle to form roughly a 20 ml gel. To check on the effects of concentration some of the gel samples were diluted by adding 10 or 20 ml of water. For oven synthesis experiments the temperature was kept at 90 °C.

Initially the phase transition behavior of the gel (20ml) was studied without additional water. Zeolite A appeared to be the first phase produced during heating. Sodalite followed within one day of aging. Prolonged heating increased the amount of cancrinite. However, the sodalite to cancrinite conversion (out to 5 days) was slow.

Dilution of the gel-like mixtures was performed to check on the effect that concentration had on the identity of the product phase. All samples were kept in an oven at 90° C for 48 hours. Sodalite is the dominant phase and without additional water only minor amounts of cancrinite were observable in the XRD pattern. The amount of zeolite A increased with dilution, suggesting lower concentrations favor the formation of zeolite A. At room temperature a mixture of equal proportions of gel and water revealed that zeolite A precipitated within 3 weeks of aging

Synthesis of Pure NO₃ Cancrinite (Sample Series # 2)

Oven synthesis experiments were conducted in an attempt to produce pure NO₃ cancrinite samples. The solutions used in the investigation are listed in Table 1.2. A different mixing strategy was employed to ensure complete dissolution of chemicals before reaction. For this series of samples, sodium hydroxide, sodium nitrate and sodium silicate were first dissolved in 70 ml water. Sodium aluminate was dissolved separately in 10 ml of water. The two solutions were mixed together afterwards, resulting in a viscous gel. The gel was then put in a lab oven and aged at 90 °C. Figure 1.1 shows the XRD patterns of samples collected with various aging time. Apparently, the gel completely crystallized within 5 hours of heating because X-ray diffraction revealed formation of a pure NO₃ cancrinite. Crystallinity of the samples improved with longer aging times (out to 7 days). One example of the high purity cancrinites produced in this manner is given by the formula: Na_{7.261}[Al_{5.854}Si_{6.146}O₂₄](NO₃)_{1.316}(CO₃)_{0.045}·2.626(H₂O) (“NCS #5”).

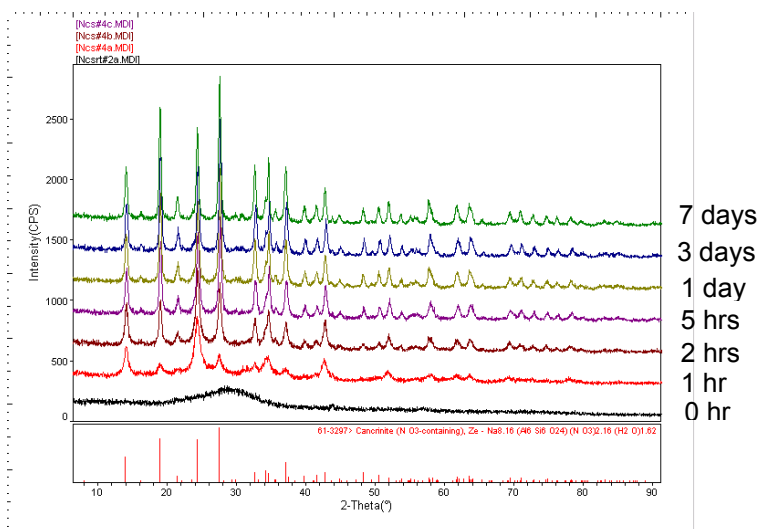


Figure 1.1: X-ray Diffraction (XRD) patterns of samples with different aging times.

Zeolite A to Sodalite Conversion

The influence of temperature on the phase transitions between zeolite A, sodalite and cancrinite was also studied. After dispersing zeolite A in a mixed solution of NaOH and NaNO₃ (see Table 1.2 for synthesis conditions), the sample was placed in a laboratory oven (that was pre-warmed to 90°C) and aged for 24 hours. The product was mostly composed of sodalite with a minor amount of cancrinite. Next, a special effort was made to check if lowering temperature would suppress cancrinite formation. XRD analysis of samples collected with different aging temperatures showed that lowering the temperature alone did not prevent the formation of cancrinite. When temperature was lower than 80°C, no significant amounts of sodalite were formed.

The kinetics of transformation from zeolite A to sodalite/cancrinite at 90°C was also investigated. X-ray analysis indicated that the reaction was completed within 8 hours of aging. No conversion was found at room temperature even after 46 days. Also, *in situ* calorimetry did not reveal any heat effects related to such a conversion process. This finding is consistent with the *in situ* experiments for the series # 1 samples where no heat event was found for the phase transition from zeolite A to sodalite.

Conclusions:

In summary, we have explored the influence of various factors on the product purity, energetics and kinetics of precipitation, and phase transition rates for a variety of sodium aluminosilicates. Valuable knowledge has been gained regarding the formation of cancrinite and sodalite materials. Pure NO₃ cancrinite samples have been successfully produced. While sodalite is readily available as one of the end products in many of synthesis experiments, we have yet to have success in synthesizing the pure sodalite needed for precision calorimetric measurements.

Calorimetric Studies

This task summarizes progress made at UC Davis in determining the energetics of various sodium aluminosilicates. A variety of analytic techniques were employed using UC Davis state-of-the-art equipment, particularly the unique Calvet calorimeters for molten salt solution calorimetry.

In situ synthesis calorimetry

Mixtures of 10 ml of gel with 10 ml additional water was further investigated by *in situ* solution calorimetry. 7.5 g of the gel was loaded into the sample vessel. The instrument was operated in a scanning mode with the objective of studying the crystallization of the gel at different heating rates.

Figure 2.1 shows how heat effects the crystallization of the gel at three heating rates. At the slower heating rate, crystallization occurred at a lower temperature. Completion of crystallization was also delayed with the slower heating rates, though all samples finished crystallization within hours. Although peak intensities decreased with slower heating, integrated exothermic heat values (not shown) were almost unchanged, indicating complete crystallization. The enthalpy of crystallization per gram of gel was about -0.34 J.

Samples were collected before, during, and after the crystallization peak for phase identification. All samples were quenched to room temperature with running water immediately after taken and repeatedly washed with de-ionized water to neutral pH. For the sample with a heating rate of 0.1 K/min, sampling temperatures were chosen as 68.36°C, 82.50°C, and 92.40°C. The sample collected before the appearance of the crystallization peak was amorphous. Significant amount of crystallization took place in the sample collected on the peak. Samples taken after the peak were completely crystallized to zeolite A.

If the *in situ* experiment was then maintained 90°C for two days the product had transformed into a mix that was mostly sodalite, with only a small amount of cancrinite and a minor amount of zeolite A. The whole heating cycle was repeated afterwards for baseline correction. The second heating showed no calorimetric peaks. Thus the initially formed zeolite A was apparently converted to mostly sodalite, but the heat effect associated with this reaction was either too small to detect or too spread out in time to be seen clearly.

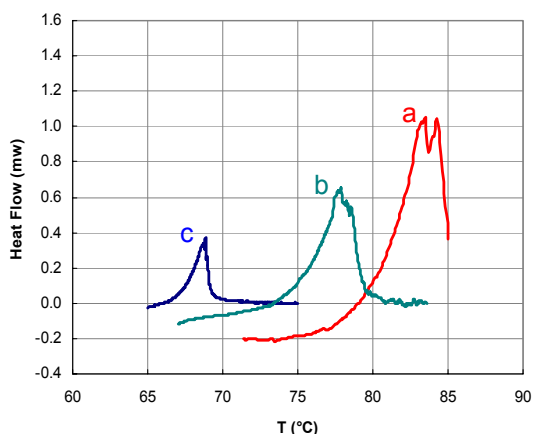


Figure 2.1: *In situ* calorimetry of gel mixtures at different heating rates. The heating sequences of the three scans were: **a.** 25 to 90°C at 0.1 K/min, **b.** 25 to 65°C at 0.1 K/min and 65°C to 90°C at 0.01 K/min, **c.** 25 to 65°C at 0.1 K/min and 65°C to 90°C 0.05 K/min.

Drop-Solution Calorimetry

All Sandia cancrinite samples listed in Table 2.1, and the pure NO₃ cancrinite sample (NCS#5) synthesized at UC Davis, were characterized with high temperature oxide melt solution calorimetry. The enthalpy of drop solution was used in a thermochemical cycle to calculate the enthalpy of formation from an oxide- nitrate-carbonate mixture and from the elements. In all experiments, the temperature of the calorimeter was maintained at 700°C. Lead borate was used as a solvent and Ar gas as a bubbling and flushing gas. 5 mg alumina calibration factors were used in heat of drop solution calculations. This is a standard method used in our laboratory.

Heats of Formation

The formulae of the samples were calculated based on composition analysis. For details of the calculation, refer to previous sections. All data were tabulated in Table 2.1.

Table 2.1 Heats of formation of cancrinite samples

Sample ID	Formula	Heat of Formation at 298.15 K (KJ/mol)	
		From oxide mixture ^a	From Elements
NC#1	$\text{Na}_{8.893}[\text{Al}_{5.777}\text{Si}_{6.223}\text{O}_{24}](\text{NO}_3)_{1.582}(\text{CO}_3)_{0.767} \cdot 1.863(\text{H}_2\text{O})$	-439.11±9.24	-14234.59±11.80
NC#2	$\text{Na}_{7.754}[\text{Al}_{6.003}\text{Si}_{5.997}\text{O}_{24}](\text{NO}_3)_{1.461}(\text{CO}_3)_{0.145} \cdot 1.726(\text{H}_2\text{O})$	-884.81±11.61	-13915.21±13.67
NCS#5	$\text{Na}_{7.261}[\text{Al}_{5.854}\text{Si}_{6.146}\text{O}_{24}](\text{NO}_3)_{1.316}(\text{CO}_3)_{0.045} \cdot 2.626(\text{H}_2\text{O})$	-924.91±15.71	-13987.50±17.37
Bennington and Brown	$\text{Na}_{7.68}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NO}_3)_{1.68} \cdot 4.1(\text{H}_2\text{O})$	-900.40±7.53	-14593.67±10.88

a. Formation from a mixture of NaNO₃ and Na₂CO₃ (enough Na to balance the anions), remaining Na as Na₂O, plus Al₂O₃, SiO₂, and H₂O (liquid).

Due to variations in sample composition, heats of formation data are different from sample to sample. This is especially true for samples with large amount of carbonate (e.g., NC#1). The enthalpy of formation from the mixture of oxides, sodium carbonate and sodium nitrate becomes less exothermic with increasing carbonate content, suggesting that the end-member carbonate

cancrinite is substantially less stable than its nitrate analogue. The results were also compared with the one available literature values. The enthalpy of formation data from oxides for samples with small amounts of carbonate are close to that reported by Bennington and Brown (Rep. Invest. 8778 - U. S., Bureau of Mines, 1983). It has been generally accepted that NO_3 cancrinite has a ideal formula of $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NO}_3)_2 \cdot 2(\text{H}_2\text{O})$. However, the sample used in Bennington and Brown's work was reported to have 4 moles of water. Details of sample preparation and compositional analysis were not presented in their work. Nevertheless, their value and ours for our most carbonate free sample practically overlap within experimental error despite probably small differences in composition.

Final State of Nitrate

To write the appropriate thermochemical cycles for the calculation of heat of formation, the final state of nitrate the after calorimetry experiments needs to be characterized. At the very least, one needs to be reasonably confident that this final state is the same regardless of which nitrate-containing sample is being dissolved. We have used weight loss experiments, evolved gas analysis, and thermodynamic calculations to investigate this problem.

Weight loss experiments

To simulate what happens in the drop solution calorimeter, pellets of NaNO_3 were dropped in both lead borate and sodium molybdate solvents and heated at 700°C for an hour. The weight differences before and after the pellet was dropped were plotted against pellet weight. Weight losses were very close to theoretical values assuming all nitrate evolves as gases in both solvents. N analyses of the solvents (e.g., the quenched fused salts) after dropping of NaNO_3 confirmed this conclusion and no nitrogen was detectable in either solvent. Thus, we conclude that all nitrate is converted to gaseous species during calorimetry. The gaseous products evolved during heating of nitrate pellets in solvents at 700°C were characterized with FTIR. From the IR spectra we conclude that nitrate salt in cancrinite and sodalite is evolved as nitrogenous gases such as NO_2 and NO . Finally, the consistency of the nitrogen-containing gases was checked with thermodynamic calculations. The following reaction was used in the calculations.



The heat of reaction calculated from literature data (heat of formation) of each species was -32.02 kJ/mol . A value of -31.6 kJ/mol was obtained from heats of drop solution of the four salts. The two values agreed very well, suggesting the gas products evolved from sodium and potassium nitrate were consistent.

Heat Capacity Measurements

Preliminary heat capacity measurements were performed on samples NC#1 and NC#2 with both low and high temperature Differential Scanning Calorimetry (DSC) using a Netzsch 404 system. For low temperature DSC, the temperature range was -100 to 200°C . High temperature DSC measurements were conducted in a range of room temperature to 1000°C . In both cases, a scanning rate of 10 K/min was used and a corundum disk was used as the standard. The results show that the sample begins decomposing above 100°C , limiting the range of heat capacity measurements. More detailed work will be done with the better samples now available.

Conclusions

Major findings of the first 2.5 years of this EMSP project at UC Davis are:

1. High temperature oxide melt solution calorimetry is feasible for nitrate-containing aluminosilicates. All nitrogen is evolved from the solvent as a consistent mixture of gases.
2. Synthetic NO_3 cancrinites contain considerable carbonate unless extreme care is taken in synthesis. The enthalpy of formation of the cancrinite phase from a mixture of sodium nitrate, sodium carbonate, sodium oxide, aluminum oxide, and liquid water becomes less exothermic as carbonate is substituted for nitrate.
3. *In situ* calorimetry can be used to follow the synthesis and transformation of zeolite phases. Zeolite A is synthesized first and then transformed to sodalite and/or cancrinite. While calorimetric peaks related to zeolite A crystallization are readily observable, the heat effect associated with this reaction was either too small to detect or too spread out in time to be seen clearly.
4. The formation of NO_3 cancrinite and NO_3 sodalite in mixed solutions of sodium silicate, sodium aluminate, sodium hydroxide and sodium nitrate are sensitive to concentration and temperature. In less concentrated systems, zeolite A appeared to be first precipitated phase and then sodalite follows. Concentrated solutions (hydroxide and nitrate) favored formation of cancrinite. Zeolite A can be easily converted to sodalite although some cancrinite remains as a minor impurity. Crystallization is usually complete within hours of aging at 90°C . However, sodalite to cancrinite transitions seemed to take much longer to reach completion.

Publications and products

“Nitrate Cancrinite: Synthesis and Determination of Enthalpy of Formation, Microporous and Mesoporous Materials”, Q. Liu, H. Xu, and Navrotsky, (in submission)