A Comprehensive Study of the Solubility, Thermochemistry, Ion Exchange, and Precipitation Kinetics of NO_3 Cancrinite and NO_3 Sodalite (Project #: 81959)

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Research Objective: NO_3 cancrinite and NO_3 sodalite haves been found as a common sodium alumino-silicate forming in strongly caustic 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 and predict the formation of NO_3 cancrinite and NO_3 sodalite.
- Provide a comprehensive characterization of the solid precipitation rates and mechanisms using novel spectroscopic (e.g., NMR) and thermochemical techniques in conditions encountered in HLW waste solutions.
- Investigate the ion exchange capacity of these zeolitic phases with respect to radionuclides and RCRA metal species.

Research Progress and Implications: This report summarizes work after a of a 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 initial solution compositions. NO_3 cancrinite precipitation has been confirmed by its previously-observed spherical 'yarn ball' growth morphology through Scanning Electron Microscopy (SEM). Other routine material characterization methods include X-Ray Diffraction (XRD), Nuclear Magnetic Resonance (NMR), and Infrared Spectroscopy (FTIR). Refinements on the NO_3 sodalite synthesis to obtain a purer composition are planned.
- Confirmation of NO_3 cancrinite stability through long-term solubility experiments at various temperatures and solution compositions in highly caustic and alkaline solutions at temperatures ranging from ambient up to 80°C. Filtered samples of aqueous solutions from all runs were analyzed at different time intervals and cancrinite solids were recovered for material characterization through XRD and FTIR. Results of these two analytical techniques confirm that the solids are NO_3 cancrinite.
- Thermochemical analysis of NO_3 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. The measured standard enthalpy of formation from the oxides is -793.1 ± 10.1 kJ/mol. The measured enthalpy of formation from the elements is -14108.1 ± 12.4 kJ/mol. To make sure on the validity of the final state of the gaseous component used in the thermodynamic cycle for standard enthalpy determination, various $NaNO_3$ pellets of different weights were analyzed by drop solution calorimetry and through weight loss experiments. Results of these analyses demonstrate that nitrate decomposed in the form of a gas during the calorimetric experiment validating the use of a gaseous final state in the reactions detailing the thermochemical cycles. Heat capacity measurements for NO_3 cancrinite were performed through Differential Scanning Calorimetry (DSC) at the temperature range of -100 °C to 220 °C. The runs

were reproducible within experimental error in three run replicates. Compositional analyses of the analyzed samples through Electron Microprobe Analysis (EMPA), thermogravimetry (TGA), and LECO methods yield a NO_3 cancrinite stoichiometry of $Na_{7.798}Al_{6.004}Si_{5.997}O_{24}(NO_3)_{1.797}\cdot 2.58H_2O$ on a 24 oxygen basis. The samples were subjected to dehydration treatment prior to EMPA anlysis to prevent material breakdown under the inciding electron beam.

- 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. Nuclear Magnetic Resonance (NMR) spectroscopy has provided valuable information on phase characterization, monitoring precipitation kinetic data, and therefore assessment of optimal synthesis chemical conditions at different temperatures. 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. This technique also allows for characterization of Al and Si speciation in the aqueous phase. Tank simulant solutions having 0.1 M Al and Si produce 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.
- Ion exchange experiments on NO_3 cancrinite to monitor the behavior of waste surrogates. Ion exchange experiments were conducted at temperatures of 22 °C and 70 °C using $NaNO_3$ as the matrix electrolyte and Cs^+, ReO_4^-, SeO_4^{--}, and I^-. Preliminary results show that Cs^+ is strongly partitioned into the NO_3 cancrinite phase (up to ~46% reduction) whereas the anions (ReO_4^-, SeO_4^{--}, and I^-) are not significantly reduced from the aqueous phases. Thus, cancrinite could act as significant sink of Cs in tanks and evaporators but long-lived anionic radionuclides will not be sequestered by this phase.
- Thermodynamic modeling, Pitzer data retrieval, and development of solution-solid-equilibria model for the system $Na\text{-}NO_3\text{-}Al(OH)_4\text{-}SiO_2\text{-}H_2O\text{-}OH$. The Pitzer approach has been adopted in this study in order to accurately model the ion activities of aqueous species present in strongly caustic and alkaline HLW solutions. To apply this model into our solubility study, temperature-dependent Pitzer parameters (temperature range of 25 to 100 °C) of some important species relevant to the system of interest such as those related to nitrate and silica were added to the database. The code used for solution speciation is EQ3/6. Testing of the upgraded database shows that predictions of saturation molalities for Al-hydroxide phases (gibbsite) conforms very well with reported values in the literature. Also, predictions of salt solubilities to high ionic strength has been also successful. Modeling of aqueous solutions sampled from solubility experiments is currently under way.

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

- Continuation of NO_3 cancrinite and NO_3 sodalite thermochemical, solubility, phase characterization, and precipitation studies. These include in situ NMR studies of precipitation kinetics and phase characterization on both phases and refinements on the experimental synthesis procedures. Other planned NMR activities include high temperature ^{23}Na MAS-NMR to accentuate differences between framework and cage or tunnel Na^+, use $^1H\text{-}^{23}Na$ CP and TRAPDOR MAS-NMR to differentiate between multiple Na sites, conduct NMR analyses on dehydrated phases to verify model compounds are correct, high resolution NMR at low temperatures to better identify Al species during Al-silicate precipitation process, and precipitation experiments also using NMR at various Al:Si ratios. Thermochemical investigations will focus on in situ calorimetry to study the formation of NO_3 cancrinite and NO_3 sodalite where heat flow will be accurately monitored through the various precipitation stages (e.g., nucleation and growth) of these phases.

- Completion of a manuscript (in preparation) on the solubility, synthesis, thermochemistry and characterization of NO_3 cancrinite for submission in a peer-review scientific journal.
- Conduct further ion exchange experiments on NO_3 cancrinite and NO_3 sodalite at various temperatures and electrolyte matrices. Cs NMR studies as a function of Cs loading are planned.
- Coupling of gathered thermochemical and solubility experimental data to generate activity phase diagrams and develop the solution-solid-equilibria model as function of temperature is under way. Further testing of the Pitzer activity model in concentrated sodium nitrate solutions and silica.
- Addition of computational investigations on the molecular dynamic description of NO_3 cancrinite and NO_3 sodalite to complement experimental observations on the ion exchange behavior of exchangeable species (e.g., Cs) and structural characterization. Also, addition of nano-scale microscopic investigations involving High Resolution Transmission Electron Microscopy (HRTEM) on the gel material and crystalline solids is planned. The latter will add knowledge on the nano-structural characterization of the synthesis and run products of the precipitation kinetic experiments.

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

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

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