Environmental Management Science Program

Colloidal Agglomerates in Tank Sludge: Impact on Waste Processing

Primary Participants:

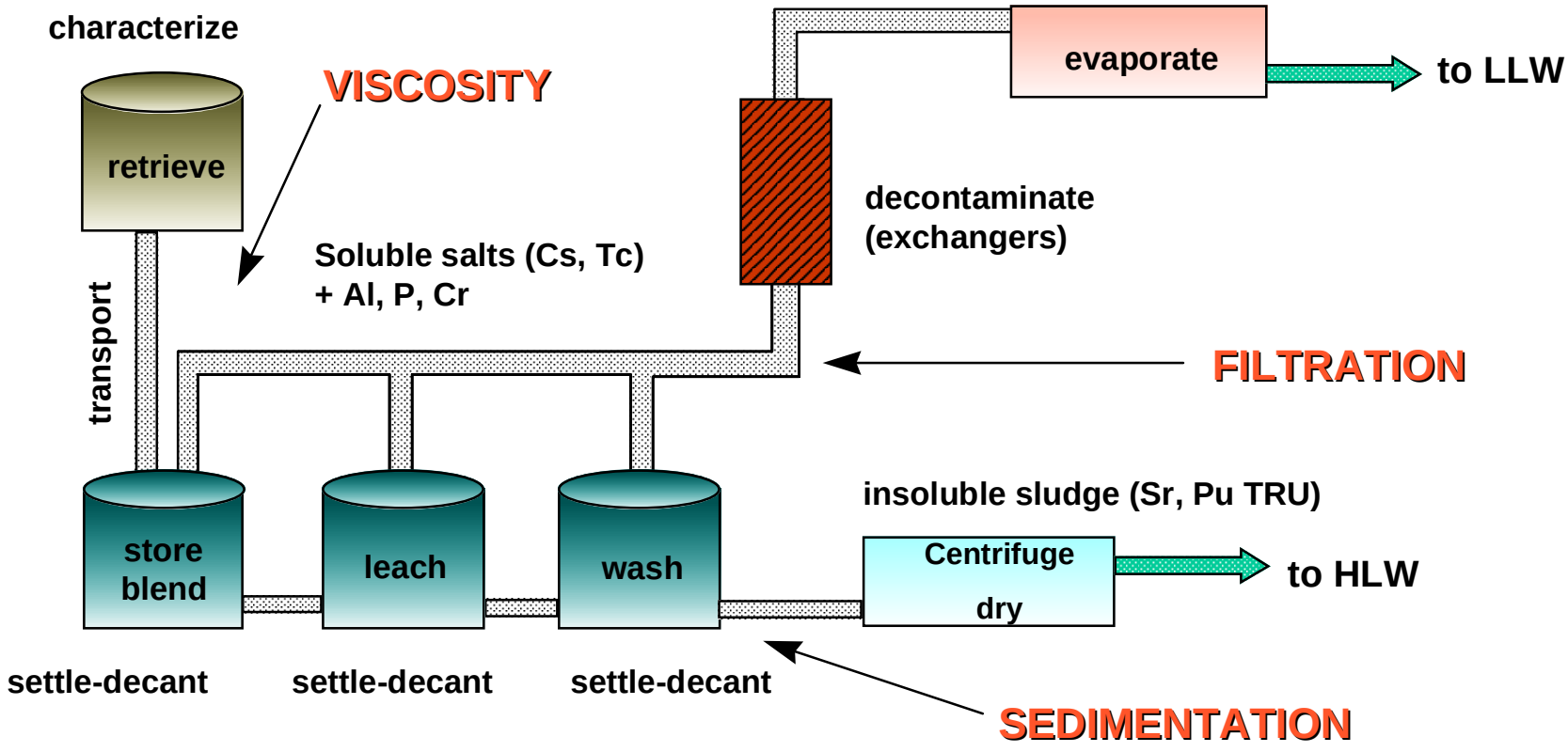
J. Tingey, B. Bunker, J. Virden, G. Graff, D. Rector, J. Liu, A. Lea, K. Keefer
Pacific Northwest National Laboratory

James Martin
Sandia National Laboratory

John Berg and Susie Stenkamp
University of Washington

Tank Waste Processing

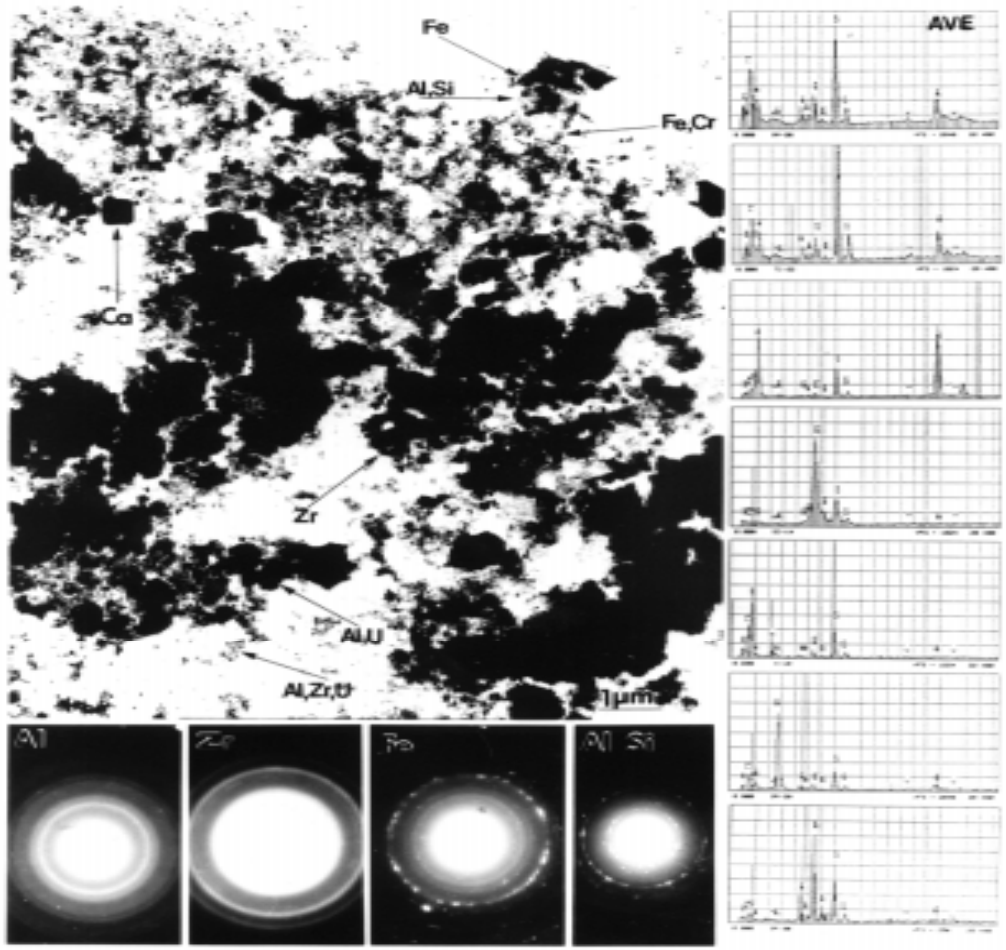
All Major Steps in Tank Waste Remediation are Influenced by Colloidal Agglomeration



Retrieval, Transport, and Safety - want dispersed, non-interacting colloids.

Settle-Decant, Centrifugation - want agglomerated colloids.

TEM Results Show that NCRW Sludge (Tank 105-AW)Contains Nanoparticles of Many Different Phases and Compositions



Impact of Colloidal Behavior on Waste Processing

1. TEM images show tank sludge consists of submicron, i.e., colloidal, particles.

2. Colloid chemistry indicates that particles agglomerate in tank solutions.

3. Consequences of agglomeration on desired processing windows:

Property	Limit	Solids Loading	Desire
viscosity	<100 cp	<1 wt% sludge	>30 wt%
sediment rate	3 cm/hr	<9 wt% sludge	>30 wt%
sediment density	80 wt%	3-12 wt% sludge	80 wt%

High dilution levels will probably be needed to process native wastes.

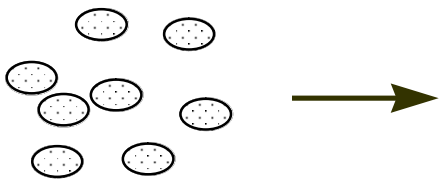
4. Flammable gases are retained in settled solids with high viscosities (yield stress of 200 to 1500 pascals).

5. Sludge processing conditions can be relaxed if larger primary particles are present or if solution conditions favor formation of dense agglomerates.

Agglomeration

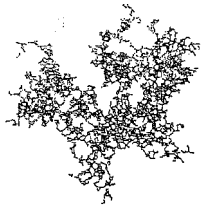
Particle Types in Tank Sludge

Primary Particles



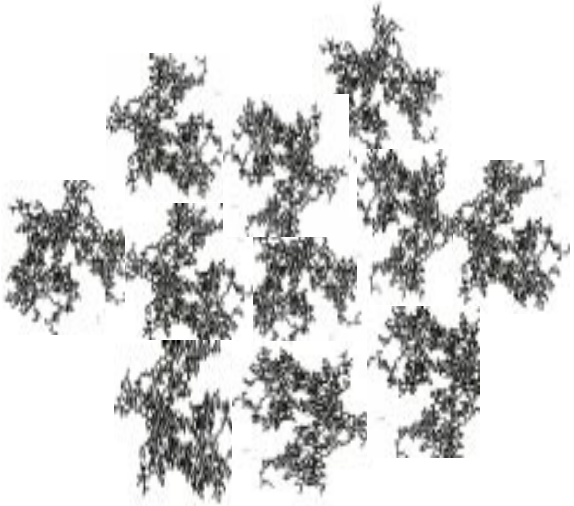
3 nm - 10 nm

Fractal Agglomerates



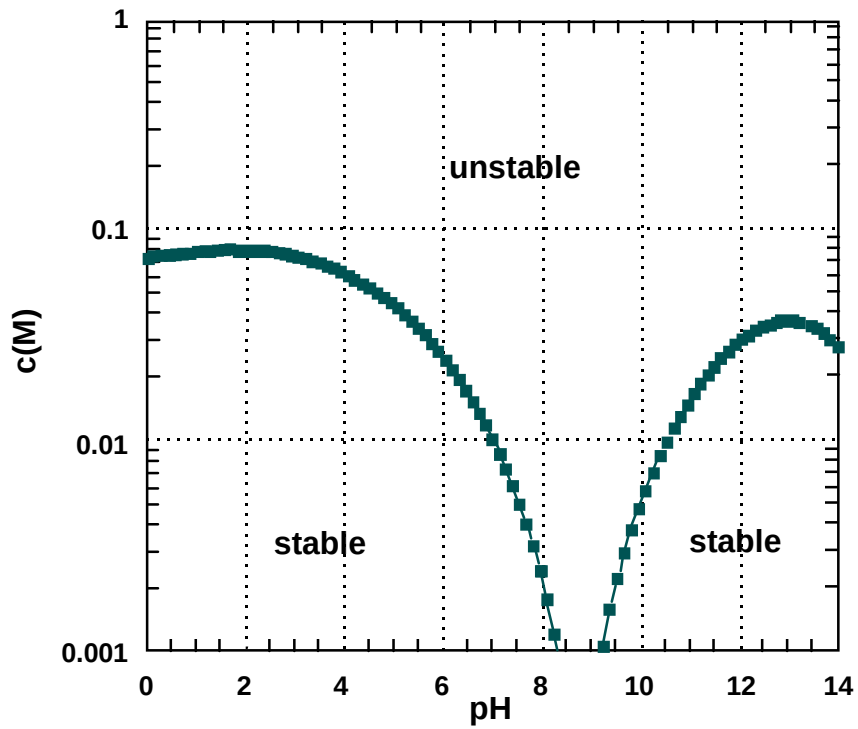
0.1 μm - 5 μm

Large Flocs



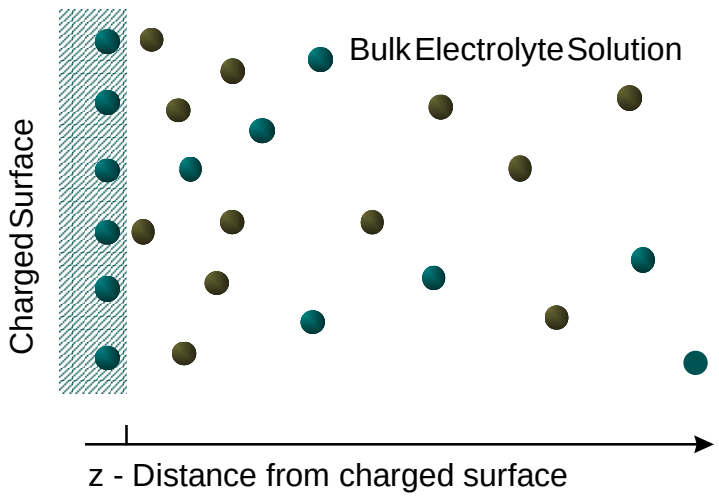
10 μm - 1 mm

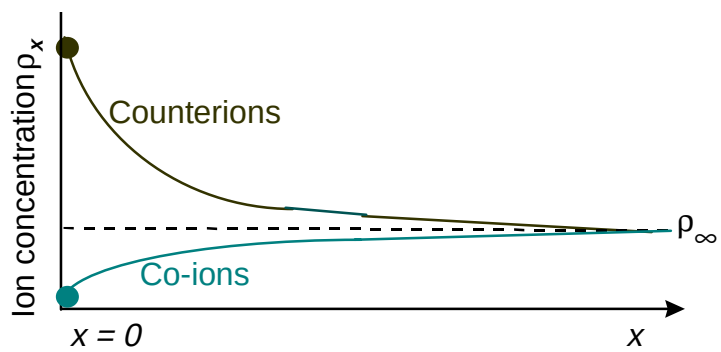
Double Layer Potentials Predict Solution Regimes That Promote Agglomeration

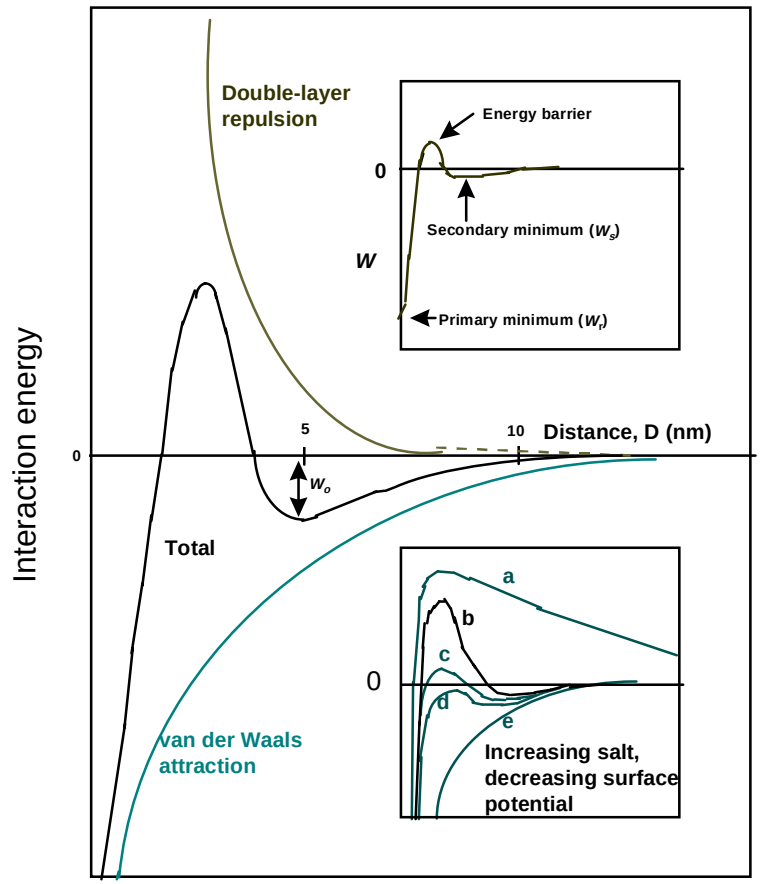


Stability map for colloidal boehmite shows that unstable, agglomerated suspensions are expected at the isoelectric point (pH9) and in solutions of high ionic strength (salt concentrations > 0.1 *M*).

Particle Behavior Changes from Repulsive to Attractive as Double Layer Repulsion Decreases

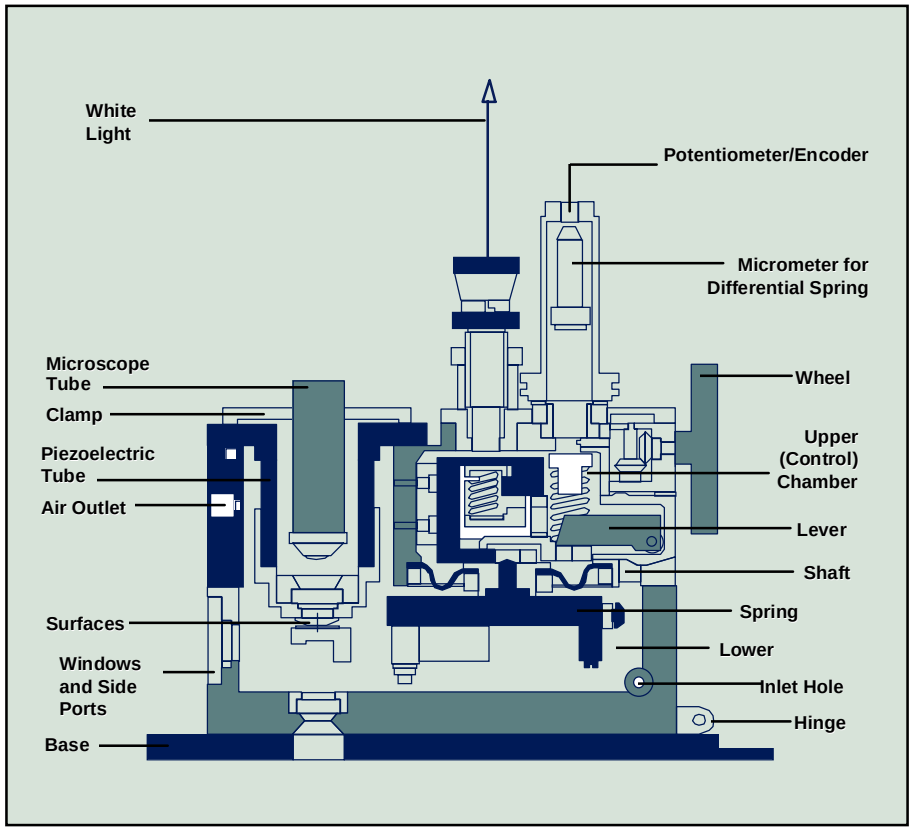






Van der Waals attraction dominates when surface charge is low (near i.e.p.) or when salt collapses the electrical double layer.

Surface Force Apparatus

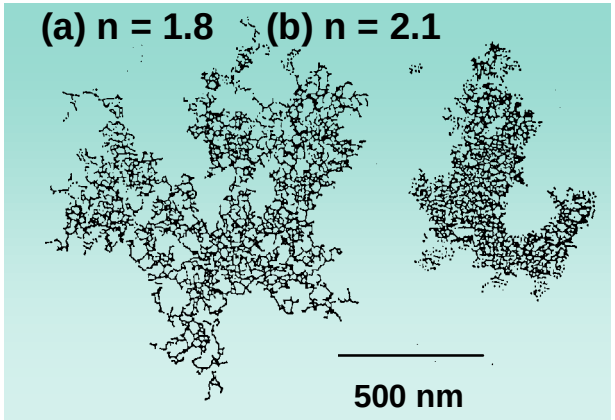


Surface force apparatus measures interparticle interactions, adhesion, shear forces.

Complementary Equipment: AFM, ESA, Zeta Plus, Rheometers, Fluid Loops, Modeling

Agglomerate Behavior Depends on Primary Particle Size, Agglomerate Size, and Fractal Dimension

Primary Diameter	Agglomerate Diameter	Fractal Dimension	Gel Point (vol%)	Settling Rate (cm/hr)
0.01 μm	100 μm	1.8	0.32	0.07
1 μm	100 μm	1.8	2.7	18
0.01 μm	100 μm	2.5	3	72
1 μm	100 μm	2.5	10	3000
0.01 μm	1 μm	2.5	10	0.036
0.01 μm	10 μm	2.5	7	1.4
0.01 μm	100 μm	2.5	3	72
100 μm	100 μm	3.0	16	6000

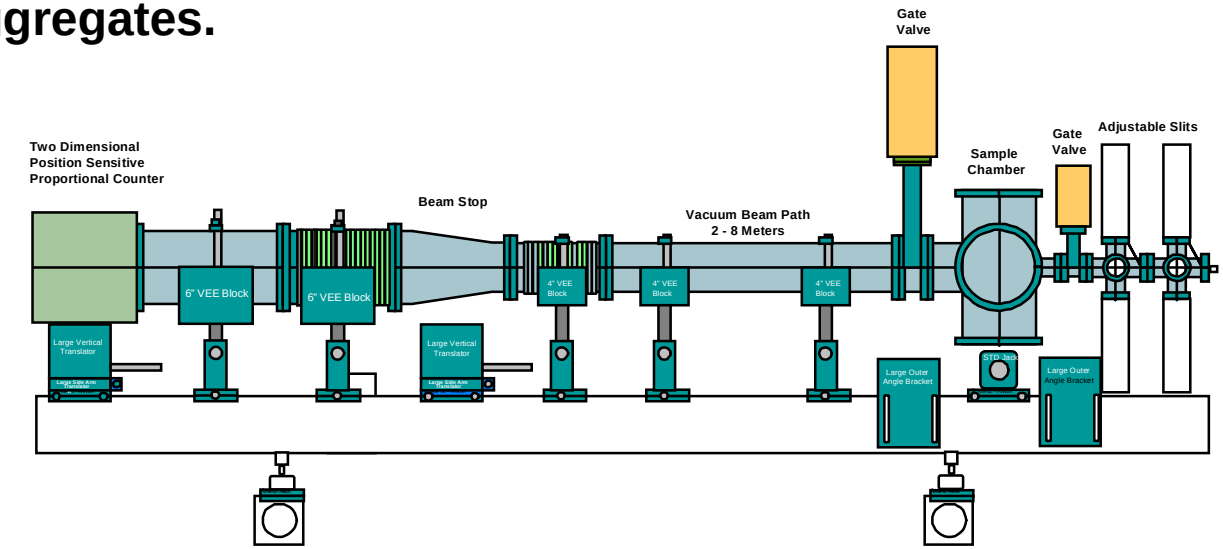


Agglomerates having the same size do not necessarily settle at the same rate or pack to the same sediment density as each other or as dense particles.

Primary particle size, fractal dimension, and agglomerate size must all be known to predict behavior of colloidal suspensions.

Small Angle X-Ray Scattering (SAXS)

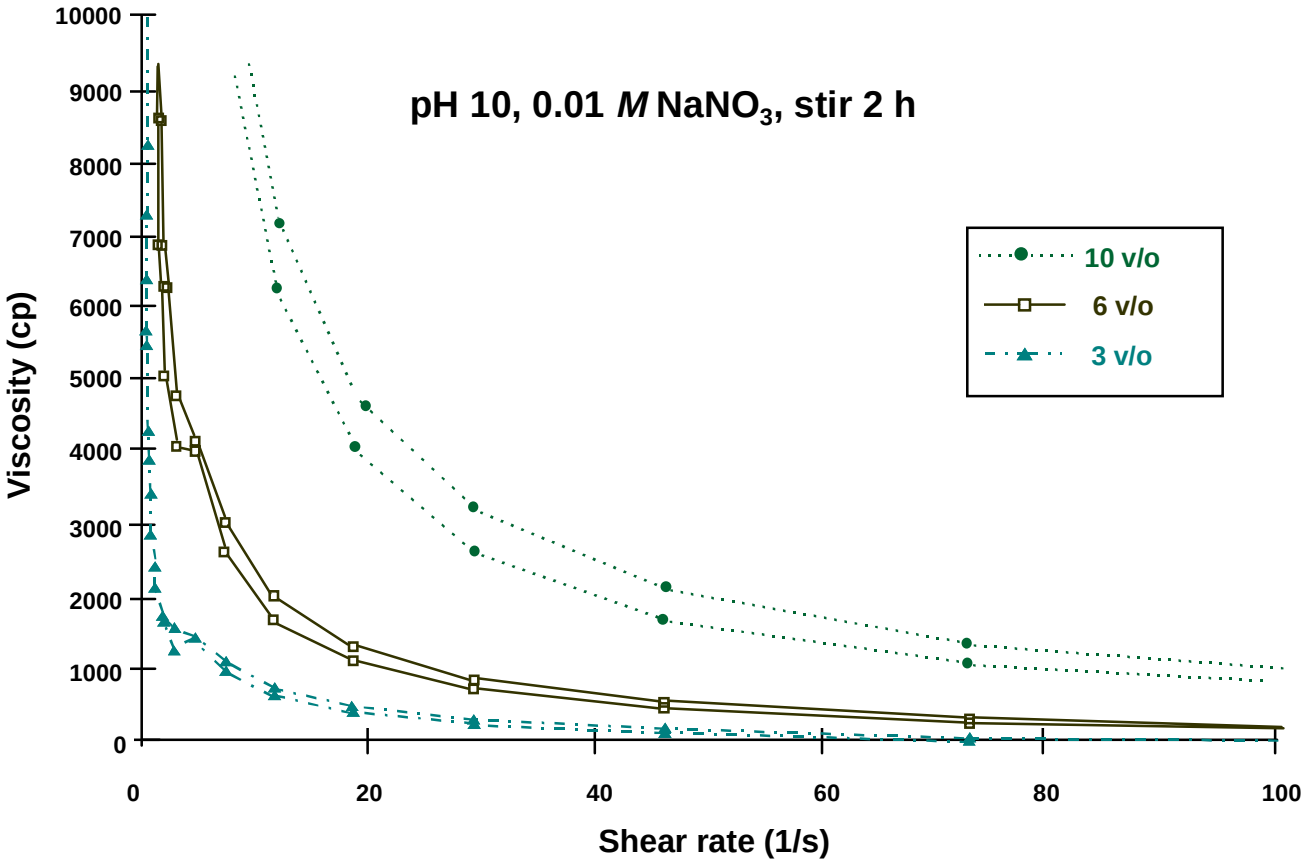
Pinhole collimated SAXS measures primary particle size, agglomerate size, fractal dimension of colloidal aggregates.



Complementary Equipment: Field Flow Fractionator, SANS (Oak Ridge), TEM, Light Scattering, Sedimentation System (sedigraph)

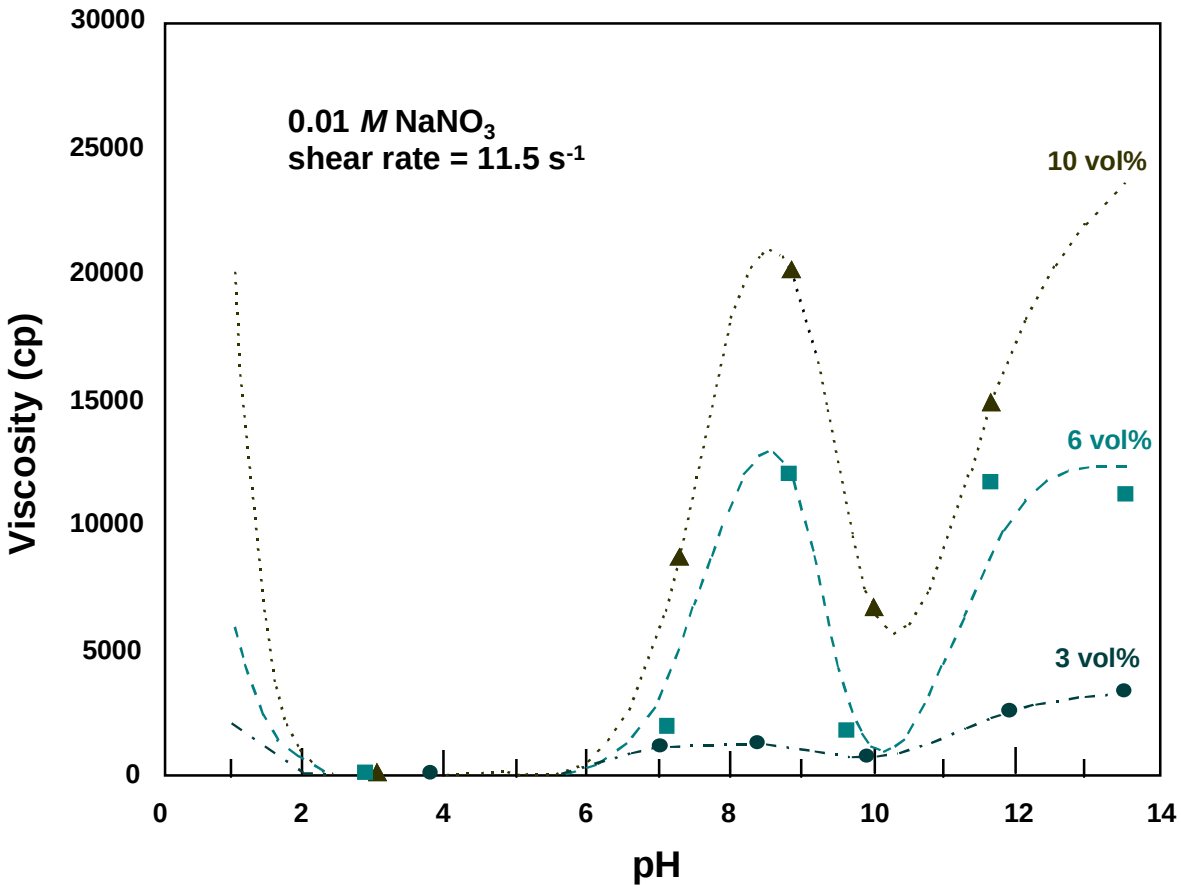
Slurry Rheology

Agglomerated Boehmite Forms Viscous, Shear-Thinning Suspensions



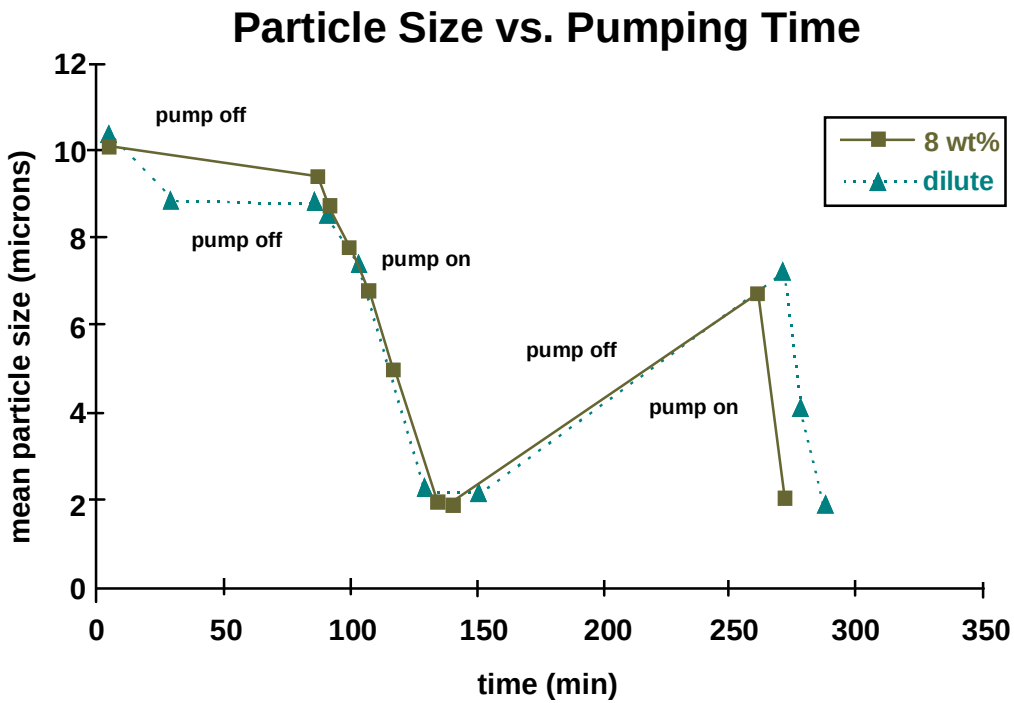
All data exhibit power law behavior:
shear stress = viscosity x (shear rate)^n

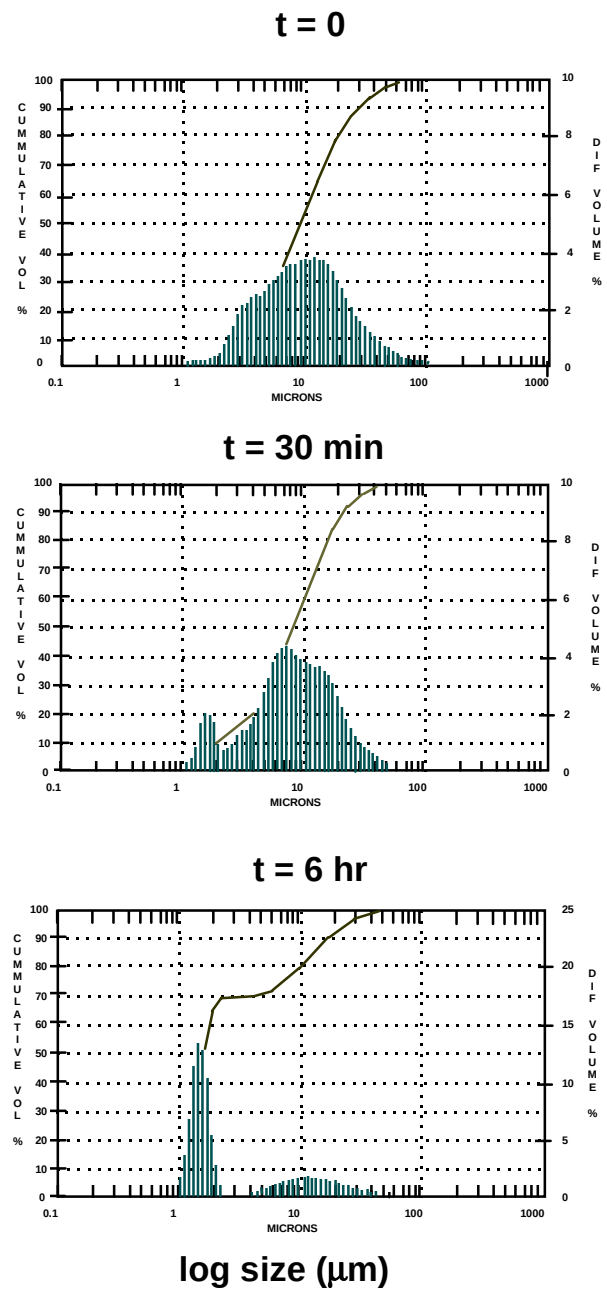
Boehmite Viscosity is Highly Sensitive to pH, Ionic Strength, and Solids Loading



Electrostatic repulsions are overcome near the isoelectric point and in high ionic strength (<0.01 *M*) solutions.

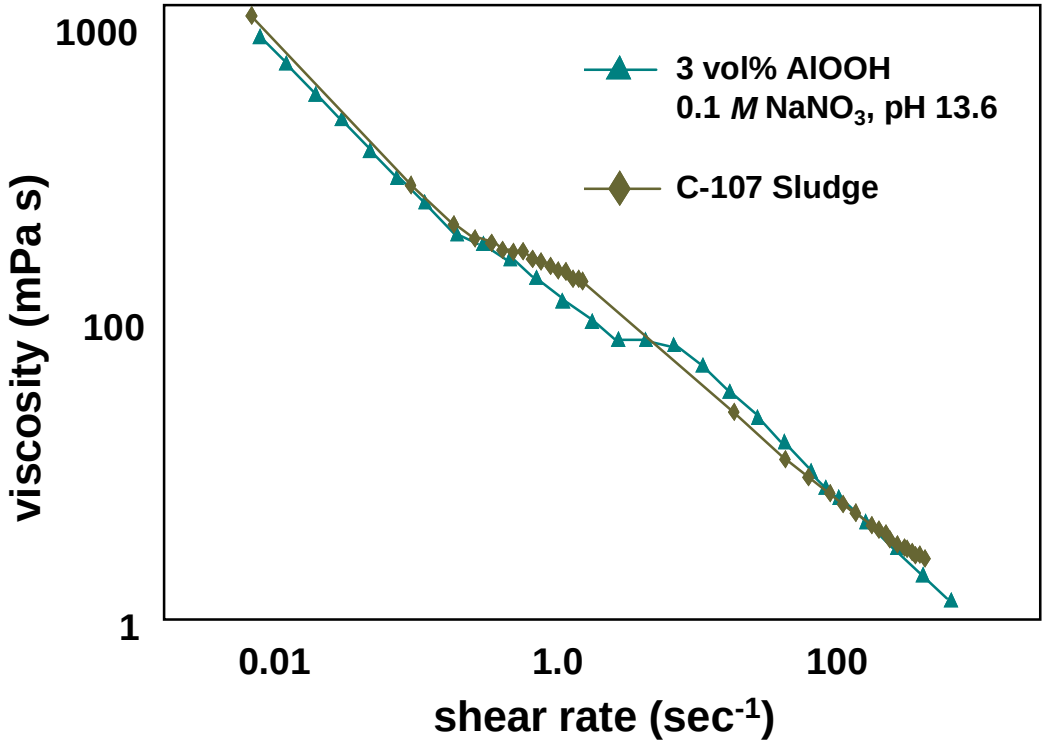
Shear Breaks Down Agglomerates





Moderate shear forces reduce 10-µm flocs to 2 µm.
Agglomerates reform under stagnant conditions.

Simple Simulants Mirror Viscosity Behavior of Actual Tank Wastes



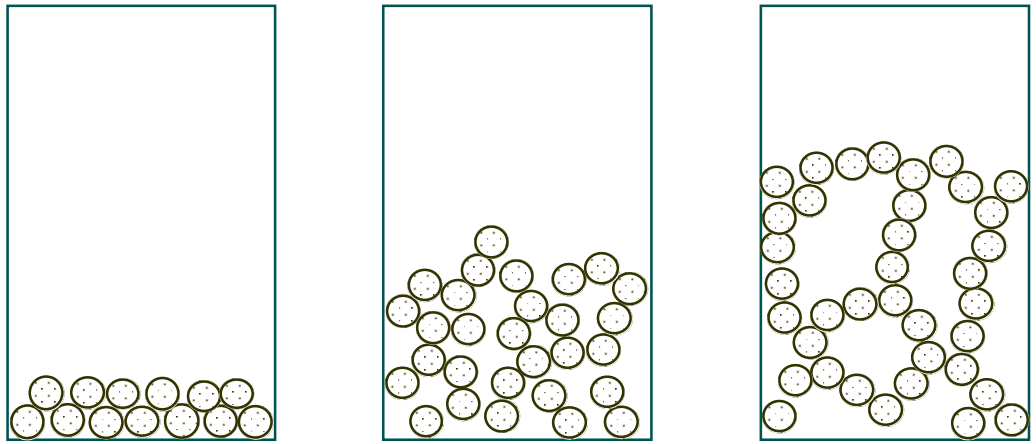
Al, Fe - rich sludge from Tank C-107 behaves like boehmite (AlOOH).

Simulants are useful if particle types and solutions are replicated.

Sedimentation

Impact of Agglomeration on Settle-Decant Steps

Example:
10 vol% slurry



	perfect packing (spheres)	25 vol% (spheres)	16 vol% spheres (percolation)
cake (total vol)	14%	40%	63%
interstitial	4	33	59
supernatant	96	66	41

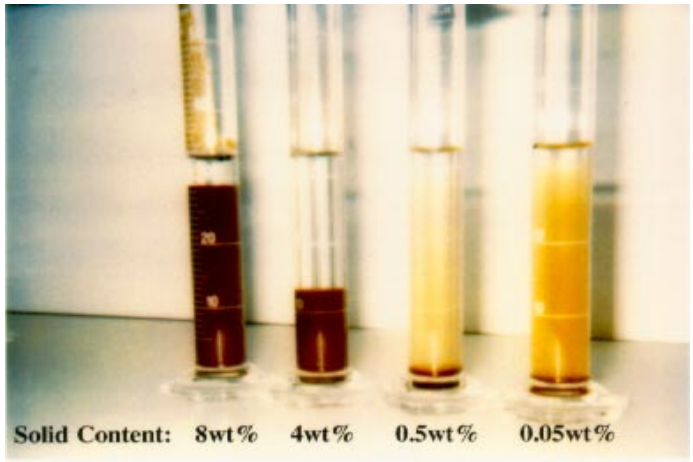
Some boehmite cakes pack to less than 10 vol% solids even after centrifugation at 20,000 G!

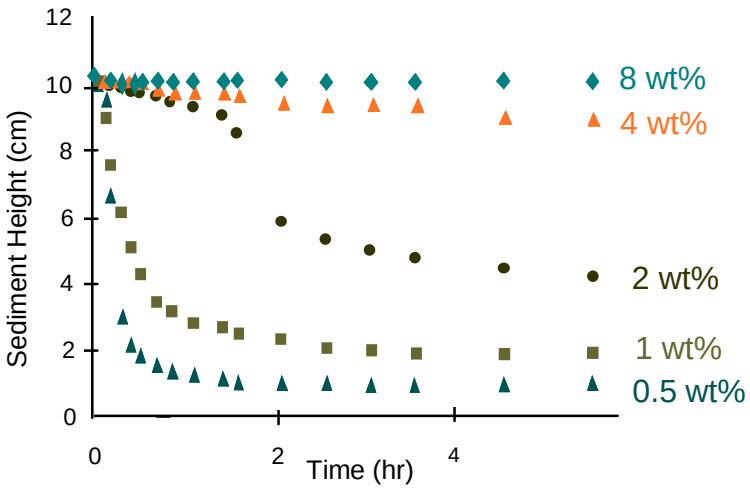
Highly dispersed boehmite does not settle at all.

Highly agglomerated boehmite can gel, even at 3 vol% and result in 0% sedimentation.

Sedimentation Behavior Varies with Solids Loading

$Fe(OH)_3$ Sedimentation





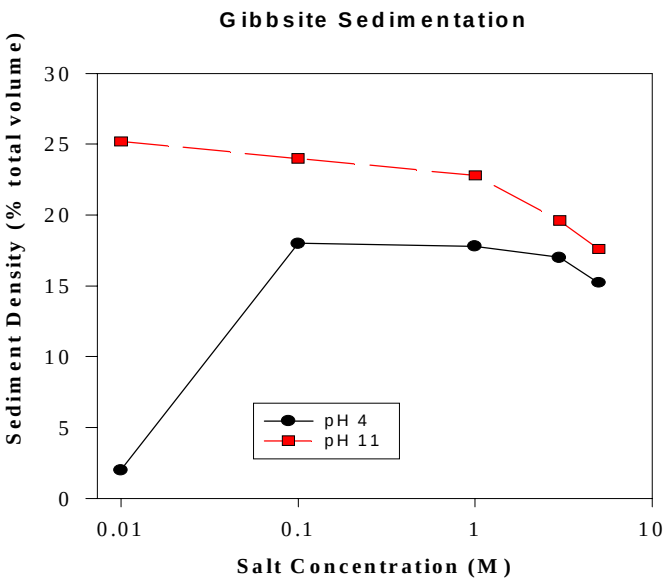
High Loading - No sedimentation. Stable particle network is already present.

Medium Loading- Hindered sedimentation. Network forms, but collapses under own weight.

Low Loading - Free sedimentation. No network forms. Individual particles sink at different rates.

Transitions between behavior are controlled by agglomerate structure.

Sedimentation Behavior Varies with pH and Salt Content



Conditions:

1 vol% Gibbsite

$NaNO_3$

50 ml centrifuge cone

sediment density measured after no further settling observed for 24 hours.

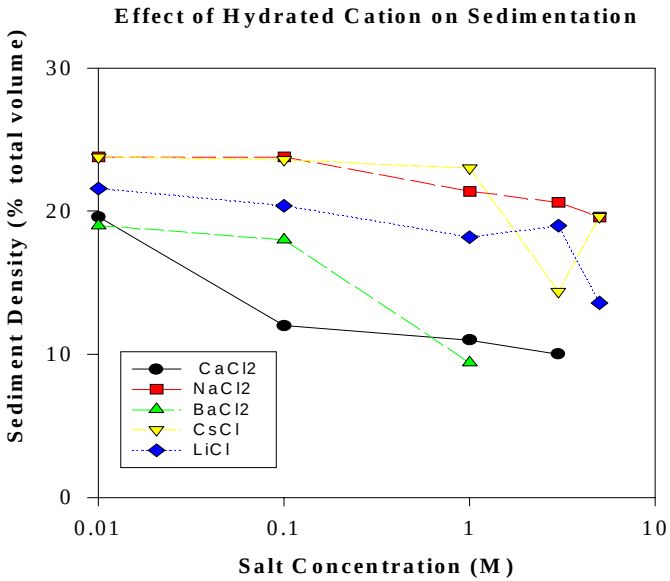
At low pH (4.0) and no salt present, gibbsite particles are dispersed and pack efficiently (2% of the total volume).

At low pH (4.0) and 0.1 M $NaNO_3$, the same gibbsite particles agglomerate and pack less efficiently (18% of the total volume).

Agglomerated sludge occupies more space and contains more non-removable interstitial liquids than dispersed sludge resulting in less efficient solids-liquids separations.

Sedimentation Behavior Varies with Salt Type

$Al(OH)_3$ Sedimentation



Conditions:

1 vol% Gibbsite

pH 10.6 to 11

50 ml centrifuge cone

sediment density measured after no further settling observed for 24 hours.

All salts tested ($NaNO_3$, NaCl, LiCl, CsCl, $BaCl_2$, $CaCl_2$ and $Mg(NO_3)_2$) promote sediment compression between 1 and 5 M.

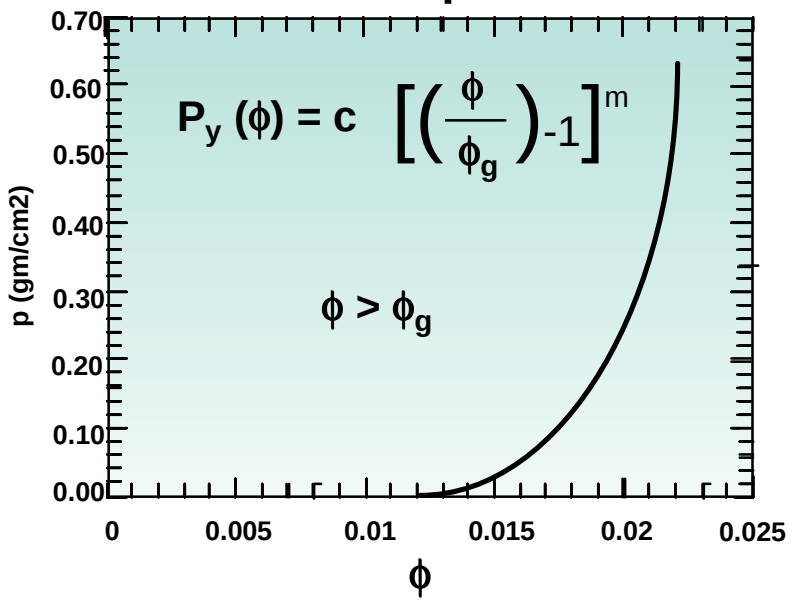
$BaCl_2$:NaCl mixtures having the same ionic strength but different Ba:Na show greater compression as the Ba content is increased.

Sediment compression does not correlate with the order of salting out, the Hofmeister series, or the order of binding.

Heavily hydrated cations allow agglomerates to deform and compact.

Sedimentation Results Yield Information Concerning Gel Point, Sediment Compressive Yield Stress

Sediment Compression Model



Reference Pressures

Condition	Pressures(psi)
10-cm lab test	0.6 psi
Normal filtration	14 psi
10-ft tank sediment	36 psi
Centrifugation (20,000 x G)	200 psi
Pressure Filtration	20-5400 psi

Compression Model Results

System	Salt	Gel Point(vol%)	C(psi)	P=0.6 psi	P=14 psi	P=36 psi
$Fe(OH)_3$, pH 12	none	0.95%	0.04	4 wt%	13 wt%	16 wt%
	1 *M*	0.64%	0.02	9 wt%	16 wt%	19 wt%
$Al(OH)_3$, pH 13 (1 μm)	0.1 *M*	6.7%	326	21 wt%	26 wt%	29 wt%

Gel point, yield stress parameters extracted from power law fit are consistent with known agglomerate interactions.

Sedimentation Studies with Actual Sludge Samples Confirm Results Obtained with Simple Simulants

Sludges Examined (Lumetta, Rapko): S-104, T-111, BX-107, T-104, B-111, T-111

Conditions:

Retrieval Wash
- 2.3 wt% insolubles
- 0.01*M* $NaOH/NaNO_2$
- 100°C, 1 hr

Caustic Leach
- 8 wt% solids
- 3 - 3.2*M* NaOH
- 100°C, 5 hr

Final Wash
- 8 wt% solids
- 0.01*M* $NaOH/NaNO_2$
- 25°C, 0.5 hr

Results:

- S-104 (boehmite) forms a sediment network with a density of 3.5 wt% (1.1 vol%). Suspensions with higher solids loadings (caustic leach, final wash) do not settle. *Results mirror results obtained on commercial boehmite.*
-
- T-111 and B-111 form sediments with a density of around 6 wt% (1.5 vol%). Again, 8 wt% suspensions do not settle, as continuous agglomerate networks form. *Results are nearly identical to $Fe(OH)_3$, which appears to model the behavior of the predominant Fe-Bi-Si phase.*
- BX-107 and T-104 form the densest sediments (10 wt% to 12 wt%, 3 vol%). Reasons for the enhanced sedimentation is under investigation.
- Initial sedimentation rates are negligible in all 8 wt% suspensions. Rates at 2.3 wt% range from 0.23 cm/hr to 3.2 cm/hr.

Capabilities

State-of-the-Art Colloids Laboratory

- Particle Size, Agglomerate Size, and Fractal Dimension
-
  - Small Angle X-Ray Scattering
  - Small Angle Neutron Scattering (Oak Ridge)
  - Particle Size Analyzers
  - Field Flow Fractionator
  - TEM
  - Sedigraph
  -
- Interparticle Interactions
-
  - Surface Force Apparatus
  - Atomic Force Miicroscope
  - ESA
  - Zeta Potential
  -
- Rheology
-
  - Rheometers
  - Fluid Loops
  - Modeling
  -

Radiocolloids Laboratory

- Fume Hood and Glovebox (Low Dose Samples)
-
  - Particle Size Analyzers
-
  - Zeta Potential
-
  - Rheology
-
  - Thermal Analysis
-
  - Sedimentation
  -
  - Solids Content
  -
  - TEM
  -
- Hot Cell

–
  - Rheology
  -
  - Sedimentation
  -
  - Solids Content
  -