Development of Rheological Modifiers

November 17, 2010

Jaehun Chun*, Erich Hansen‡, and John Berg§

DOE-EM Tech Exchange

*Pacific Northwest National Laboratory
‡Savannah River National Laboratory
§University of Washington

Pacific Northwest
NATIONAL LABORATORY

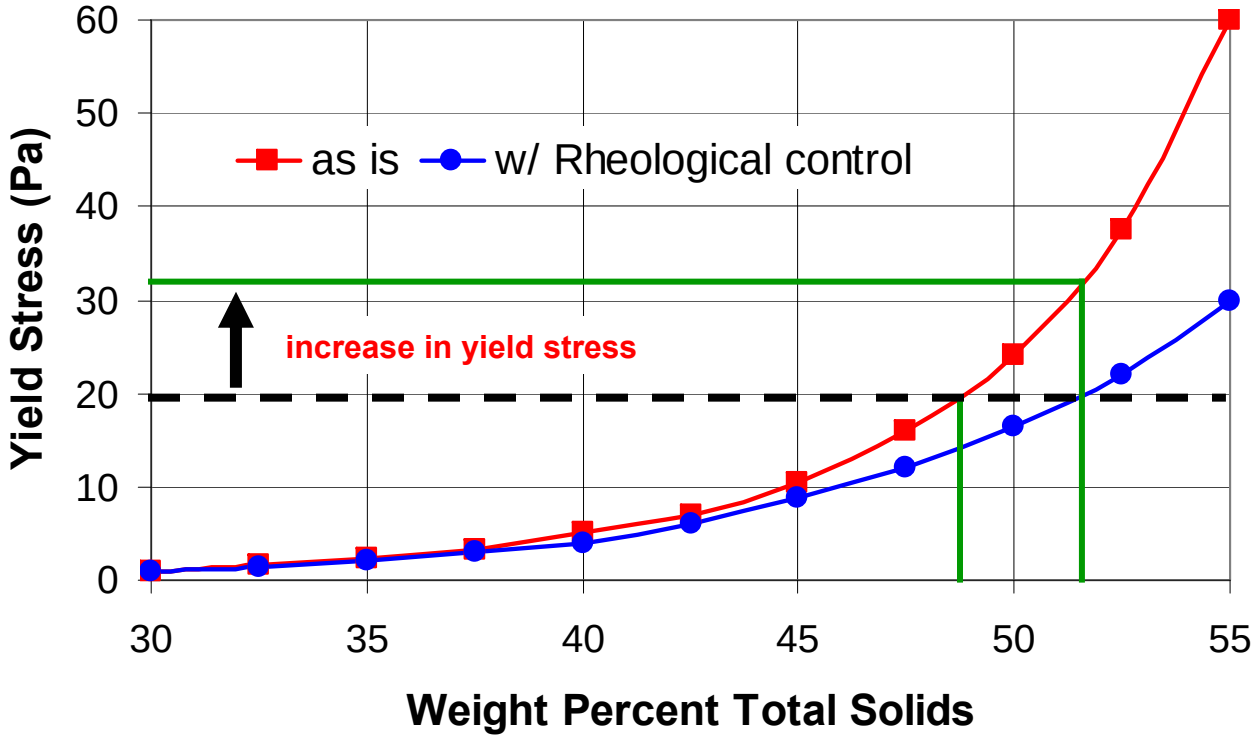
Outline

- Motivation
- Approach
- Experimental/Method
- Initial Studies with AZ-101 simulant
- SRNL Results
- LAW Melter Feed Results
- UW Contribution
- Summary
- Acknowledgements and Future Work

Pacific Northwest
NATIONAL LABORATORY

Motivation

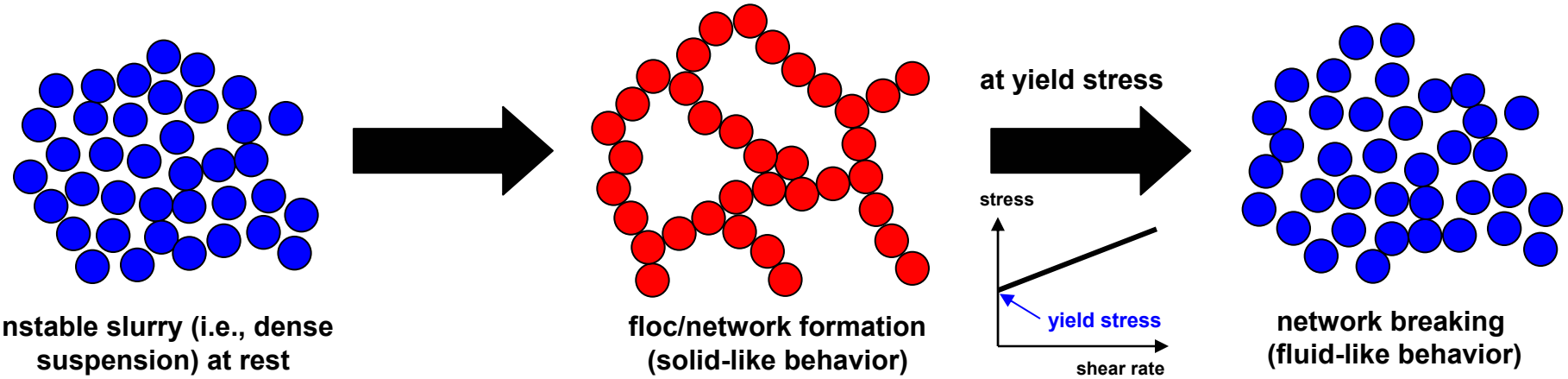
A higher throughput in tank waste treatments (WTP at Hanford and DWPF at Savannah River Site) is desirable due to both cost and time, but requires processing waste slurries at higher solids content → **requires control of the rheological properties of slurry**



Pacific Northwest NATIONAL LABORATORY

Print Close

Approach



unstable slurry (i.e., dense suspension) at rest

floc/network formation (solid-like behavior)

network breaking (fluid-like behavior)

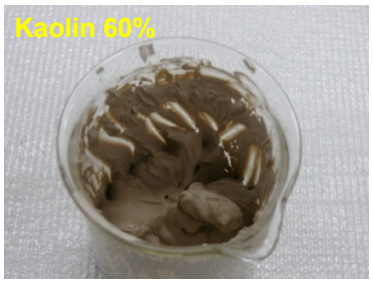
→ **Minimizing the floc/network formation is a key to reducing the yield stress**

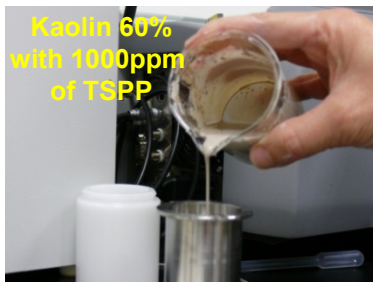
Introduce a small amount of "**Rheological Modifiers**"

depending on type of colloidal interactions

build additional steric repulsion : nonionic/polymeric surfactants

strengthen electrostatic repulsion : weak organic acids





TSPP (Tetra Sodium Pyrophosphate)

Pacific Northwest NATIONAL LABORATORY

Experimental/Method

Rheology measurement

Flow curve measurement (bob /cup) with 0-1000 sec^{-1}

Rheology

Relative change in yield stress (%)

$$= \left(\frac{\tau_y^{\text{with R.M.}} - \tau_y^{\text{control}}}{\tau_y^{\text{control}}} \right) \times 100$$

< 0 : favorable
> 0 : unfavorable

Size measurement

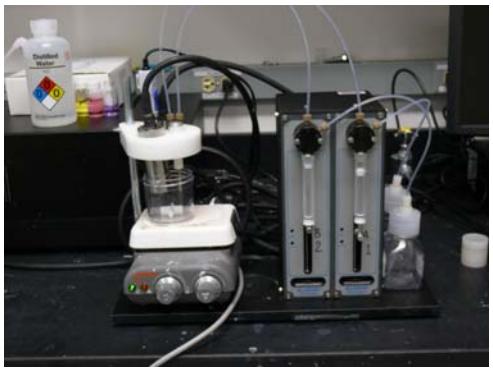
Particle size analysis (laser light scattering)

PSD

Other measurements

Solids content (UDS), pH, and possibly zeta potential

UDS



Zeta Potential

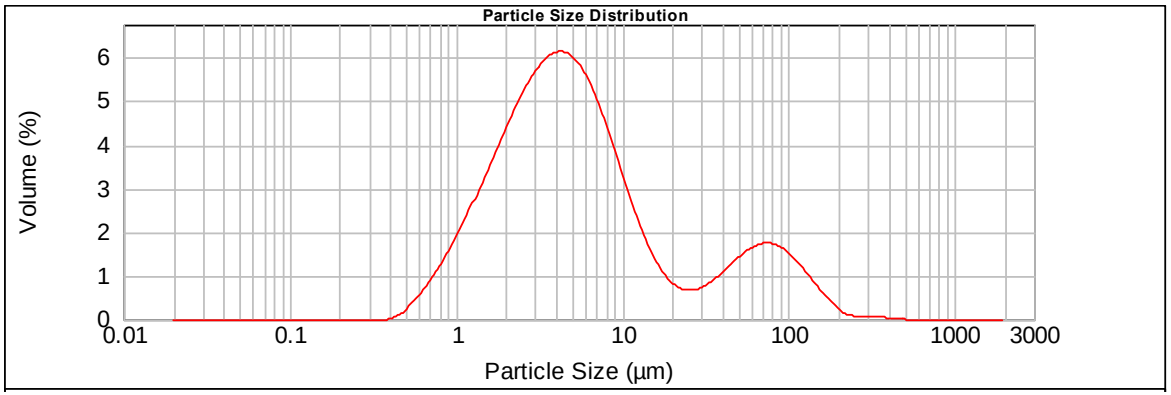
Qualitative understanding based on fundamentals of colloidal suspensions

Pacific Northwest NATIONAL LABORATORY

Initial Studies with AZ-101 simulant - Simulant characteristics

AZ-101 complex nuclear waste simulant: representative HLW simulant

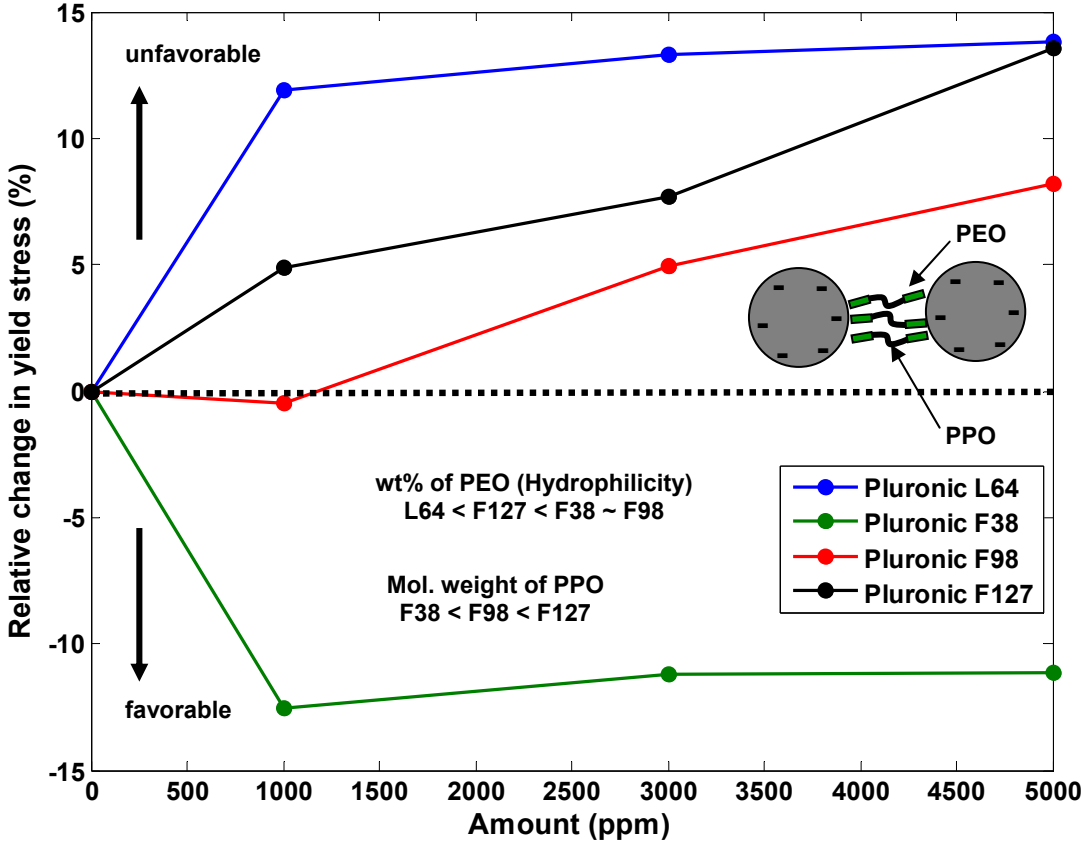
- Highly basic : pH ~11-12
- Oxide/hydroxide particles (mainly Fe_2O_3 and $Al(OH)_3$) :
  negative charges due to amphoteric nature (zeta potential ~ -4mV)
  hydrophilic particle surface
- Abundant electrolytes (from inorganic salts including NaOH ~ 0.5M) :
  very weak electrostatic repulsion and unstable slurry
- Reasonably high solids content → ~ 26 wt% : unstable slurry
- Colloidal slurry : bimodal distribution, *O*(1-100) µm, and ~ 70% of particles are 1 to 10 µm

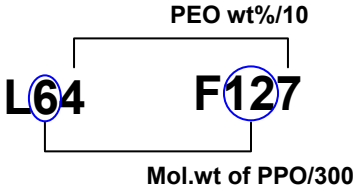


Pacific Northwest NATIONAL LABORATORY

Print Close

Initial Studies with AZ-101 simulant - Nonionic/polymeric surfactants (1)



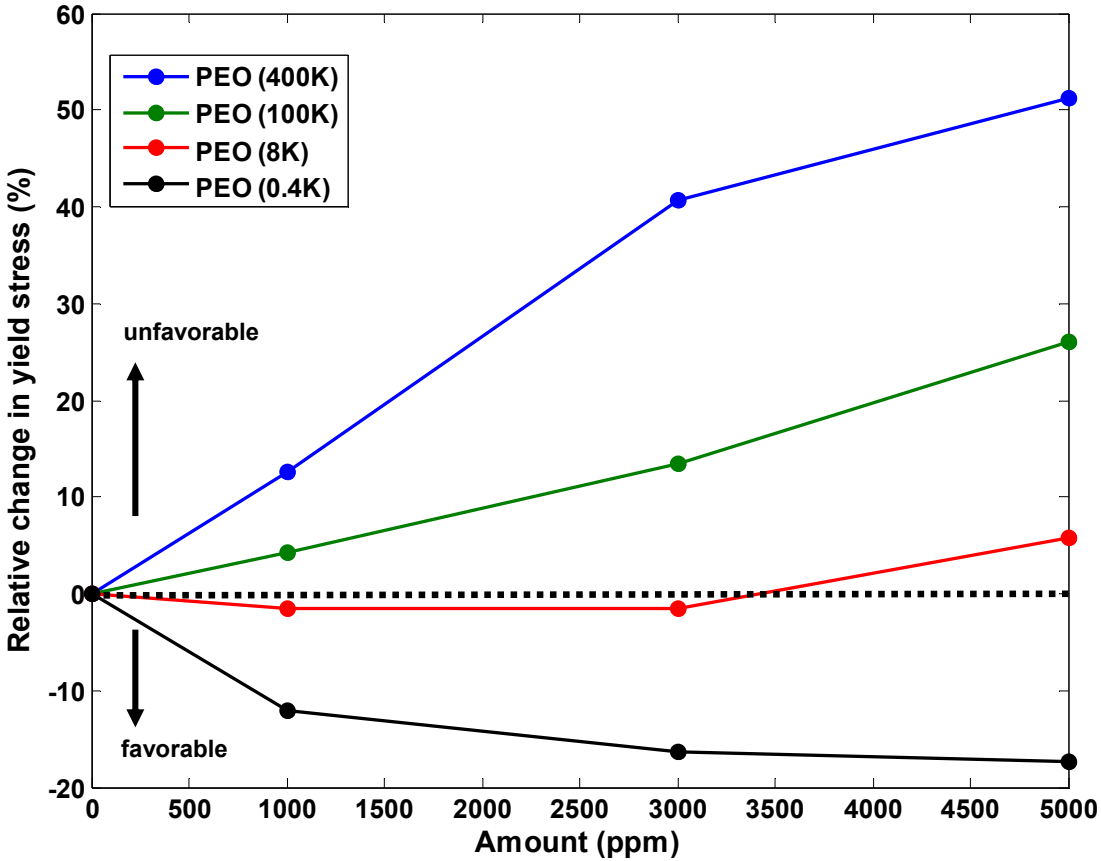


Efficiency depends on weight % of PEO and molecular weight of PPO, which are essentially connected to two issues
→ adsorption on the surface and bridging between particles

Pacific Northwest NATIONAL LABORATORY

Print Close

Initial Studies with AZ-101 simulant - Nonionic/polymeric surfactants (2)

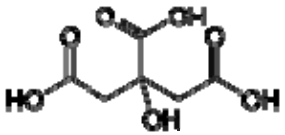


Possible bridging between particles would provide additional destabilization, which appears to be proportional to the molecular weight

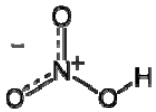
Pacific Northwest NATIONAL LABORATORY

Print Close

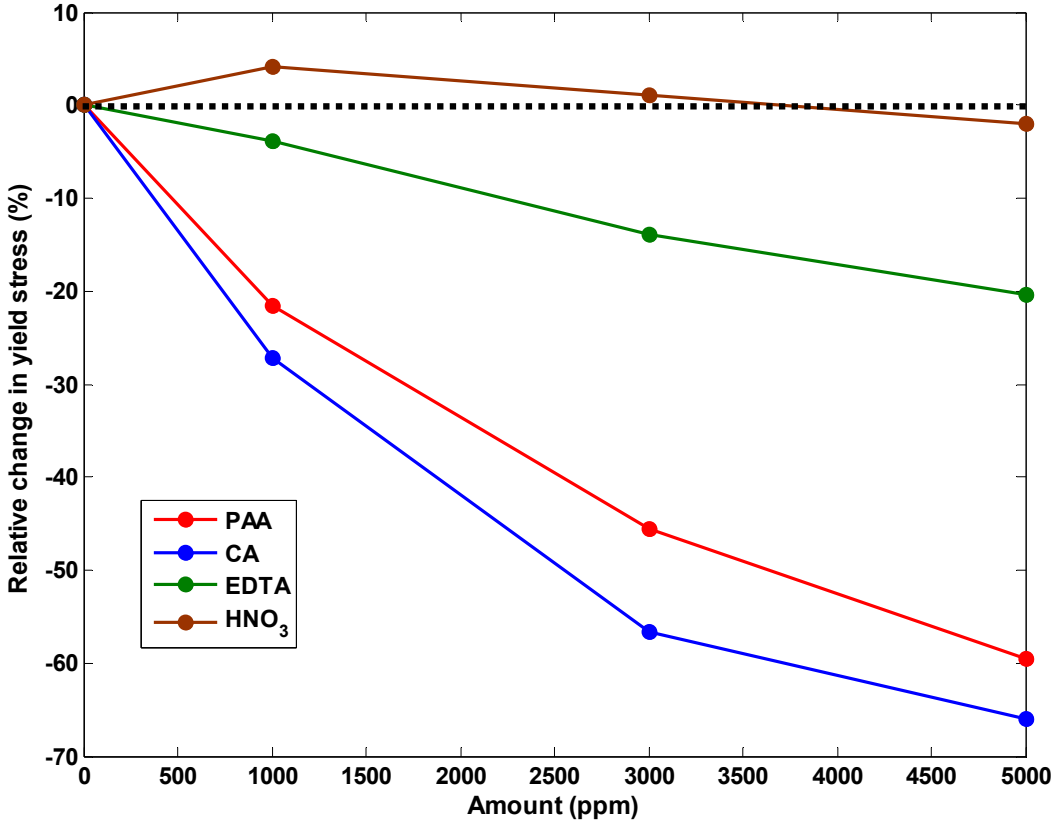
Initial Studies with AZ-101 simulant - Weak acids (1)

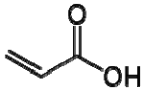


citric acid (CA)

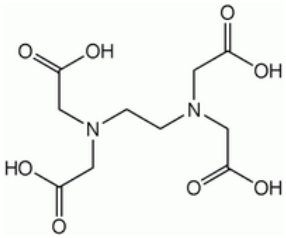


nitric acid





polyacrylic acid (PAA) (monomer unit)



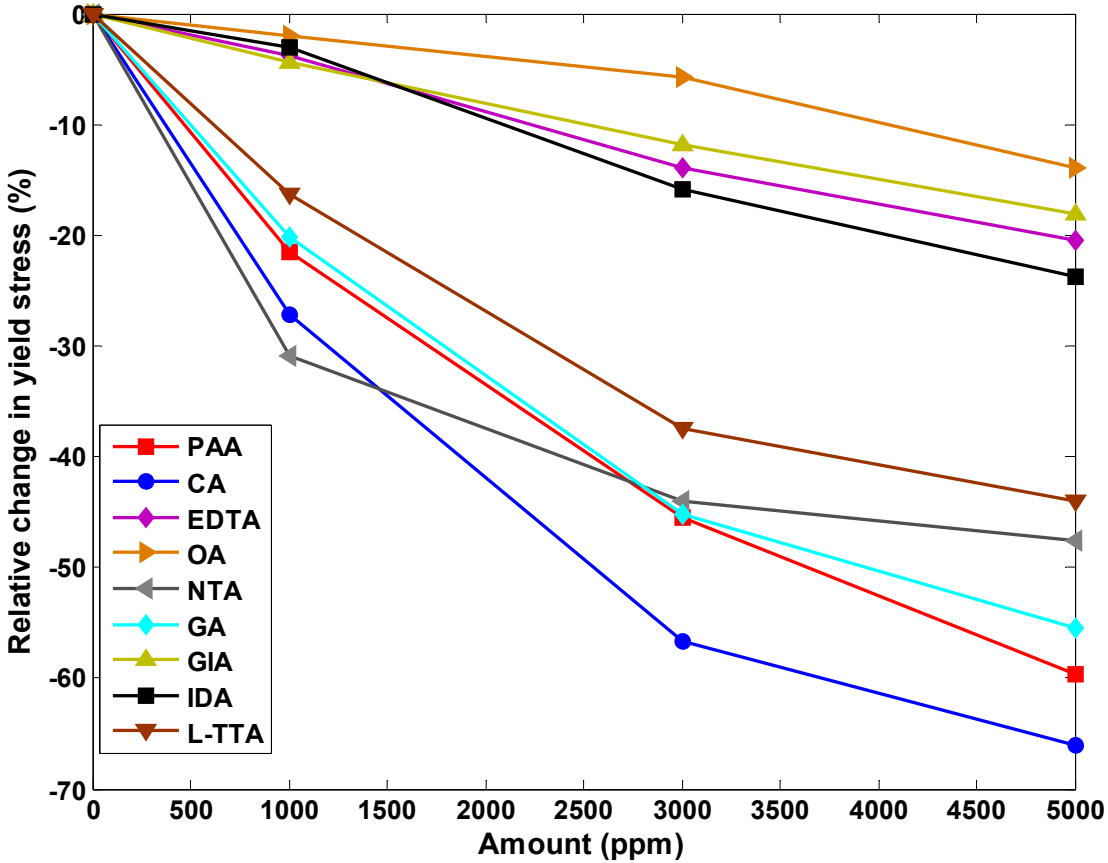
EDTA

- **Weak acids are more efficient than nonionic/polymeric surfactants**
- **Efficiency does not depend on the number of carboxyl groups**
- **A decrease in yield stress is not from a direct pH effect (cf. nitric acid)**

Pacific Northwest NATIONAL LABORATORY

Print Close

Initial Studies with AZ-101 simulant - Weak acids (2)



- **CA and PAA are most promising weak acid type rheological modifiers**
- **Various weak carboxylic acids reduce the yield stress more than ~15%**

OA: Oxalic acid GA: Gluconic acid IDA: Iminodiacetic acid
NTA: Nitrilotriacetic acid GIA: Glycolic acid L-TTA: L-tartaric acid

Pacific Northwest NATIONAL LABORATORY

Print Close

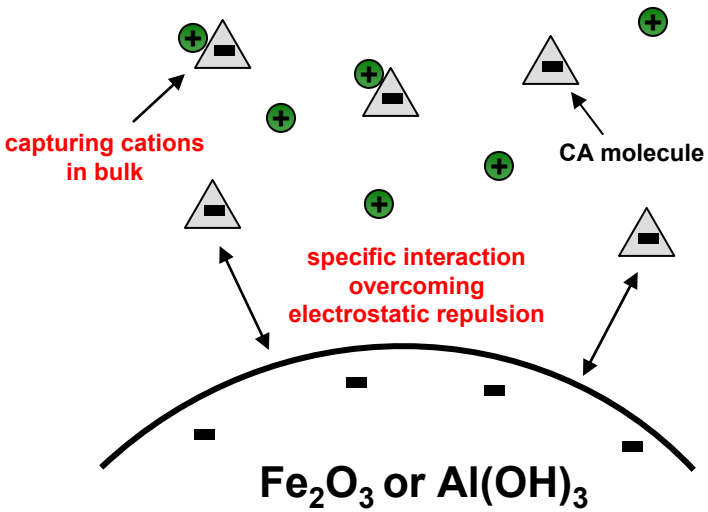
Initial Studies with AZ-101 simulant - Weak acids (3)

At pH ~12, charges on the particle (mainly Fe_2O_3 and $Al(OH)_3$) and weak acids (e.g., PAA and CA) are both negative. How do weak acids enhance the rheological/flow properties of the slurry?

< Key experimental observations >

- Specific interactions between carboxyl (COOH) and hydroxyl group (MOH) - Kummert et al (1980), Karaman et al (2001), and Wisniewska et al (2009)
- Number of MOH groups is dominant over MOH_2^+ or MO^- irrespective of pH - Parks et al (1962), Chibowski et al (2002)
- Adsorbed amount of PAA on Fe_2O_3 becomes half at pH=3, compared to that at pH=9 - Chibowski et al (2002)
- At pH~7, no adsorption of PAA on silica (PZC ~ 2.5) but appreciable adsorption on alumina (PZC ~8.5) - Zaman et al (2002)
- CA and PAA are well-known sequestering agents for water treatment

Citric acid at pH~12



Electrostatic repulsion and specific interaction are keys to understanding the mechanism by which these modifiers work

Pacific Northwest NATIONAL LABORATORY

SRNL Results - Overview

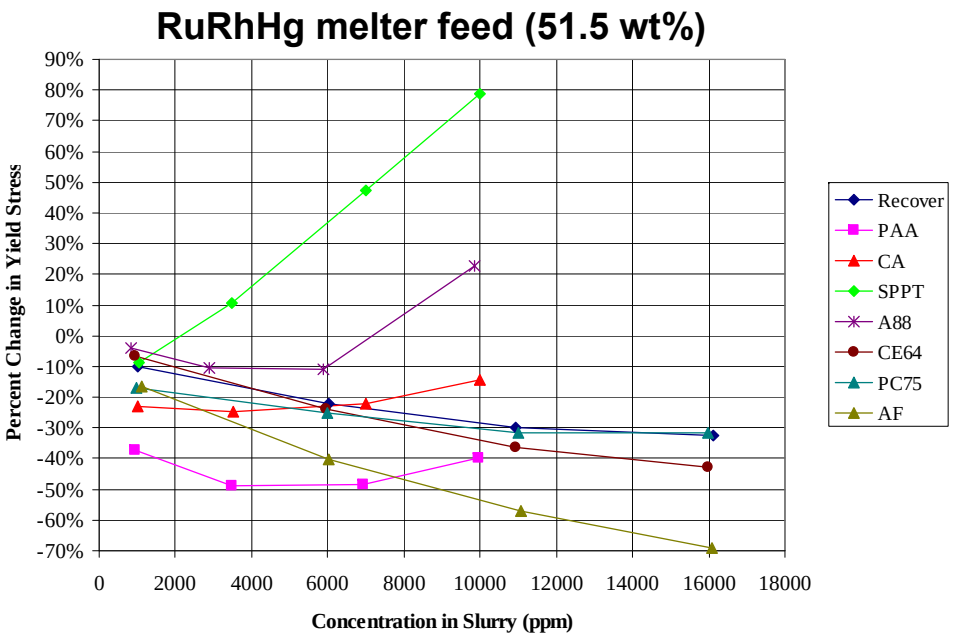
Various rheological modifiers, in addition to the promising candidates (PAA and CA) identified by PNNL, were tested on five different melter feed simulants at SRNL

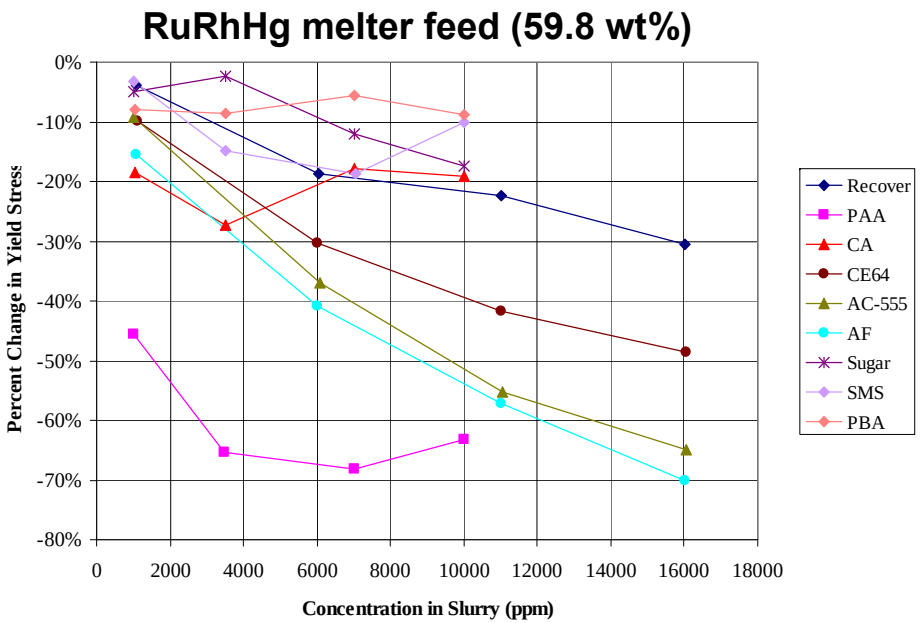
Tested simulants	Tested rheological modifiers
RuRhHg melter feed (two different solids contents) SB5-12/13 melter feed SB6-1,2,3,4 melter feed 09-SB5-23 melter feed 09-SB5-24 melter feed	- Weak acids polyacrylic acid (PAA), citric acid (CA), phenylboronic acid (PBA) - Sodium pyrophosphate tetrabasic (SPPT) - Sugar, Sodium metasilicate - Dolapix A88, CE64, and PC75 - Antifoam 747 - W. R. Grace ADVA Cast 555 - W. R. Grace ADVA Flex - W. R. Grace Recover

Pacific Northwest NATIONAL LABORATORY

SRNL Results
- RuRhHg simulant

Testing of RuRhHg melter feed simulants (used to determine the impact of noble metals on the DWPF process)





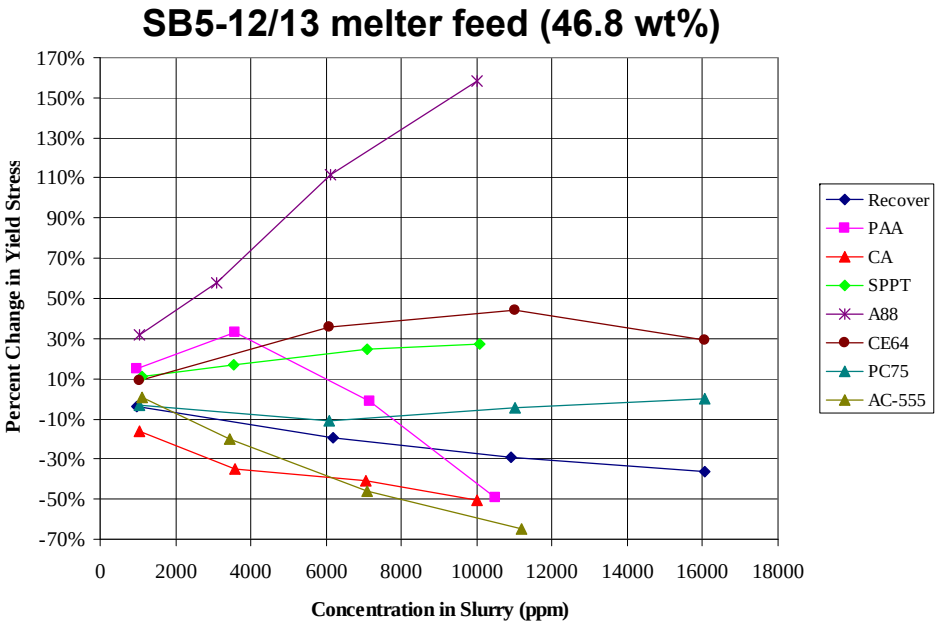
- **PAA, CE 64, and ADVA Flex (AF) are effective in decreasing the yield stress for two different solid wt% simulants**
- **Sugar and sodium metasilicate appear to have little impact**

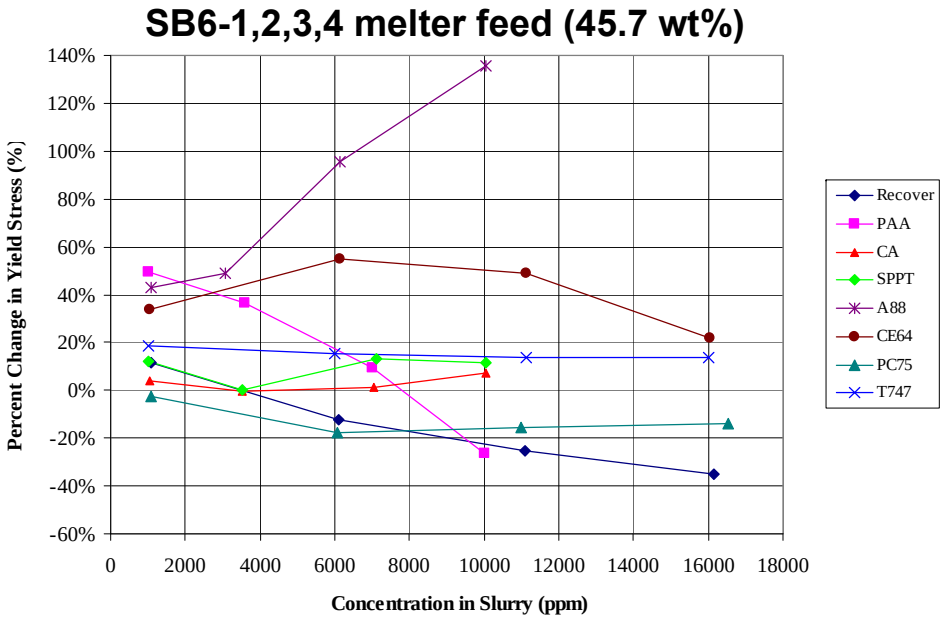
Pacific Northwest NATIONAL LABORATORY

Print Close

SRNL Results
- SB5-12/13 and SB6-1,2,3,4 melter feeds

Testing of SB5-12/13 (to support the processing of sludge batch 5) and SB6-1,2,3,4 (to support initial scoping studies for processing sludge batch 6) melter feed simulants





- **Recover, PAA, CA, and ADVA Cast 555 (AC-555) are effective in decreasing the yield stress for the SB5-12/13 simulant**
- **Recover, Dolapix PC 75, and PAA are effective for the SB6-1,2,3,4 simulant**

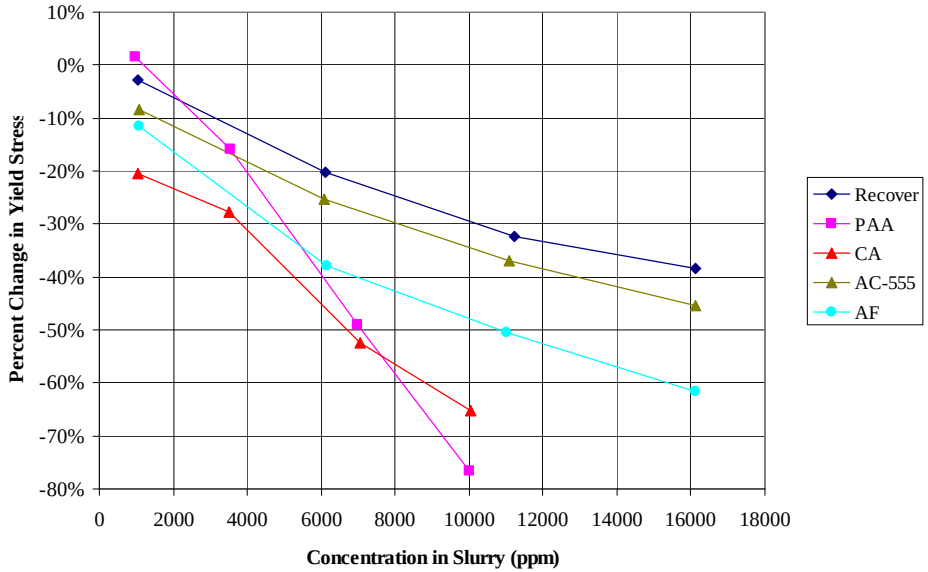
Pacific Northwest NATIONAL LABORATORY

Print Close

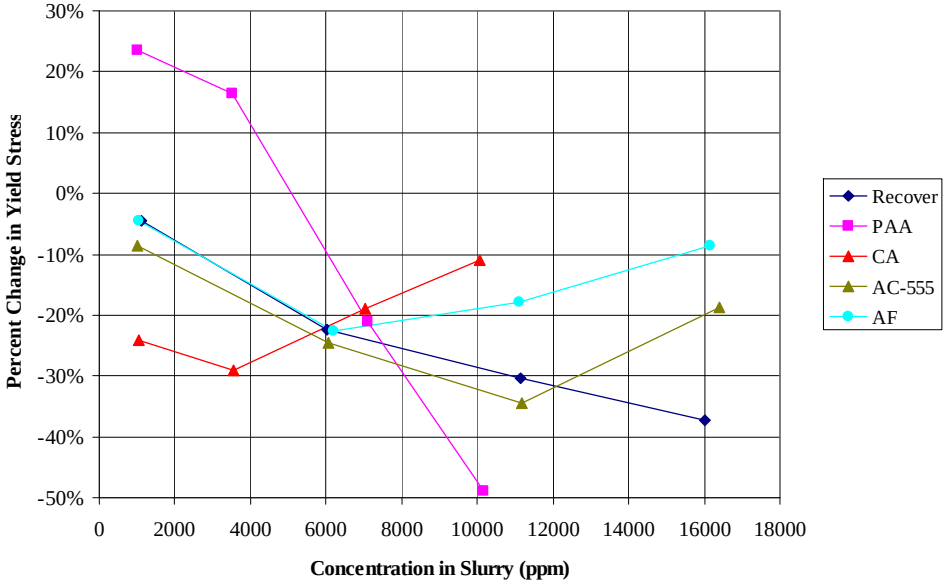
SRNL Results
- 09-SB5-23 and 09-SB5-24 melter feeds

Testing of 09-SB5-23 and 09-SB5-24 (to support the processing of sludge batch 5, especially for the effect of pH) melter feed simulants

09-SB5-23 melter feed (50.2 wt%, pH ~7.4)



09-SB5-24 melter feed (49.0 wt%, pH ~5.1)



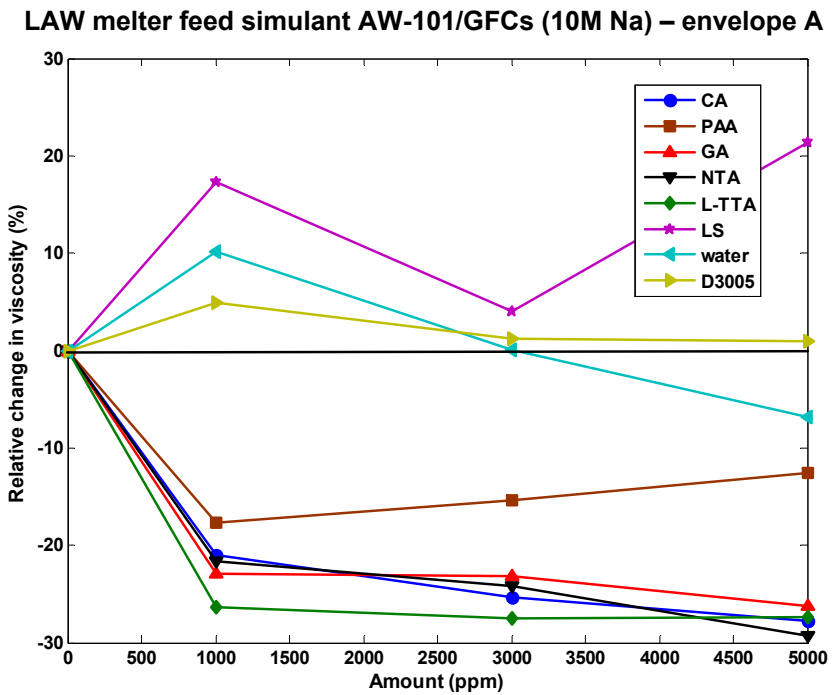
- **Most of the modifiers reduce the yield stress for both simulants**
- **Modification appears to be less effective as pH decreases**
  → possibly related to dissociation of carboxyl groups

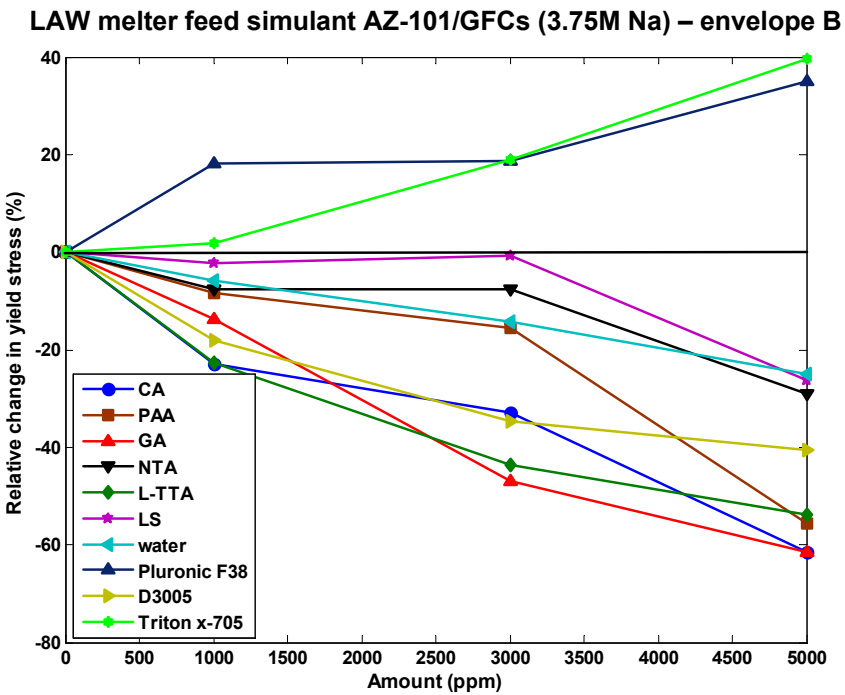
Pacific Northwest NATIONAL LABORATORY

Print Close

LAW Melter Feed Results - Envelopes A, B, and C

Three different LAW melter feeds with glass former chemicals (GFCs, mainly SiO_2)
- envelope A: AW-101/GFCs (with anti-foaming agent (AFA) and sodium oxalate (SO)), envelope B: AZ-101/GFCs, and envelope C: AN-107/GFCs

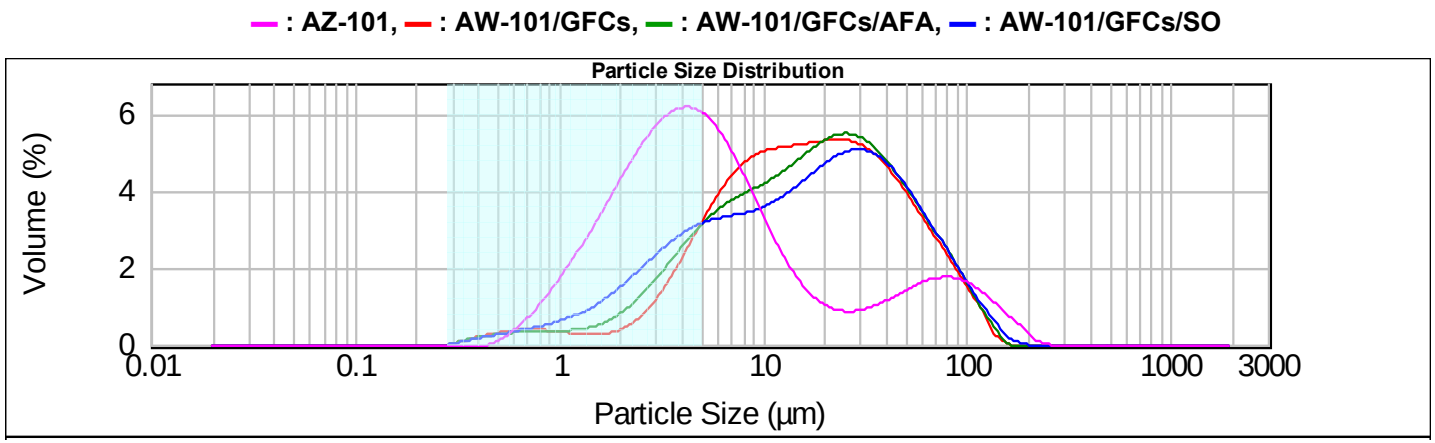


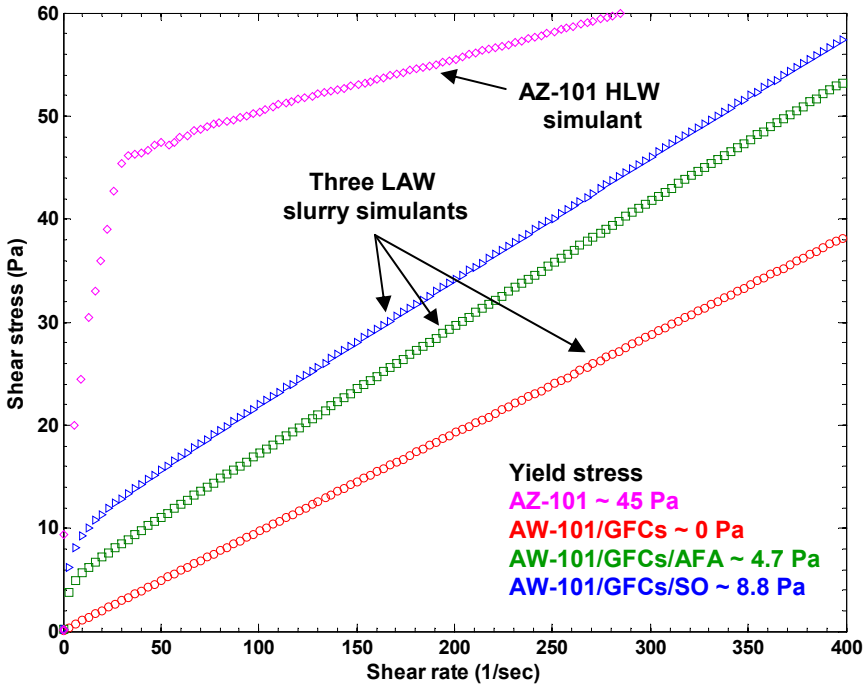


CA, PAA, GA, and L-TTA are effective in decreasing the yield stress for various LAW melter feeds

LS: Sodium lignosulphonate

LAW Melter Feed Results
- Effect of particle size distribution





- **Higher percentage of small particles (d ~ 5 µm) corresponds to higher yield stress**
- **d_{50} of AW-101 simulants are very similar (~ 17 µm) so the yield stress does not scale as 1/ $(d_{50})^2$ with broad size distributions**
- **Shear-attraction number :**

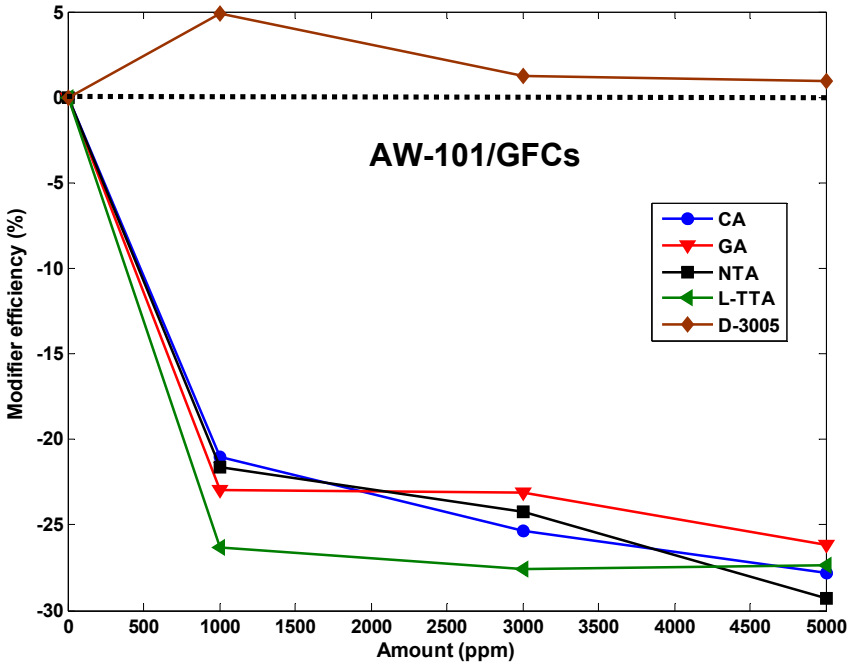
$$N_{SA} = \frac{\mu a^3 \dot{\gamma}}{A} \sim O(1)\dot{\gamma}$$ with d ~ 5 µm and A ~ 10^{-20} J

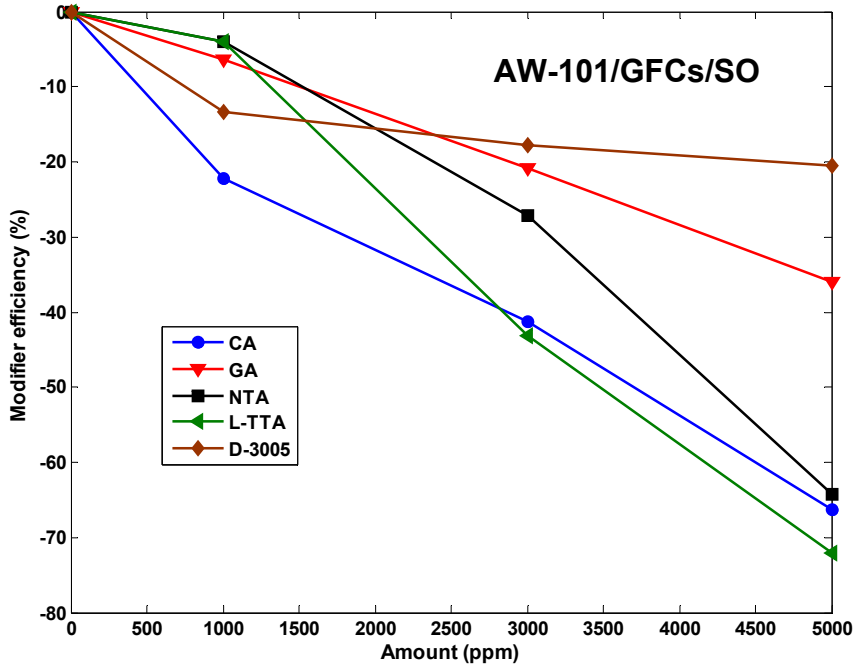
particles less than ~ 5 µm are important for van der Waals interaction (i.e., yield stress)

Pacific Northwest NATIONAL LABORATORY

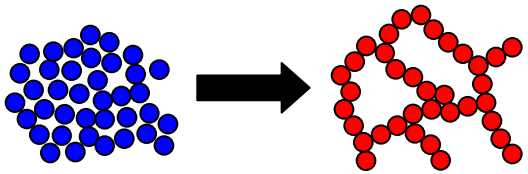
Print Close

LAW Melter Feed Results
- Implication to rheological modification





Modifier efficiency (i.e., relative change in rheological property) appears to be correlated with percentage of small particles (d ~ 5 μm)



unstable slurry (i.e., dense suspension) at rest

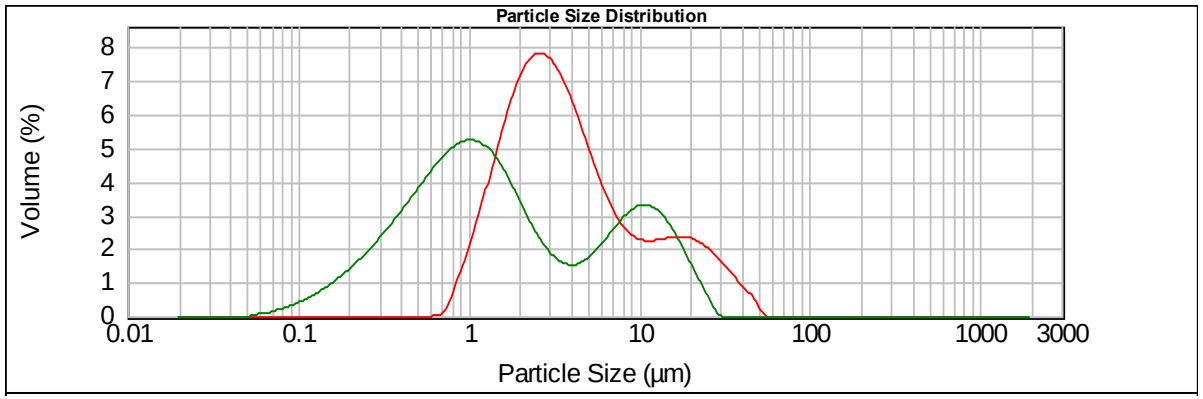
floc/network formation (solid-like behavior)

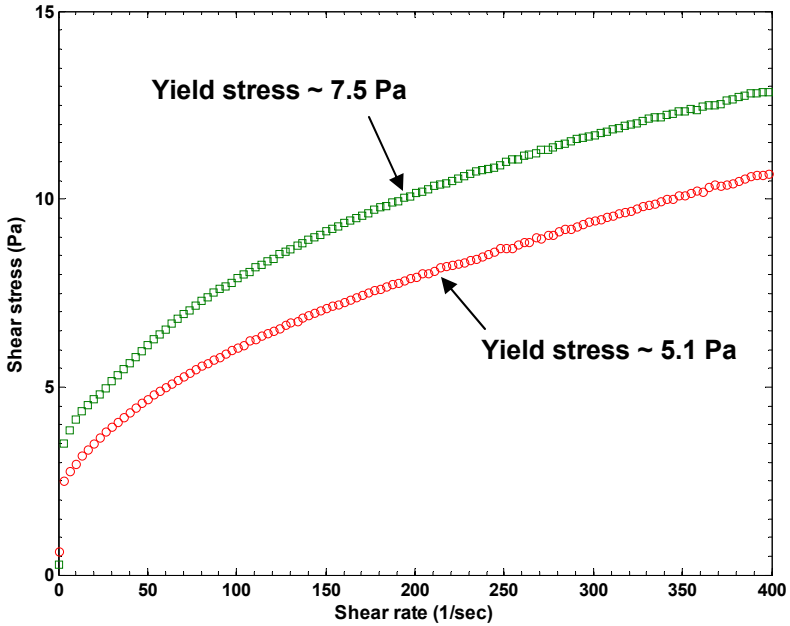
Pacific Northwest NATIONAL LABORATORY

D-3005: Duramax D-3005

LAW Melter Feed Results
- Coupling with electrostatic repulsion

35 wt% gibbsite (α-$Al(OH)_3$) with different size distribution under low salt concentration (0.01M $NaNO_2$ and 0.01M NaOH)





- **Higher percentage of small particles (d ~ 5 µm) corresponds to higher yield stress**
- **Coupling with electrostatic repulsion is significant:**
  - **pH of the slurries ~ 11**
  - **PZC of gibbsite ~ 5**
  - **(higher surface potential)**

$$N_{SR} = \frac{\mu a^2 \dot{\gamma}}{\varepsilon \xi^2} \leq O(1)$$

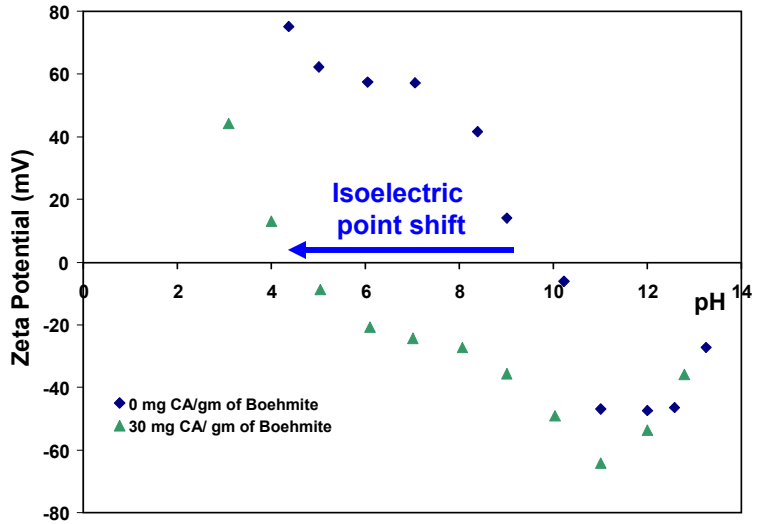
(Shear-repulsion number)

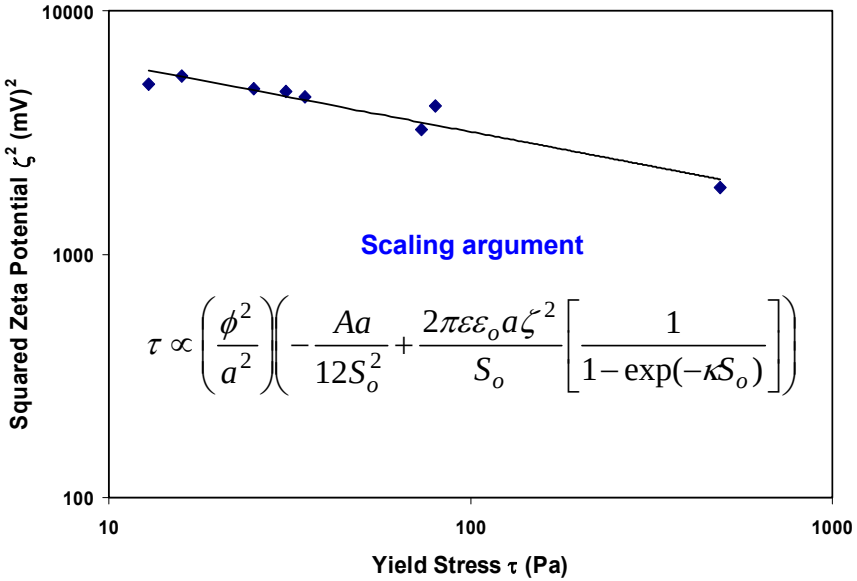
Pacific Northwest NATIONAL LABORATORY

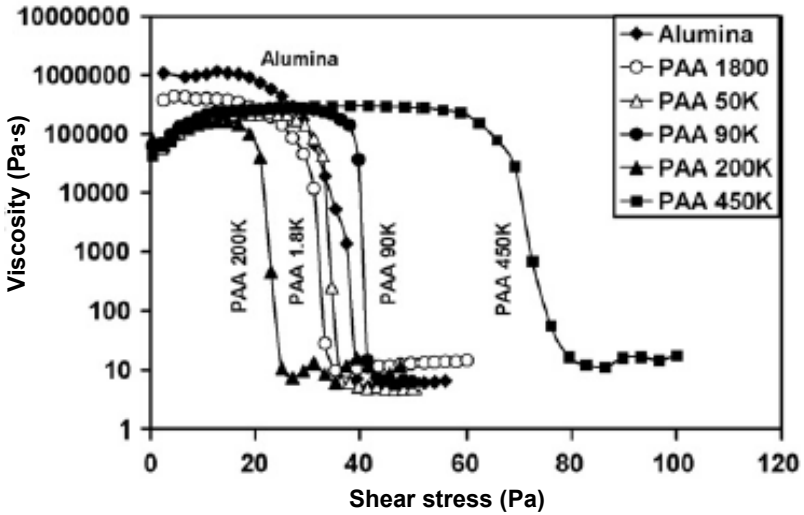
Print Close

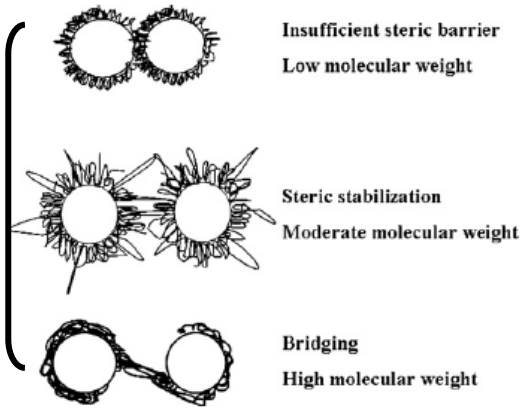
UW Contribution (Berg group, Dept. of ChemE) - Detailed understanding on working mechanism

Detailed understanding of PAA and CA rheological modifiers on a simple but reasonable system (~ 35 wt% alumina with high pH and high salt conc.)









Pacific Northwest NATIONAL LABORATORY

Print Close

Summary

- Weak acids are typically more efficient rheological modifiers than nonionic/polymer surfactants.
- Overall, citric acid and polyacrylic acid are the two most promising candidates (~ up to 70% decrease in yield stress) as rheological modifiers for the nuclear waste simulant slurry tested at PNNL .
- A "qualitative" understanding can be obtained by considering electrostatic interaction and specific interaction between the metal oxides and weak acid rheological modifiers.
- Overall, citric acid and polyacrylic acid are effective for five different SRNL melter feed simulants, and Grace ADVA class rheological modifiers are also effective.
- Particle size distribution appears to be important for modifier efficiency based on LAW simulant testing.
- Studies were recently published in *Journal of Colloid and Interface Science* (PNNL/SRNL) and *Colloids and Surfaces A* (UW). Additionally, the results were presented at four national conferences.

Pacific Northwest
NATIONAL LABORATORY

Acknowledgements and Future Work

Acknowledgements

- Adam Poloski (DNFSB)
- Carolyn Burns, Richard Daniel, Elizabeth Golovich, Maria Luna, Tak Keun Oh, Don Rinehart, and Michael Schweiger (PNNL)
- Paul Bredt and Reid Peterson (PNNL)
- U.S. Department of Energy's Office of Technology Innovation and Development (EM-30)

Future Work

- Testing with three different groups of actual wastes
- More detailed analysis and better qualitative and quantitative understanding of rheological modification
- Apply our understanding to other related problems/tasks

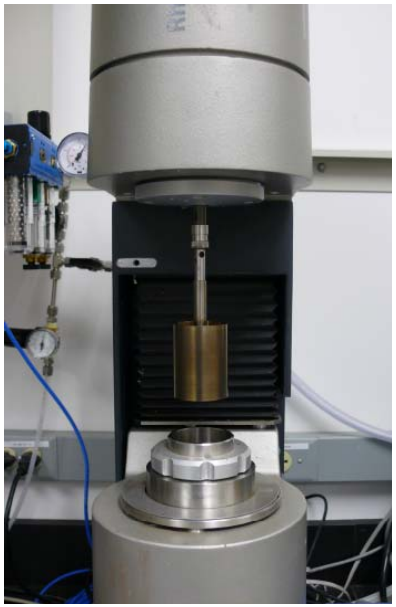
Pacific Northwest
NATIONAL LABORATORY

Questions ?

Pacific Northwest
NATIONAL LABORATORY

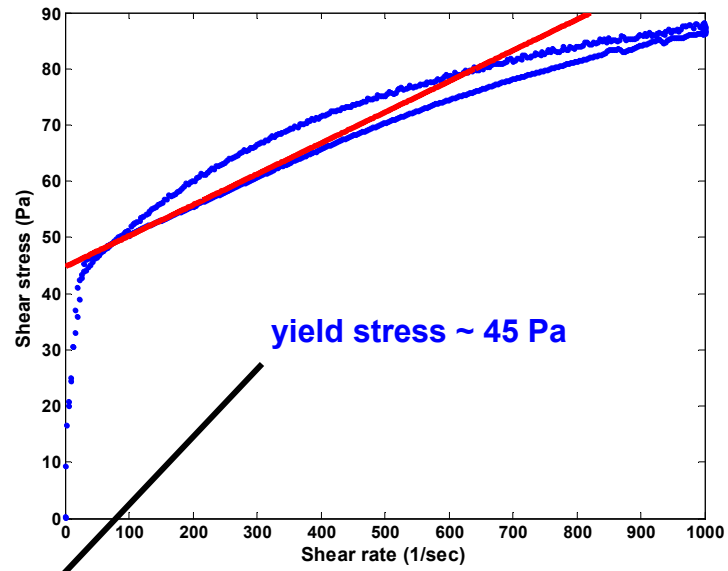
Rheological measurements

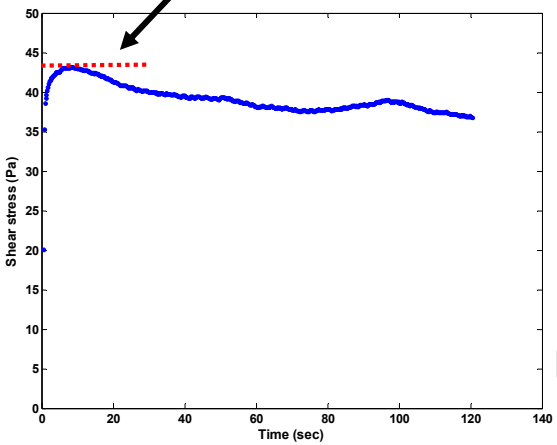
Flow curve measurements using Haake RS-600 and Anton Paar MCR 301 rheometers (concentric cylinder)



Haake RS-600

Anton Paar MCR 301





stress response (vane/cup), 43.16 Pa at 0.03 sec^{-1} : No significant slip effect

Relative change in yield stress (%)

$$= \left(\frac{\tau_y^{\text{with R.M.}} - \tau_y^{\text{control}}}{\tau_y^{\text{control}}} \right) \times 100$$

Pacific Northwest NATIONAL LABORATORY

Print

Close