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

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 cementitious Al-Si phases.
Objectives

✓ Formation, solubilities, and transformation 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 ºC
Predominance Diagrams

Precursor Phase

Zeolite A
Crystallization Kinetics
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

√ Formation and solubilities of aluminosilicates

\[ \text{Al: } 0.01 - 0.2 \text{ M, Si: } 0.04 - 0.2 \text{ M, OH: } 6.0 - 10.0 \text{ M, } \]
\[ \text{NaNO}_3 \text{ 5.0 M, Temperature 40 - 175}^0 \text{ C} \]

√ Gibbsite/Boehmite/Dawsonite Transformation

\[ \text{NaOH: } 1.0 - 6.0 \text{ M, NaNO}_3 \text{ 1.0 - 6.0 M, NaNO}_2 \text{: } 1.0 - 3.0\text{M} \]
\[ \text{Temperature 75 - 200}^0 \text{ C} \]

√ Formation of Uranium silicates phases with NAS

✓ 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 relevant 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

- Complete characterization of precipitates
- Solution phase characterization
- Tank and Process Relevant conditions
- Phase Equilibrium Studies
- Role of Organics

Guidelines for preprocessing schemes