Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes

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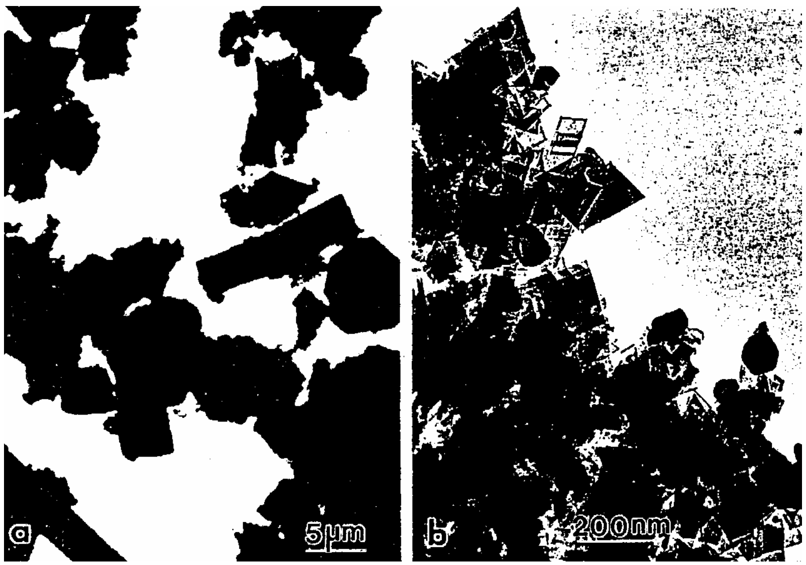
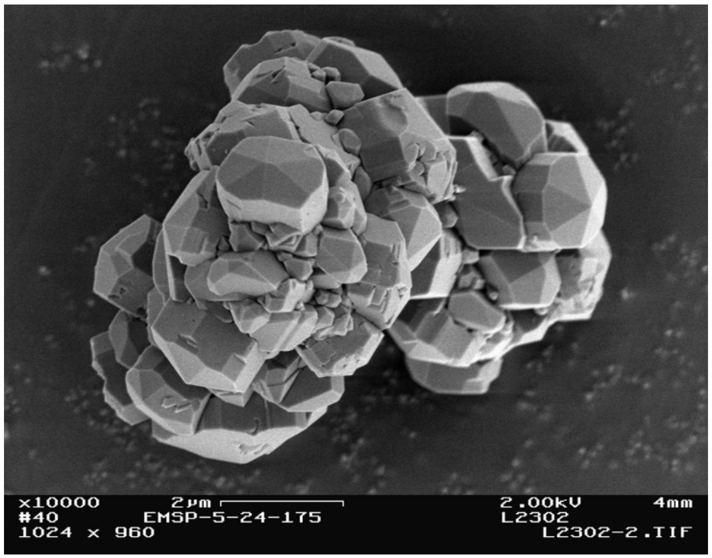
Relevance



- Tank sludge retrieval and pretreatment precede vitrification.
- Al is a major component of both sludge and supernate fractions of HLW.
- Minimization of HLW glass volume requires sludge washing and leaching to dissolve Al-containing wastes.

Processing Hiatus

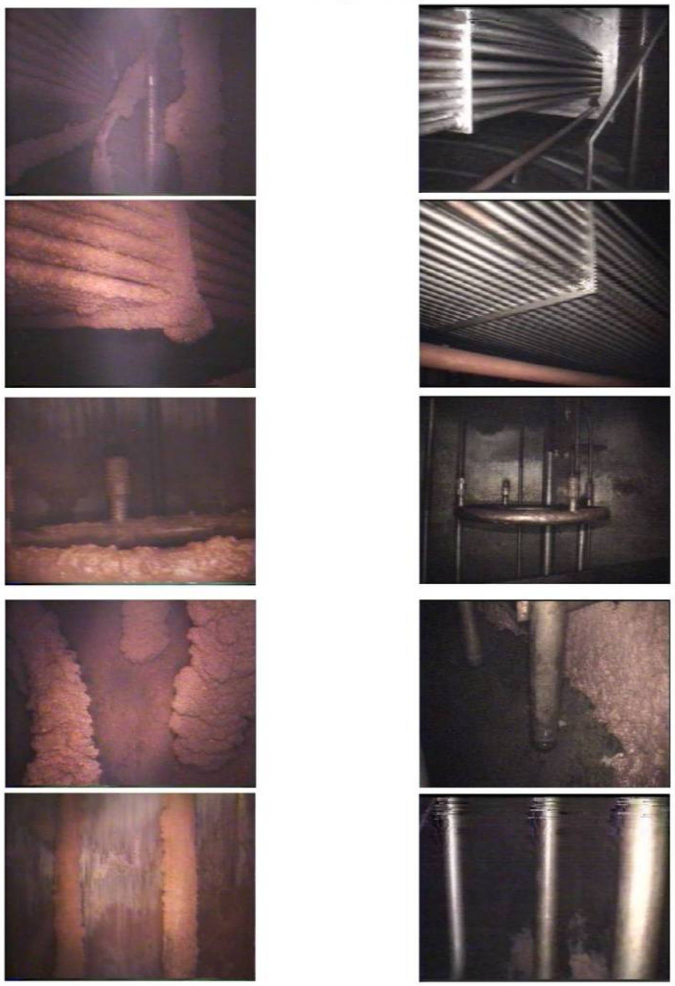


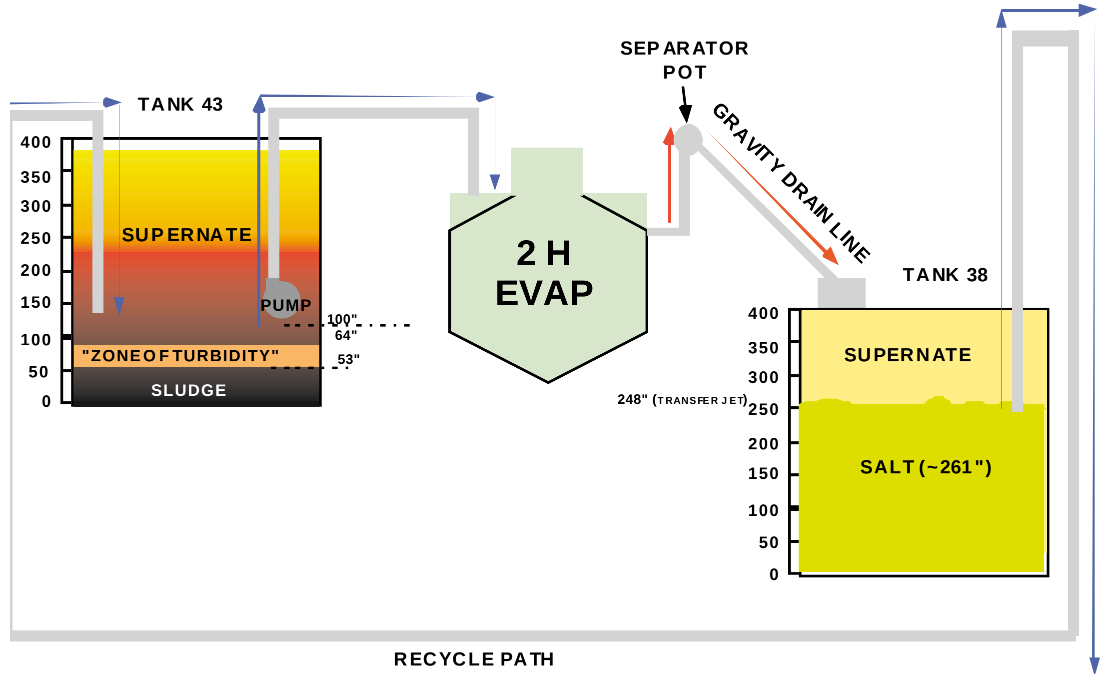
- Scaling and clogging from Al-Si phases:
  - 2H evaporator at SRS shutdown
  - Plugging of Cs-removal columns at SRS from mineral formation.
  - Occasional blocked pipes at Hanford tank farm due to aluminous precipitates.

- Processing hiatus results in escalated cost and extended time for treating tank wastes

SRS 2H-Evaporator

4/30/01 2H Evaporator 6/07/01





v **Precipitates**

Plugged concentrate line (97 - 98)
>3000 kg solids in evaporator (99)

v **Down time and Cost**

Gravity Drain Line: 4 mo - $4M
Evaporator: >22 mo, $10+ M

Critical Need

- Limited knowledge about mechanisms of formation and transformation of Al-Si phases under tank and pretreatment conditions (Si/Al ~ 0.003, high salt and OH^-, range of temperature)
- Understand factors that control the extent and the rate of formation of Al-Si phases that form hard cementitious scales
- Develop process schemes to avoid/inhibit formation of cementitous Al-Si phases.

Objectives

- Formation, solubilities, and transormation of Al-bearing phases under processing conditions
- Factors that promote formation of mixed aluminosilicate and uranium bearing phases
- Inhibiting effects of organics on scale formation.
- Thermodynamic modeling of aluminosilicate and uranium solid phase formation

Previous Work

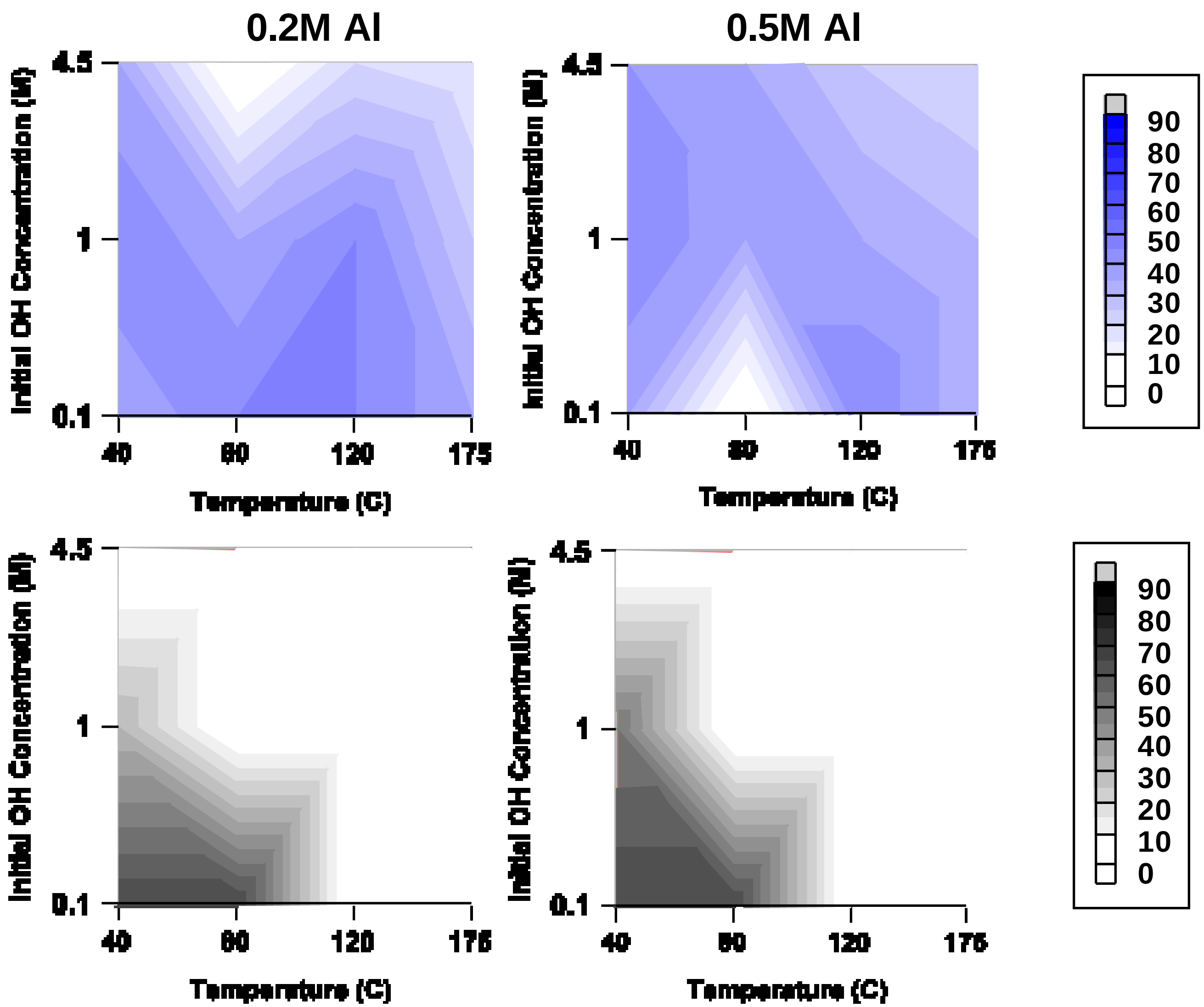
Identify and characterize aluminosilicate precipitates

Al/Si molar ratio: 20, 50
OH: 0.1, 1, 4.5M
NaNO3: 3M
Temperature: 40, 80, 120, 175 $^{\circ}$C

Predominance Diagrams

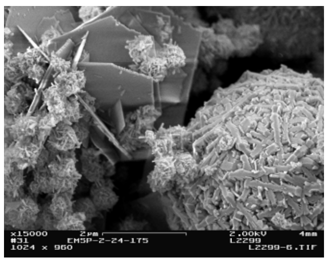
Precursor Phase

Zeolite A

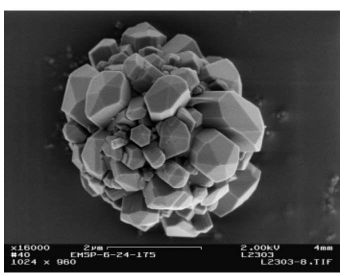


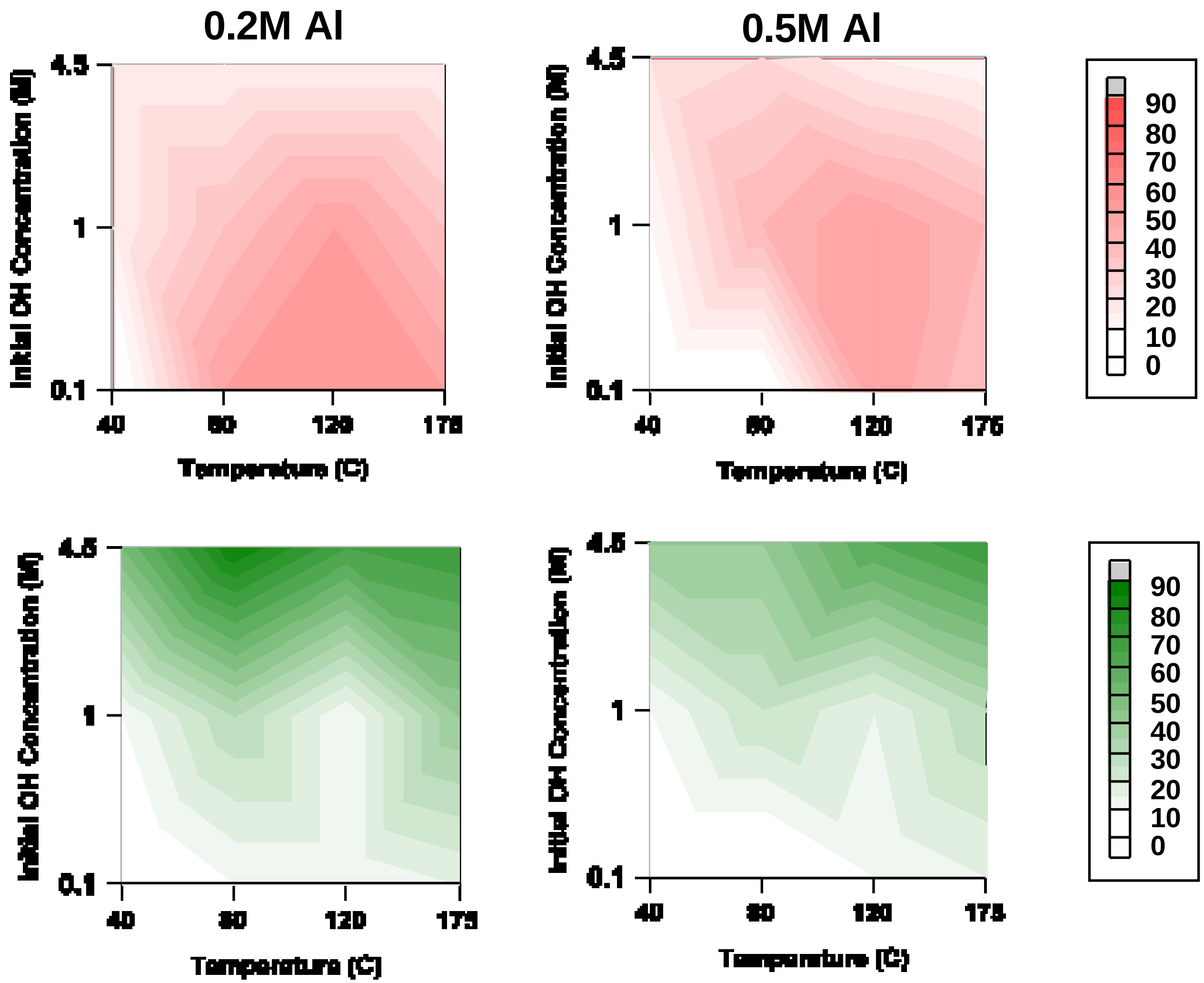
Predominance Diagrams

Sodalite



Cancrinite





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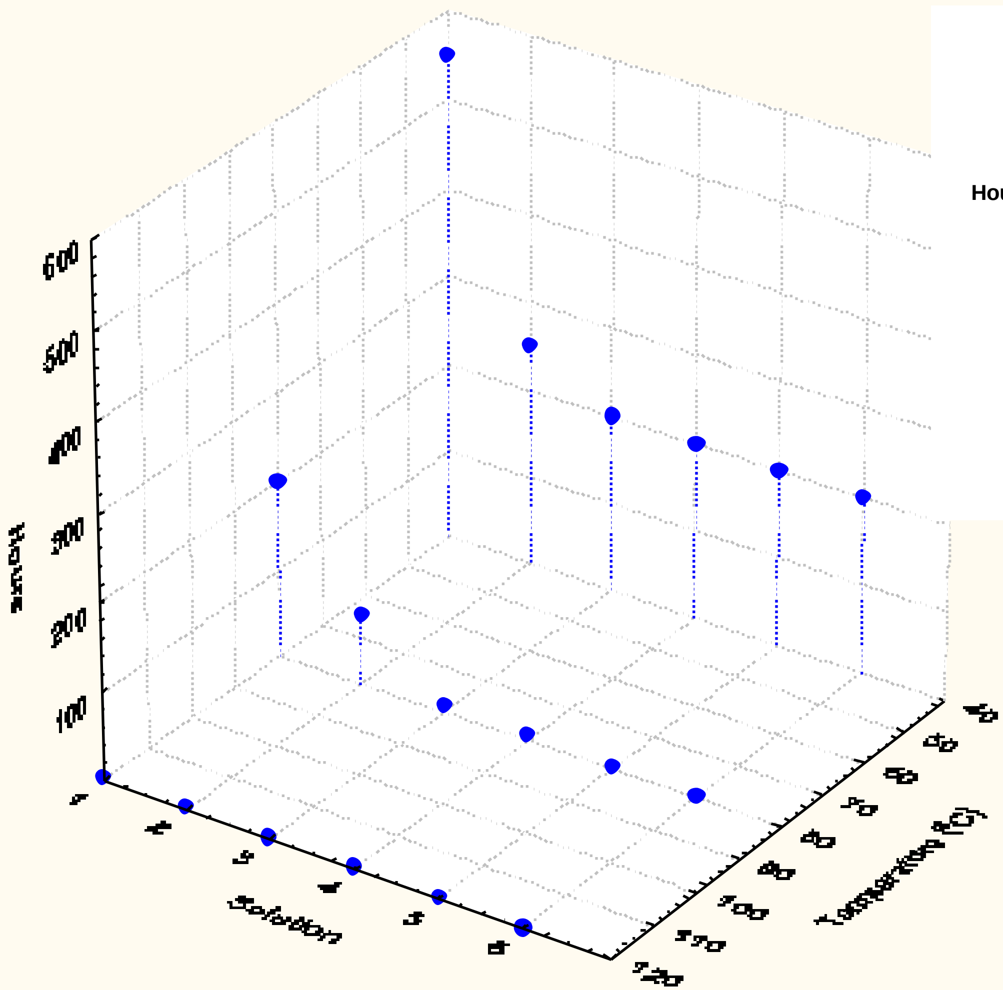
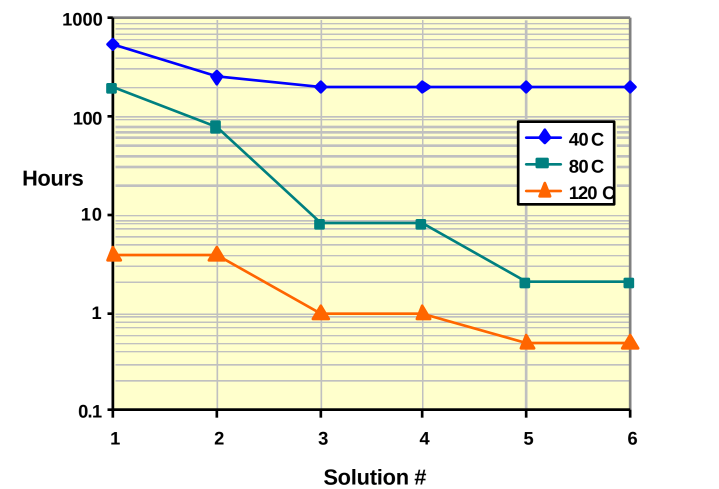
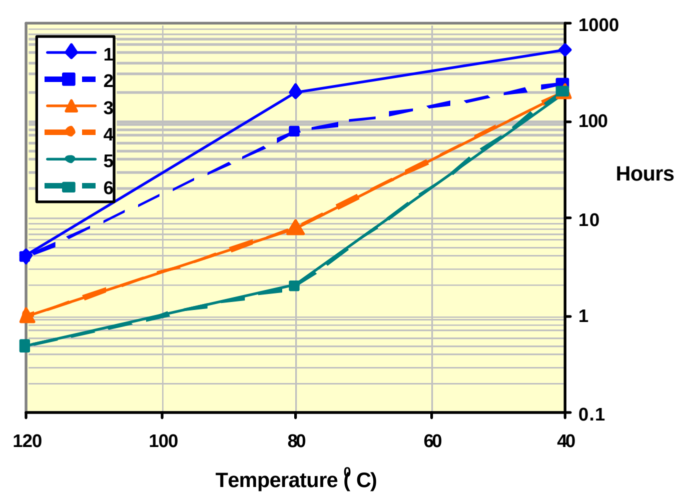
Crystallization Kinetics







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Synopsis

- ***Solid Phase Formation***

  Amorphous precursor phase precipitates initially - with time converts to mainly zeolitic crystalline phases
- ***Al/Si Ratio in Precipitates***

  Precipitates become more aluminous with increasing temperature and Al concentration
- ***Crystallization Kinetics***

  Higher OH^-, increasing temperature promote more rapid crystallization of the precursor phase
- **Dominant Crystalline Phases**

  <80 C - <1M OH: zeolite A, sodalite

  >80 C - <1M OH: sodalite, cancrinite

  >80 C - >1M OH cancrinite, sodalite

Summary

- Provide sound scientific knowledge for processing schemes to avoid and/or inhibit formation and growth of Al-Si phases
- Knowledge of aluminosilicate chemistry critical to glass waste minimization
- Develop insights into industrial fouling problems
- Gather data on geochemistry of two most abundant and ubiquitous elements (Al and Si) in earth's crust

Research Plan (2005 – 2007)

- Formation and solubilities of aluminosilicates

  Al: 0.01 – 0.2 M, Si: 0.04 - 0.2 M, OH: 6.0 - 10.0 M,
  $NaNO_3$ 5.0 M, Temperature 40 - 175^0 C

- *Gibbsite/Boehmite/Dawsonite Transformation*

  NaOH: 1.0 - 6.0 M, $NaNO_3$ 1.0 - 6.0 M, $NaNO_2$: 1.0 – 3.0M
  Temperature 75 - 200^0 C

- *Formation of Uranium silicates phases with NAS*

Research Plan (2005 – 2007)

- Role of organics in inhibiting precipitation and scale formation
  1. *Low-chain polyols to stabilize aluminosilicate particles.*
  2. *Polyelectrolytes and diblock copolymers to prevent nucleation and particle growth*
- Thermodynamic Modeling
  1. *^{27}Al and ^{29}Si NMR – determine speciation of Al and Si under relevent conditions for use in Pitzer model development*
  2. *Model U(VI) solution chemistry in high ionic strength solutions*

Approach

- NMR (^{27}Al, ^{29}Si, and ^{23}Na) – structures of soluble and insoluble species.
- SAXS – size and structure of precipitates.
- TEM, ED, SEM, EDA – morphology, structure and composition.
- XRD – identify and quantify precipitated and transformed species.

Integration