A Comprehensive Study of the Solubility, Thermochemistry, Ion Exchange, and Precipitation Kinetics of NO₃ Cancrinite and NO₃ Sodalite (Project #: 81959)

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Research Objective: NO_3 cancrinite and NO_3 sodalite have been found as a common sodium aluminosilicate forming in strongly caustic and alkaline aqueous solutions associated with radioactive High Level Waste (HLW) stored in many underground tanks and also in nuclear waste treatment facilities such as the Savannah River Site (SRS). The appearance of these phases have created very expensive problems in waste treatment plants by fouling process evaporators in the SRS waste processing facility. Therefore, in order to prevent their formation an assessment of the relative stability, formation kinetics, and the ion-exchange characteristics of these two phases in HLW solutions needs to be investigated. The goals of this project are to:

- Develop a robust equilibrium thermodynamic framework to accurately describe the formation of NO_3 cancrinite and NO_3 sodalite.
- Provide quantification and characterization of the solid precipitation rates through long-term batch kinetic experiments and novel analytical techniques.
- Investigate the partitioning and ion exchange properties of these zeolitic phases with respect to radionuclides and RCRA metal species. This also includes compositional and structural characterization of ion exchanged solids elucidate the exchange properties of these phases.

Research Progress and Implications: This report summarizes work after a two of a three year project. To date, the following achievements have been accomplished:

- Successful laboratory synthesis and characterization of crystalline NO_3 cancrinite and NO_3 sodalite. The synthesis of NO_3 cancrinite has been conducted on SRS simulant feed solutions and other types of solutions. Also, synthesis from kaolinite in contact with alkaline solutions have generated NO_3 cancrinite. NO_3 cancrinite precipitation has been characterized through various analytical techniques such as Scanning Electron Microscopy (SEM). Other routine material characterization methods include X-Ray Diffraction (XRD), Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (FTIR), and Thermogravimetric analysis (TGA). Refinements on the NO_3 cancrinite synthesis to obtain a purer composition have been successful in reducing the amount of carbonate content which is the most important impurity.
- Seeded batch solubility experiments were carried out using various concentrations of electrolyte matrices at a temperature range of 25–90 °C to investigate its effect on cancrinite solubility. After successful synthesis and characterization of NO_3 cancrinite seeds, several solubility experiments were conducted using NaNO_3 – NaOH solutions. The main effect of increasing electrolyte concentration on solubility is the continuous decrease in both Si and Al concentrations in solution. This is the result of the so-called “salting-out” effect observed with increasing ionic strength as effected on the activities of the main salt components (Na^+ and NO_3^-) and the activity of water. Another important observation is the decrease on the effect of salt content with increasing ionic strength and temperature. There is no apparent increase in NO_3 cancrinite solubility with increasing salt concentration within the studied temperature range.
- Compositional characterization of synthesized material has a significant impact on the thermodynamic properties of materials. The effect on the thermochemical cycles used to calculate heats of formation can be significant, since mass balance must be conserved in each step. 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 summarize the phase compositional data for the SNL (Sandia National Laboratories) 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 Composition and formulae of Sandia National Laboratories (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

- Thermochemical analysis of NO₃ cancrinite: enthalpy of formation and heat capacity.
Standard enthalpy of formation has been conducted by drop solution calorimetry using a high temperature Tian-Calvet type microcalorimeter at 974 K utilizing molten lead borate as the solvent media. Table 2 show the measured standard enthalpy of formation from the oxides and the elements for the two of the cancrinite syntheses. The values are compared to those obtained previously by Bennington and Brown (1983).

Table 2 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	Na _{8.893} [Al _{5.777} Si _{6.223} O ₂₄](NO ₃) _{1.582} (CO ₃) _{0.767} ·1.863(H ₂ O)	-439.11±9.24	-14234.59±11.80
NC#2	Na _{7.754} [Al _{6.003} Si _{5.997} O ₂₄](NO ₃) _{1.461} (CO ₃) _{0.145} ·1.726(H ₂ O)	-884.81±11.61	-13915.21±13.67
NCS#5	Na _{7.261} [Al _{5.854} Si _{6.146} O ₂₄](NO ₃) _{1.316} (CO ₃) _{0.045} ·2.626(H ₂ O)	-924.91±15.71	-13987.50±17.37
^b Bennington and Brown (1983)	Na _{7.68} [Al ₆ Si ₆ O ₂₄](NO ₃) _{1.68} ·4.1(H ₂ O)	-900.40±7.53	-14593.67±10.88

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

^bBennington and Brown (Rep. Invest. 8778 - U. S., California Bureau of Mines, 1983)

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 (1983). It has been generally accepted that NO₃ cancrinite has a ideal formula of Na₈[Al₆Si₆O₂₄](NO₃)₂·2(H₂O). However, the sample used in Bennington and Brown's work was reported to have 4 moles of water. Their value and ours for our most carbonate free sample practically overlap within experimental error despite probably small differences in composition.

In situ solution calorimetry in scanning mode was used to investigate zeolite crystallization from starting gel material at different 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. The enthalpy of crystallization per gram of gel was about -0.34 J. 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. A second heating cycle indicates that 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. Heat capacity measurements for both low and high temperature were conducted Differential Scanning Calorimetry (DSC). Results of these measurement indicate that the NO_3 cancrinite sample begins to decompose above 100°C limiting the range of validity for these measurements.

- MAS-NMR characterization of synthesized solids using nuclei such as ^{29}Si , ^{27}Al , and ^{23}Na : NO_3 cancrinite, NO_3 sodalite, zeolite A, and aluminosilicate gels. The stages for formation of NO_3 cancrinite from tank simulant solutions were monitored by high resolution NMR from the aqueous phase to the inception period for solid precipitation as a function of time and temperatures. Monitoring of tank simulant solutions having 0.1 M Al and Si produced NO_3 cancrinite precipitation at 90°C on a time scale observable with ^{27}Al NMR. Also, characterization of NO_3 sodalite to NO_3 cancrinite conversion has been monitored as a function of the Al:Si reactant ratio. Long-term batch kinetic experiments for NO_3 cancrinite precipitation have been conducted at 55°C , 72°C and 90°C from alkaline starting solution mixtures. Upon mixing the starting solutions, even at room temperature, a very abundant amorphous aluminosilicate precipitate or gel forms immediately. From this amorphous precipitate, the first phase to crystallize is zeolite A. At 55°C , zeolite A is the only crystalline phase detected after 6 hours of reaction; it then converts partly to sodalite. NO_3 cancrinite and sodalite are the only crystalline phases present in the samples after respectively 5 days at 55°C , 2 days at 73°C and less than 4 hours at 90°C . The rate of conversion of sodalite to cancrinite increases with temperature, but the transformation becomes very slow after an extended period of time and the weight fraction of cancrinite reaching an apparent steady state. This steady state value increases with temperature, from about 27 wt% at 55°C to 45 wt% at 73°C and 75 wt% at 90°C . The Rietveld method for structural refinement based on XRD data was utilized to quantify the weight fraction of the precipitated phases. The steady state values also coincides with quasi steady-state concentrations of dissolved aqueous components of Si and Al for the corresponding time frame.
- Several experiments have been conducted to study the ion exchange properties in the conversion of hydroxysodalite or basic sodalite ($\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$) to hydrosodalite ($\text{Na}_6[\text{SiAlO}_4]_6 \cdot 8\text{H}_2\text{O}$). Ion exchange experiments for this phase transformation reaction were conducted by contacting hydroxysodalite with an ammonium nitrate solution for less than half an hour at a temperature of 60°C . This amount of time was sufficient to attain the phase transition. The phase transformation experiments generated interesting results in regards to the removal of cations such as Na^+ and elucidating important aspects of the ion exchange behavior for this phase. Various analytical techniques have been used such as XRD, NMR, TGA, and IR to examine conversion products and advance mechanistic interpretations of the process.

- Partition of radionuclide surrogates (Cs^+ , ReO_4^- , SeO_4^{2-} , and I^-) was studied by conducting NO_3 cancrinite synthesis experiments from solution (gel synthesis) and from kaolinite. Both types of experiments generated similar results indicating that overall the Cs partition coefficient ($[\text{Cs}/\text{Na}]_{\text{(solid)}}/[\text{Cs}/\text{Na}]_{\text{(fluid)}}$) is about 52. The anions (ReO_4^- , SeO_4^{2-} , and I^-) are not significantly reduced from the aqueous phases. Thus, cancrinite could act as sink of Cs in tanks and evaporators but long-lived anionic radionuclides will not be sequestered by this phase.
- Sequestration of radionuclides through ion exchange; in this case, the sodium aluminosilicate phase being studied was synthesized (and washed free of soluble impurities) prior to starting the test. The materials used in these experiments include cancrinite and sodalite. Results from these experiments suggest that sodalite (synthesized in the presence of large organic anions) appears to participate in ion exchange processes, and Cs uptake diminishes significantly with increasing initial load of Cs in solution and NaNO_3 concentration. Therefore, these experimental results suggest that Cs uptake in high-Na fluids indigenous to the tanks at Hanford and Savannah River it is likely that the process would not be significantly favored. Thus, the Cs contained of cancrinites found in such settings probably reflects the chemistry of the fluids from which they formed rather than the transient changes in tank fluid chemistry that are the consequence of mixing that occurs during day-to-day management of the tank farms.
- The retrieval of a solubility constant for NO_3 cancrinite using solubility data was done using the computer code EQ3/6 (v. 8.0) and the recently-developed thermodynamic database operational at elevated temperatures using the Pitzer approach for the system $\text{Na}-\text{NO}_3-\text{Al}(\text{OH})_4-\text{SiO}_2-\text{H}_2\text{O}-\text{OH}$. The Pitzer approach has been adopted in this study in order to accurately model the ion activities of aqueous species present in concentrated solutions. This database was developed for the Yucca Mountain Project (YMP) to support geochemical calculations using the above-mentioned computer code. However, solubility data gained as part of the EMSP program along with further development of Pitzer parameters to include relevant Si species was performed to retrieve the thermodynamic constants used to model solubility.

2. **Planned Activities:** Future and/or planned research activities related to work remaining or in progress are as follows:

- A renewal proposal for the current EMSP project was submitted in April 2004. Continuation of NO_3 cancrinite and NO_3 sodalite thermochemical, solubility, phase characterization, and precipitation studies. Solubility and precipitation experiments are planned at temperatures exceeding 100°C . Precipitation kinetic studies will be conducted using solutions having different levels of ionic strength and various Si/Al ratios to characterize the effect on transformation rates. Also, characterization of solid phases using SEM will be conducted to elucidate on the textural details of the transformation process. Heat capacity measurements will be completed using DSC, in the temperature range below decomposition for NO_3 sodalite and NO_3 cancrinite. The energetics of ion exchange, both by solution calorimetry of ion exchanged samples. Calorimetric studies will be carried out on ion exchanged materials of various compositions between the NO_3 - CO_3 compositional range. This studies will also include Na poor aluminosilicates produced by ion exchange.
- Experimental investigation of ion exchange to produce the mixed anion species. The synthesized and ion exchanged materials will require careful characterization including XRD, solid-state NMR (^{23}Na , ^{27}Al , ^{29}Si , ^1H , predominantly), compositional analysis of

solids, and thermogravimetry in particular. Conduct Cs and Sr partitioning and ion exchange experiments on NO_3 cancrinite and NO_3 sodalite at various temperatures and electrolyte matrices. In addition to the characterization techniques mentioned before; Cs and Sr exchanged materials will be characterized by Sr and Cs NMR, as well as Cs and Sr compositional analysis.

- Continued development and evaluation of the Pitzer activity model used with the code EQ3/6 (v. 8.0) in concentrated sodium nitrate solutions and silica. Thermodynamic modeling using thermochemical and solubility data gathered in this EMSP project.
- Completion of a manuscripts documenting results (in preparation) on various task of this project for submission in a peer-review scientific journal.

3. **Information Access:** N/A

4. **Optional Additional Information:** N/A

5. **Optional Proprietary Information:** N/A