Dynamics and Mechanism of Aluminosilicate Crystal Particle Formation in Bulk Solutions and on Stainless-Steel Surfaces

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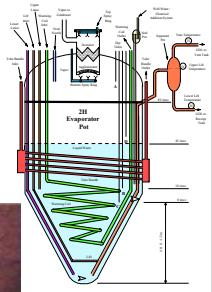
Background

- Scale formation due to mineral particle deposition is a common industrial problem
  - Heat exchanger surfaces
  - Digestor & evaporator in alumina refining
  - Crystallizer
- Aluminosilicate fouling in liquid waste evaporators has caused significant problems in DOE waste treatment
- Nonuniform deposition suggests that scale formation depends on
  - Heat and mass transfer
  - Hydrodynamics
  - Reaction mechanisms and kinetics
  - Particle-particle, particle-wall interactions



Goals and Strategies

Goal

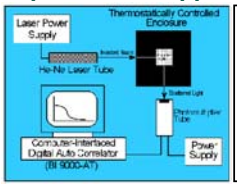
- Prohibit or minimize the solid deposition
- Maximize the cycle time between evaporator cleanings

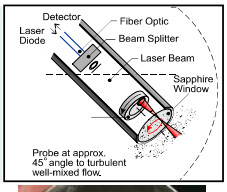
Technical Approach

- Investigate the formation of aluminosilicate solid/particle in 4*M* caustic solutions that contain soluble (supersaturated) Si and Al.
- Collect information on nucleation, growth, transport, and transformation of particle/solids in bulk solutions
- Investigate major chemical/physical factors that affect solids formation on metal surfaces
  - Reaction kinetics (process conditions: temperature, [Si], [Al], etc.)
  - Addition of chemical additives
  - Fluid hydrodynamics
  - Mixing
  - Seeding

Experimental Approaches

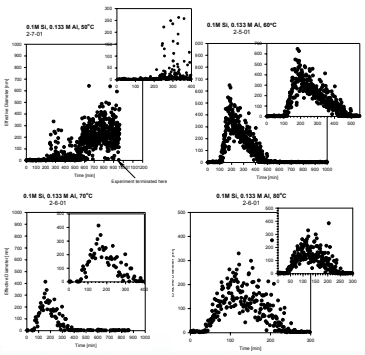
- **Dynamic Light Scattering and Focused Beam Reflectance Method:** particle formation and growth.





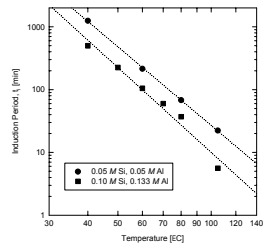
- **Surface-Solids Formation Tests**: solids deposition and growth on steel surfaces

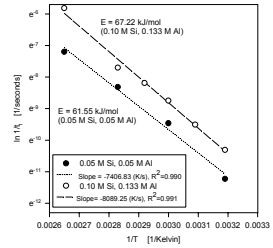
DLS Data Follow the Course of Particle Growth



- The induction time is the onset time required for particle to grow to ~ 5 nm in bulk
  - a way to quantify how fast solid particles form in solution
  - possibly could be used to estimate onset time for scale formation

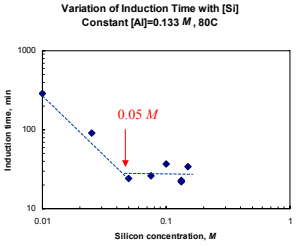
DLS Results: Effect of Temperature

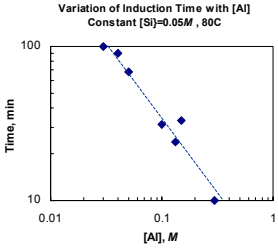




- **At conditions tested, induction time varies linearly with temperature on log-log plot**
  - Extrapolate to less than 10 minutes at evaporator temperature
- **Activation energy of ~65 kJ/mol approx. twice that measured for Al and Si consumption (Mattus, 2001; Barnes et al., 1999; Addai-Mensah, 2001)**
  - **multiple chemical and physical processes in particle solid formation and growth**

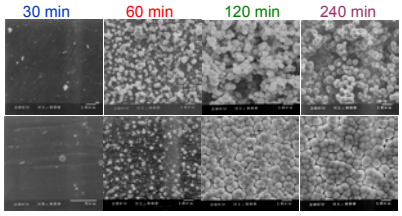
DLS Results: Effect of [Si] and [Al]



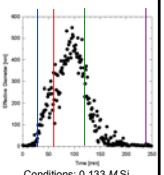


- **At [Al] = 0.133*M*, nucleation is faster as [Si] is increased from 0.01 to 0.05 *M*. Little effect on induction time is measured as [Si] is increased above 0.05 *M*.**
- **At [Si]=0.05 *M*, induction time is shorter as the concentration of aluminum is increased throughout the range from 0.03 to 0.3 *M*.**

Aluminosilicate Solid Scale Formation: kinetics & mechanism



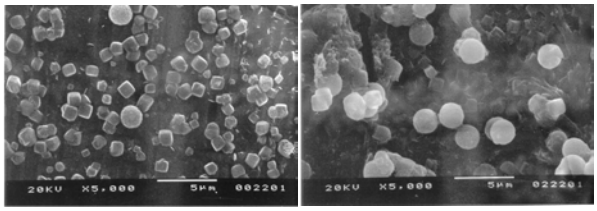
Particle growth in bulk solution



Conditions: 0.133 *M* Si, 0.133 *M* Al, 6 M Na^+, 80°C

- Heterogeneous growth of particles at the surface observed
- Particle growth in the bulk and surface particle growth are similar
- Surface solids begin as small particles on the surface and grow bigger and thicker into monolayer form.
- The strength of the material connecting two particles appears to be as strong as the particle material itself.
- Precursor depletion may stop further solid growth in this experiment

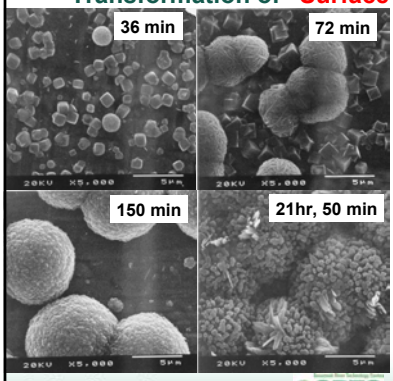
Quiescent Test at 100°C: 36 min



SEM of Bottom Surface | SEM of Top Surface

- Initial surface-grown particles are cube-shaped crystals, different from bulk particles (microspheres)
- Surface solid growth occurs on both sides of the foil

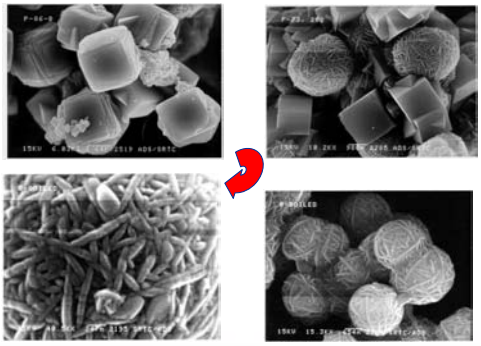
Quiescent Test at 100°C: Transformation of "Surface-Grown" Particles



- Surface-grown particles seem to evolve:
  - cube crystals
  - "balls of yarn" grown on top of cube crystals,
  - lumpy balls
  - "coral-like"
- Consistent with transition (Addai-Mensah 2001, Dworjanyn 2001):

Amorphous
↓
Zeolite A
↓
sodalite
↓
cancrinite

Aging of Aluminosilicate in Bulk Solution

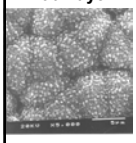


Activation Energy for Crystal Growth

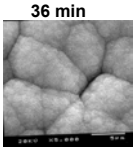
Growth conditions	Desilication Ea (kJ/mol)	References
Sodalite seeding	30	Barnes et al., 1999a
CO_3^{2-}–sodalite/cancrinite mixed phase seed crystal	52	Barnes et al., 1999b
NO_3^{2-}–cancrinite seeding	63-92	Barnes et al., 1999b
No seeding	35	Mattus et al., 2001
	Solid-Forming Ea (kJ/mol)	
Our work by DLS measurement	65	Hu et al., 2001

Multiple Monolayers of Aluminosilicate

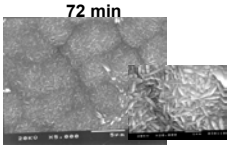
Initial layer

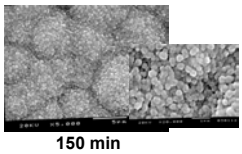


36 min

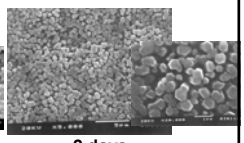


72 min





150 min



2 days

Solids can grow on top of existing solid layer

Hydrodynamic Effect: Stirred foil deposition test at 80°C

1 hour

2 hours

Stir bar rotates clockwise

Rotation rate = 850 rpm

Rough estimate of energy dissipation:
0.07-0.12 W/Kg

top

bottom

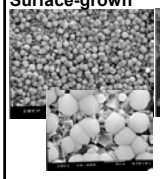
- Fluid flow significantly affects growth and particle deposition (even on bottom side)
- Solids deposited under these conditions are more strongly adhered than those from settling

Hydrodynamic Effect: Stirred foil deposition test at 80°C

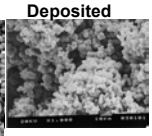
(1 hour)

bottom

Surface-grown

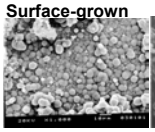


Deposited

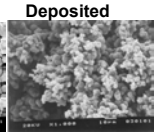


top

Surface-grown



Deposited



- Surface growth occurs everywhere
- Particle deposition occurs on both sides of foil, governed by the hydrodynamics
- Moderate flow velocity seems to induce particle deposition and aggregation

Fluid Flow Affects Solids Deposition

No Mixing

Low Mixing (<0.2W/kg)

High Mixing (0.4-0.8 W/kg)

Batch Beaker Tests: Mixing and Aging Effect

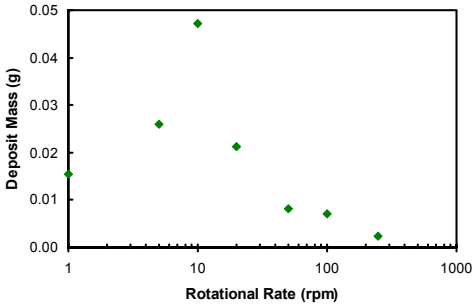
Experiment Type	*Mean for Deposition*	*Confidence Interval$_{80}$*
No Mixing	65%	± 9%
Low Mixing (<0.2W/Kg)	49%	± 17%
High Mixing(0.4-0.8W/Kg)	15%	± 3
Preform (2 hours)	22%	± 3%
Preform (4 hours)	19%	± 6%
Preform (8 hours)	9%	± 2%
High Mixing/Preform (8hours)	4%	2%

Rheometer Experiments

- **Mass of solids deposited onto rheometer spindle measured as function of rotational speed**
  - **Conditions: 16 mL of 0.133 *M* Si/0.133 *M* Al in 4 *M* OH^-, 80ºC**

•Provide a target level for local energy dissipation and/or fluid velocity in the evaporator

Rheometer Results - Average Deposit Mass



- **Appears to be significant effect of flow on deposition**
- **Maximum at ~10 rpm (shear rate = 12 s^{-1})**

Summary of Results

- **DLS and FBRM measurements indicate induction time for particle growth can be quite short under conditions in the evaporator**
- **Both "surface growth" and "particle deposition" appear to contribute to scale formation**
- **Particles grow and undergo phase transformations**
- **Significant hydrodynamic effects were observed on deposition**
  - **flow velocity and pattern affect the location of solids**
    - **more particles appear to deposit in moderate shear-regions**
    - **less deposition in high-shear regions**
  - **deposits are tougher, and adhere more strongly in moderate-flow zones than settled solids from quiescent tests**
  - **scaling can be significantly reduced with sufficient agitation**
- **Less deposition measured with aged/preformed particles suggesting relative interaction affinity for various aluminosilicate phases**