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Rheology Modifiers – Historical Aspect on Actual and Simulants

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Definition Rheology – Modifiers

- What is Rheology? It is the science of deformation and flow.[1]
  - Under flowing conditions (mixing, pipe flow, gravity flow)
  - Under stagnant conditions (settled solids shear stress)

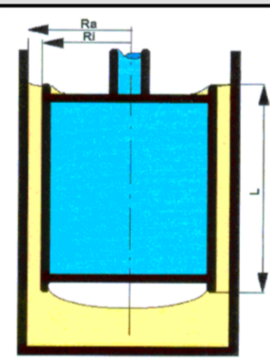
- What are Rheology Modifiers? It adjusts the flow (rheological) behavior.
  - Have been used for flowing conditions at DOE
    - *mixing*
    - *Transport*
    - *Flowability*
    - *Settling (not a flowing system)*

[1] Mezger, T. G., "The Rheology Handbook", 2nd Edition,2006

- The rheological properties are obtained using a bench scale rheometer, were a small samples can be analyzed.
- Typical measuring geometry is the concentric cylinder, gap between cup and rotor determined by particle size in the slurry (solids + liquid).
- Rheometer used to measure flow curve by increasing/decreasing shear rate and measuring shear stress response.

Rheometer

MV2 Rotor

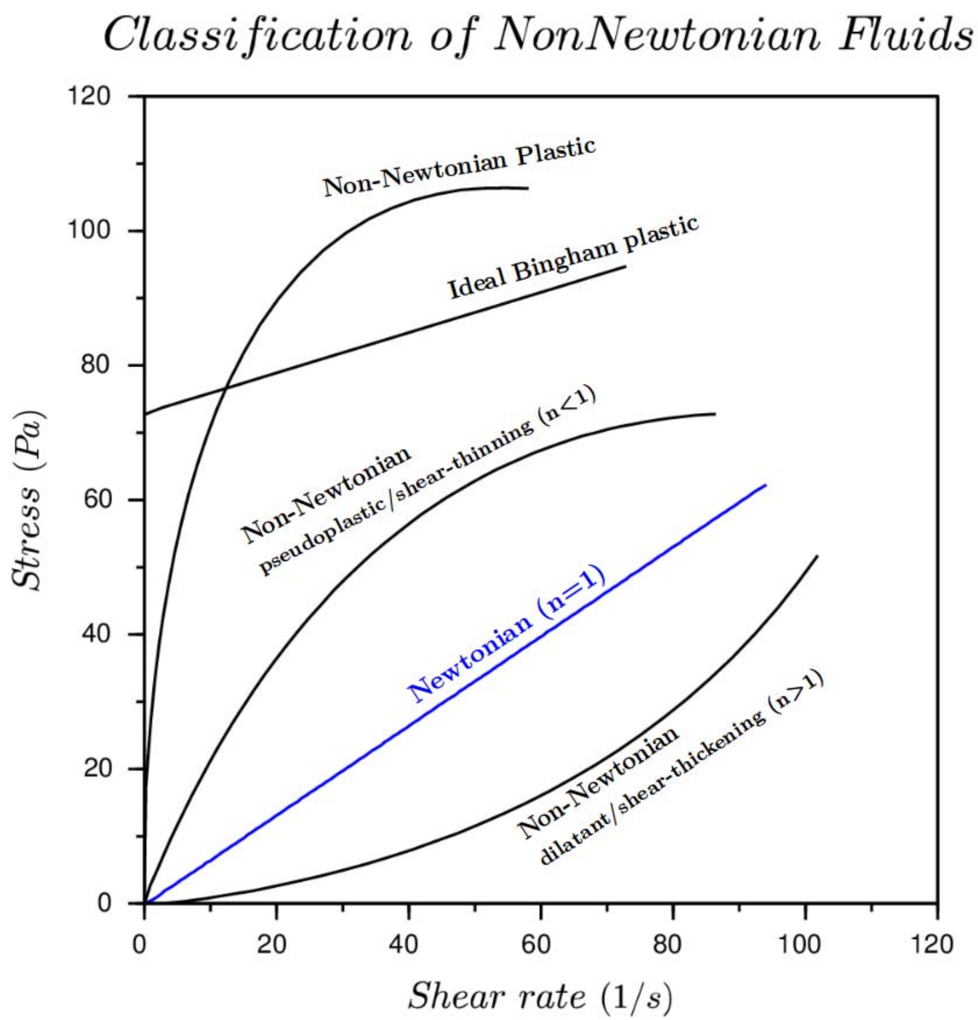


Dimensions and Flow Curve Program

Rotor radius (mm)	$R_i = 18.40$
Cup Radius (mm)	$R_a = 21.0$
Height of rotor (mm)	L = 60
Sample Volume (cm^3)	50
A factor (Pa/(N·cm))	76.8
M factor (min/sec)	0.900
Shear rate range (s^{-1})	0 – 300
Ramp up time (seconds)	210
Hold time (seconds)	30
Ramp down time (seconds)	210

Typical Measuring Geometry

- Typical flow curve obtained using rheometer.
- Most slurries analyzed by DOE have been classified as non-Newtonian fluids based on flow curve. A non-Newtonian fluid does not have a linear response, such as a Newtonian fluid (see blue line).
- The non-Newtonian fluids have typically been modelled as a Bingham Plastic fluid.
  - $\tau = \tau_o + \mu_\infty \cdot \dot{\gamma}$
    - τ = *measured shear stress (Pa)*
    - $\dot{\gamma}$ = *measured shear rate (1/sec)*
    - μ = *viscosity (Pa-sec)*
    - τ_o = *Bingham Plastic Yield Stress (Pa)*
    - μ_∞ = *infinite viscosity (Pa-sec)*



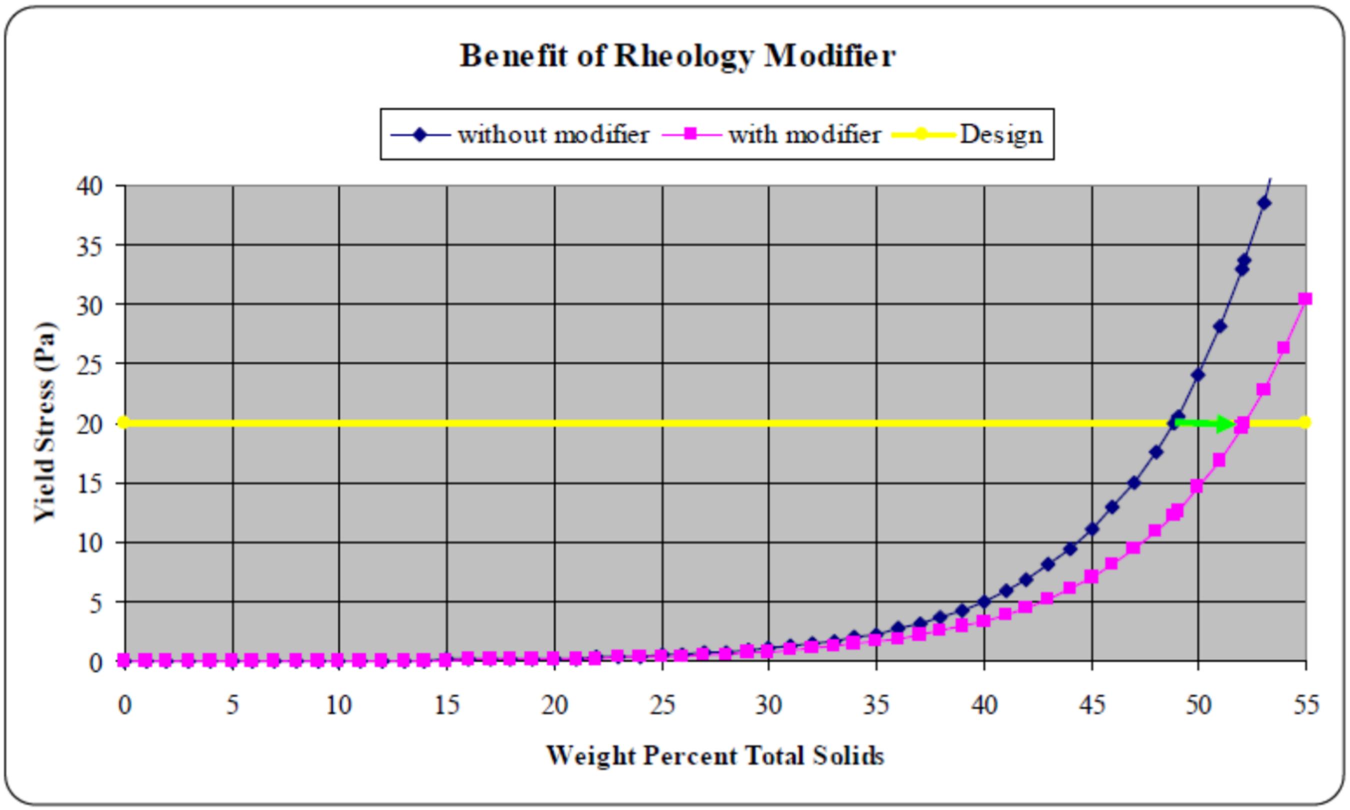
Typical Flow Curves

Rheology – Modifiers

- What types of rheology modifiers have been studied:
  - Inorganic
    - *Clays (including specialty)*
    - *Fumed silicas*
    - *Physical (changing properties of the materials)*
    - *Acids*
  - Organic
    - *Acids*
    - *Complex organics*
- Rheology modifier addition to stream:
  - Typically 1000 to 20000 ppm
  - If physical, can be much larger

Rheology – Modifiers - Expectation

- Rheology modifier have been used to reduce the rheological properties in the DOE complex. The objectives (directly or indirectly) of the modifiers have been used to allow for processing at higher solids content or to allow for materials to flow prior to setting. Below is a condition to increase solids content.



Rheology – Modifiers – Simulant -

- Waste Stream
  - non-Radioactive Simulant for testing was based on WVDP-185[2, 3].
    - *Complex simulant made at 15 – 17 wt% total solids*
    - *Simulant concentrated via boiling by 40, 50 and 60 volume percent reduction.*
    - *50 volume percent determined point for comparing effect of rheology modifier*

Chemicals	mass fraction	Chemicals	mass fraction
Ferric hydroxide	0.71026	Zinc oxide	0.00012
Boron oxide	0.00037	Sodium molybdate	0.00034
Barium hydroxide	0.00198	strontium hydroxide	0.00015
Cerium hydroxide	0.00241	Silicon dioxide	0.01971
Cesium hydroxide	0.00058	Aluminum hydroxide	0.00825
Copper hydroxide	0.00037	Calcium carbonate	0.00311
Lanthanum oxide	0.00024	Potassium hydroxide	0.02896
Magnesium hydroxide	0.00015	Sodium hydroxide	0.00755
Manganese dioxide	0.00426	Monosodium phosphate	0.01237
Neodymium oxide	0.00110	Sodium nitrate	0.02004
Nickel hydroxide	0.00189	Sodium nitrite	0.01553
Palladium oxide	0.00018	Zirconyl nitrate solution	0.06621
Rhodium oxide	0.00012	Titanium dioxide	0.00204
Ruthenum oxide	0.00049	Zeolite IE-96	0.08872
Sodium sulphate	0.00250		

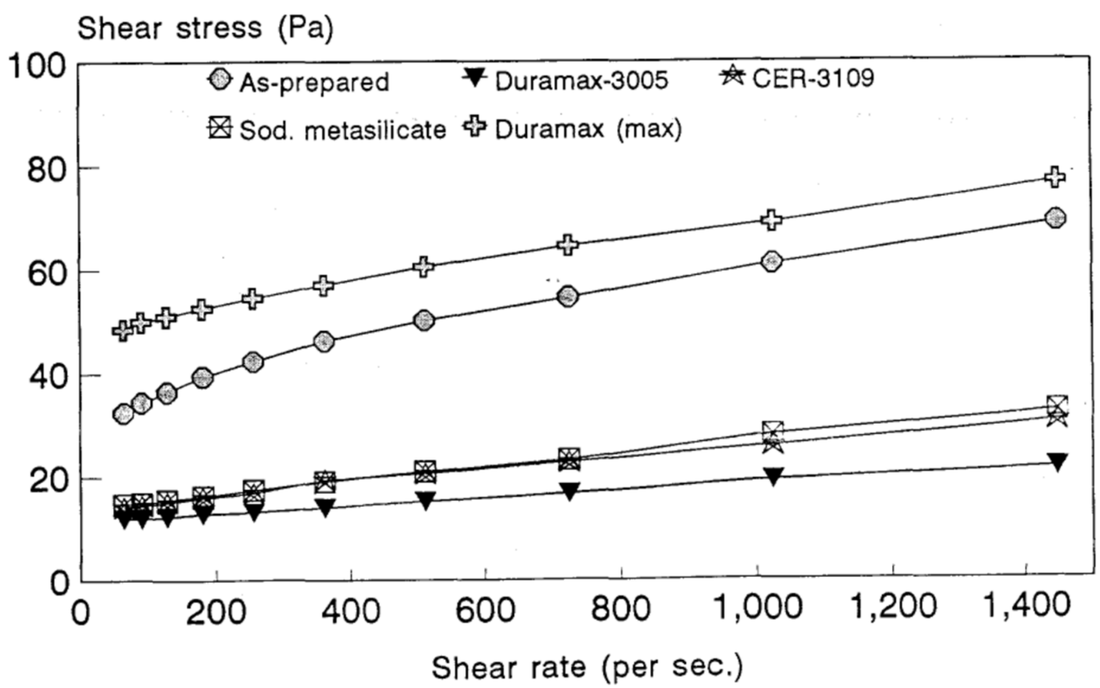
WV Complex Waste Simulant

[2] "Waste Form Compliance Plan for the West Valley Demonstration Project High-Level Waste Form", WVDP-185, Rev. 8, 1995

[3] Firstenberg, K, and et al., "The Role of Deflocculants During Concentration of the Simulated High-Level Radioactives Wastes",

Rheology – Modifiers – West Valley - 2

- Modifiers added to waste simulant, concentration and volume reduced via boiling, [3]
  - Sodium metasilicate (inorganic), 1000 ppm, 50 vol.%
  - Duramax-3005, acrylic emulsion polymers (organic) , 1000 ppm, 50 vol.%
  - CER-3019, acrylic emulsion polymers (organic) , 1000 ppm, 50 and 60 vol.%
  - 70 wt% nitric acid, 80 mL added to 600 mL, 50 vol.%
  - Performance compared on apparent viscosity at shear rate of 256 sec^{-1}
- Recommended and used Sodium Metasilicate[3], modified flowsheet
- Reduced mixing and pumping power requirements, allowed feeding of the melter.



Flow Curves

Waste Simulant	Volume Reduction (%)	Viscosity (cP) (@256 /sec.)	Total Solids (%)
As-prepared	0	177	16.1
	40	177	21.2
	50	181	24.0
	60	542	29.7
With HNO_3	50	46	39.0
With Duramax-3005	50	51	29.4
	60	211	33.7
With Sodium Metasilicate	50	65	29.6
With CER-3019	50	65	29.6

Results

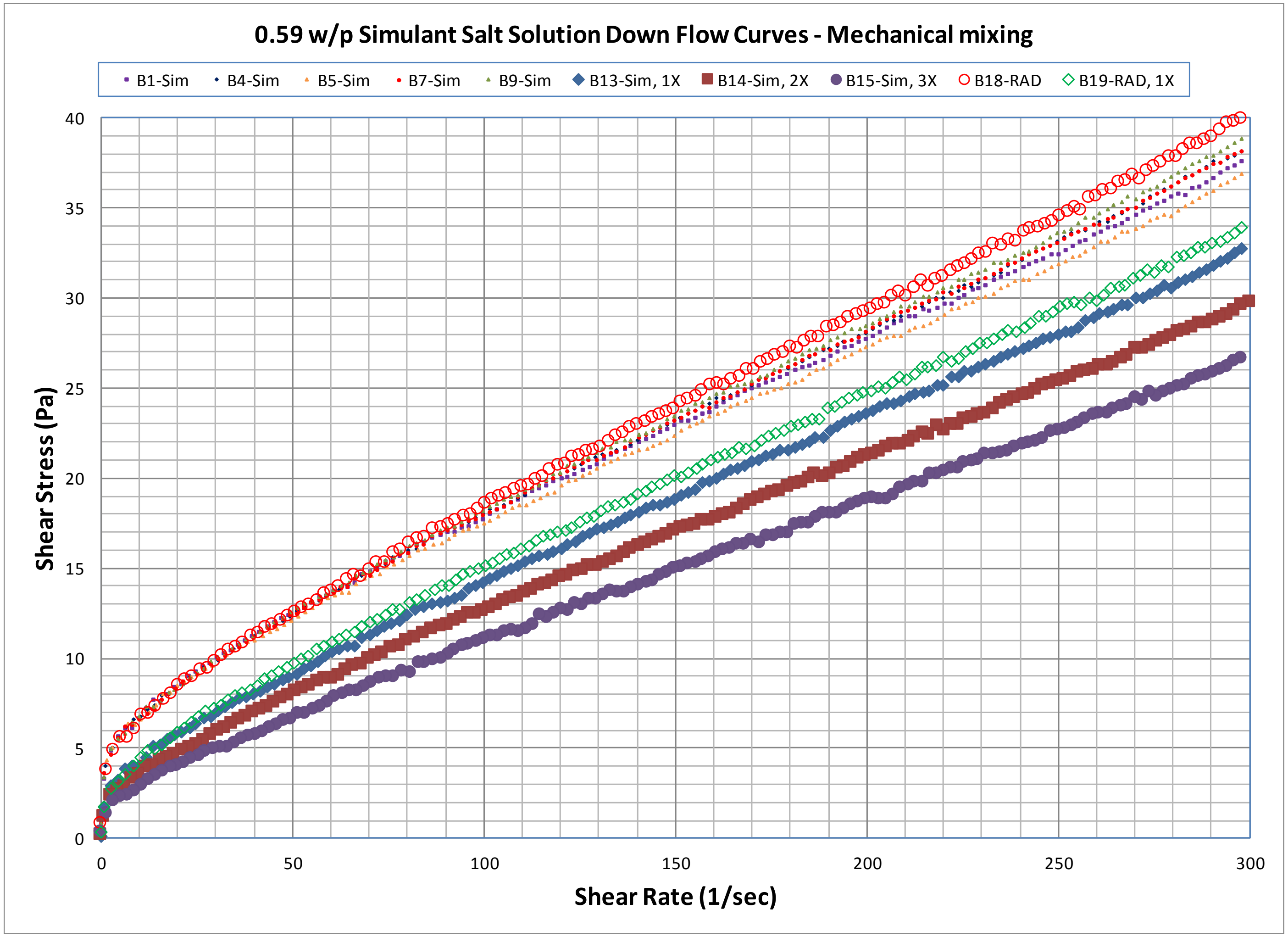
Rheology – Modifiers – Saltstone Facility

- Salt solutions[4]
  - Decontaiminated Tank 50 salt solution
  - Simulant developed based on characterization of Tank 50
- Salt solutions are mixed with dry premix (45 wt% Flyash, 45 wt% slag, 10 wt% cement) at a water to premix ratio of 0.59.
- Simulant was developed to determine uncertainty in mixing/rheological measurements due to single point measurements of actual waste.
- Property important to saltstone is the gel time, which impacts the ability of the grout to flow in the Saltstone vaults.
- Duratard 17 is a concrete Type B and D set retarder/water reducer admixture. Used in Saltstone to extend gel time. Is considered an organic modifier.
- First characterization of the impact of Duratard 17 on rheology properties.
- Duratard 17 added at a dosing rate of 0.00075 grams (750 PPM) per gram of premix, considered 1X. Based on dry premix mass.
- Flowcurves were analyzed as Bingham Plastics.

[4] Hansen, E.K., Cozzi, A.D., and Edwards, T. B., “Physical Property Measurements of Laboratory Prepared Saltstone Grouts”, SRNL-STI-2014-00169, May 2014

Rheology – Modifiers – Saltstone Facility

- Grouts without admixtures were slightly thixotropic
- Down curve results provided below.



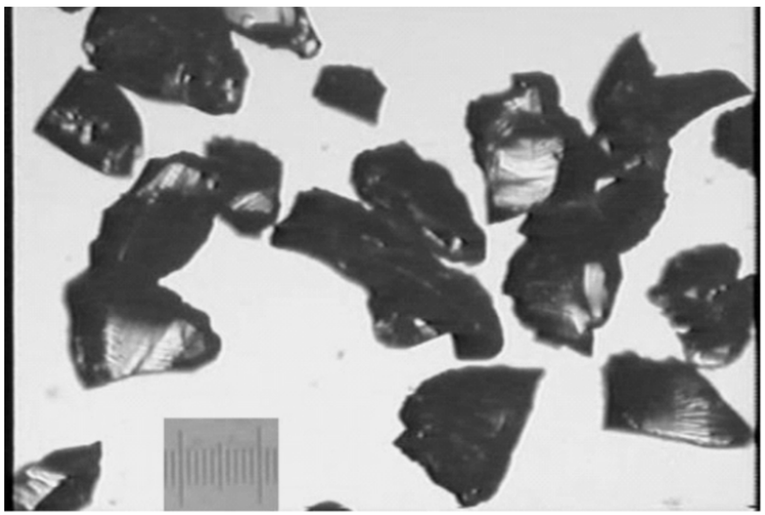
Rheology – Modifiers – Saltstone Facility

- Downcurve results are provided below.
- Admixture (Daratard 17) impacts Plastic Viscosity and Bingham Plastic yield stress, reducing these parameters as admixture concentration increases.
- Simulant and rad waste results are similar.
- Results show grout will be easier to pump and can be pumped further as the Daratard 17 dose is increased.
- Gel time increases, allowing grout to flow further in the vaults.

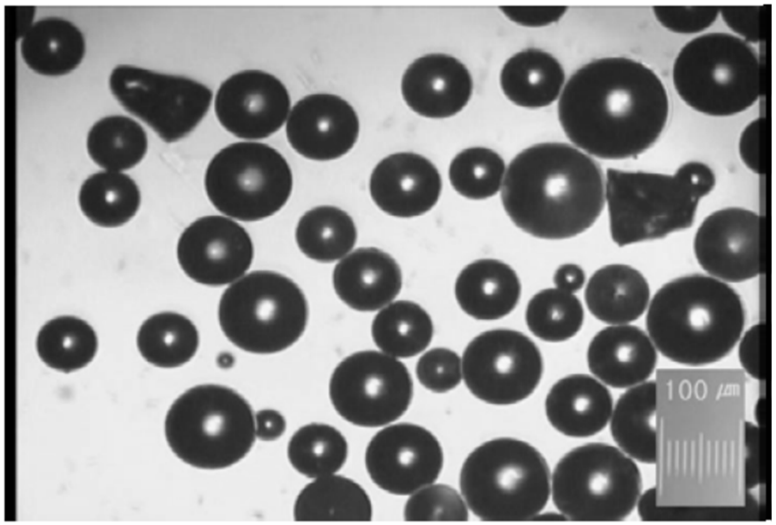
Mix	Density (g/mL)	Gel Time (min)	% Bleed	admixture addition	Plastic Viscosity (cP)	BP Yield Stress (Pa)
B1-Sim	1.731	10.0	0	0	99.9	7.75
B3-Sim	1.720	4.8	0	0	102.7	7.57
B5-Sim	1.723	5.0	0	0	97.8	7.58
B7-Sim	1.715	4.8	0	0	102.9	7.55
B9-Sim	1.716	5.0	0	0	104.6	7.57
B13-Sim	1.730	8.8	0	1X	93.6	4.73
B14-Sim	1.719	8.8	0	2X	85.9	3.94
B15-Sim	1.720	17.5	0	3X	79.1	2.91
B18-Rad	n/m	7.5	0	0	110.5	7.04
B19-Rad	n/m	8.5	0	1X	96.8	5.20
	n/m = not measured					

Rheology – Modifiers – DWPF – Simulant – Physical Modifier

- Simulant testing on SB3 SRAT/SME product.[5]
- Total replacement of FRIT with beaded FRIT.
- Beads were produced by spherizing FRIT using a flame former device.



As-received Frit

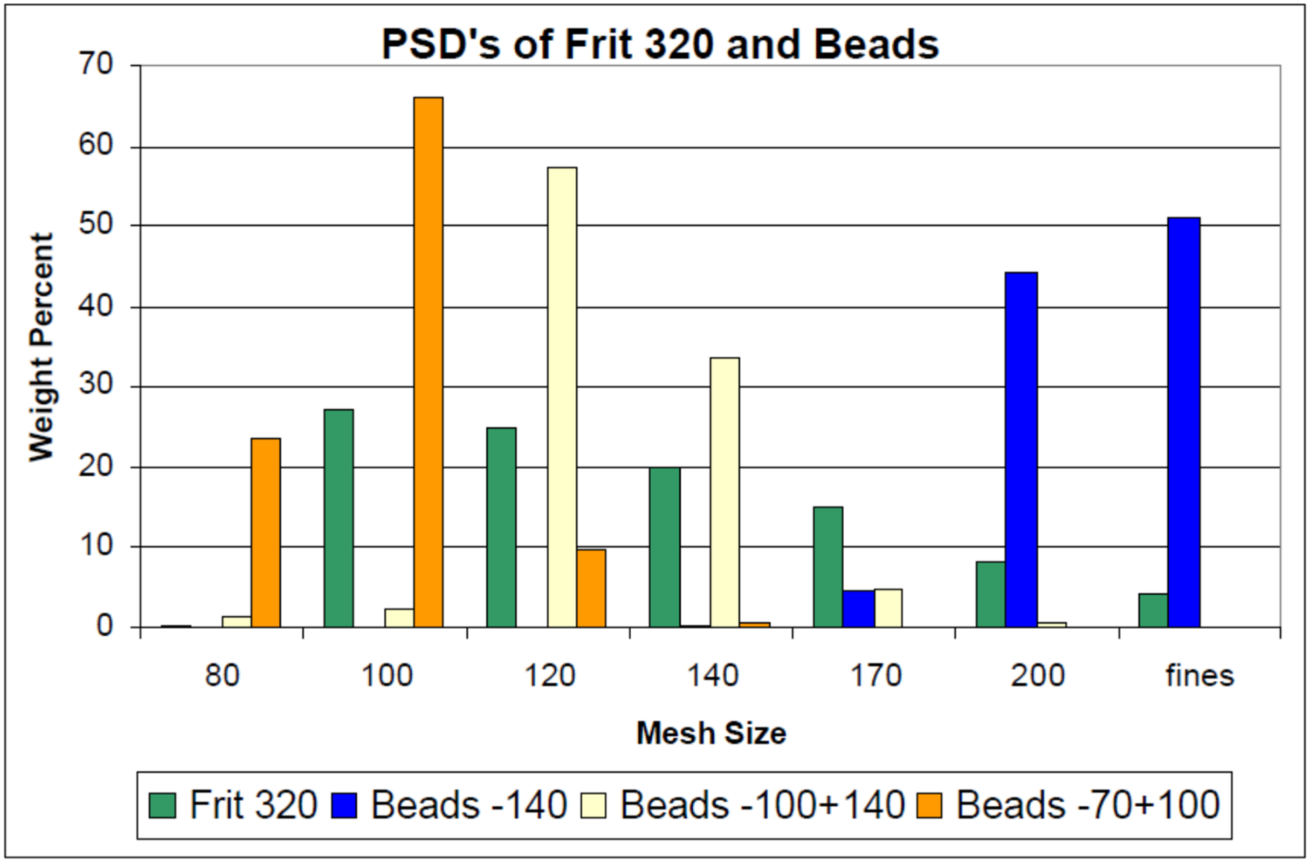


Bead Frit

[5] Smith, M.E., Stone, M.E., and Miller, D. H., "Impact of Spherical Frit Beads on Simulated DWPF Slurries", WSRC-TR-2005-00418, September 2005

Rheology – Modifiers – DWPF – Simulant – Physical Modifier

- Size of beads used in full replacement of FRIT



Composition of beads tested

- Resulting flow curves analyzed as Bingham Plastic, upcurve only.
- Reports also invested erosion and transport.

Rheology – Modifiers – DWPF – Simulant – Physical Modifier

- Results
  - 40% Waste Loading, SB3
    - *Difference between Frit and Beads, though not as much when comparing the different size beads.*

Frit/Bead (Sample ID)	Yield Stress (Pa)	Consistency (cP)	* % Reduction in Yield Stress /Consistency
Frit 320 (Bead-0015)	3.26	20.53	N.A.
-140 Bead (Bead-0016)	2.64	16.05	23 / 28
-100+140 Bead (Bead-0017)	2.51	15.27	30 / 34
-70+100 Bead (Bead -0018)	2.61	12.88	25 / 59

* Relative to Frit 320 SME product

  - 45% and 52% Waste Loading SB3

	Beads		Frit	
Up Curve	45%	52%	45%	52%
Yield Stress (Pa)	14.7	34.0	13.2	41.1
Consistency (cP)	18.9	48.2	27.3	52.2

  - Reduction of yield stress would permit increasing solids content and increasing throughput
  - Control of pumping an issue when flowrate reduced to region where sliding or fixed bed occurs in scaled transfer line.

Rheology – Modifiers – SRS Tank Farm - Settling

- Tank 51 SB4 settled slower and to a higher settled volume, impacting throughput.
- Investigated GE flocculants (organic)
  - Polyfloc AP1110, AP1120, and AP1138
  - KlarAid PC1192
- Targeted 320 ppm in SB4 sludge simulant
- Results show flocculants were not effective.
  - Not implemented
  - If implemented
    - *Downstream effects*
    - *Recycle*

Settled Solids Height (inches)					
Run Time	05-SB4-00546	05-SB4-00547	05-SB4-00548	05-SB4-00549	05-SB4-00550
Hours	Baseline	Polyfloc AP1110	Polyfloc AP1120	Polyfloc AP1138	KlarAid PC1192
0	2.5	2.69	2.69	2.69	2.69
17	2.44	2.69	2.69	2.63	2.56
41	2.25	2.56	2.56	2.50	2.31
113	2.19	2.44	2.44	2.44	2.19
137	2.13	2.44	2.44	2.38	2.13
167	2.13	2.44	2.44	2.38	2.13

[6] Stone, M.E., "Evaluation of GE Flocculant Test Kit with SB4 Simulant", SRNL-ITS-2005-00299, December 2005

Rheology – Modifiers – SRS/Hanford simulated HLW waste streams

- SRNL-STI-2013-00493 summaries the impact of rheology modifiers on simulated based on the following documents [7]:
  - Herman, C. C., et al., "*Preliminary Assessment of the Hanford Tank Waste Feed Acceptance and Product Qualification Programs",* SRNL-STI-2012-00776/PNNL-22116, 2013
  - Hansen, E. K., "*Summary of 2009 Rheology Modifier Program",* SRNL-STI-2009-00697, 2009
  - Hansen, E. K., "*2011 EM/SRNL Rheology Modifiers Summary Report",* SRNL-STI-2011- 00670, 2011
  - Kay, E. D., and et al., "Rheology Modifiers for Radioactive Waste Slurries", WSRC-MS-2003-00136, July 2003
  - Stone, M. E, Marinik, A. R. and Marsh, D. M., "*Rheological Modifier Testing with DWPF Process Slurries",* WSRC-TR-2004-00082, 2004.
  - Chun, J. Poloski, A. P. Hansen, E. K., "*Stabilization and control of rheological properties of Fe2O3/Al(OH)3-rich colloidal slurries under high ionic strength and pH*", *Journal of Colloid and Interface Science* 2010, 348, 280-288
  - Stone, M.E., "*Summary of Rheological Modifier Testing on RPP Simulants*", SRNL-GPD-2004-00040, 2005
- Modifiers tested on:
  - SRS, HLW melter feed (HLW sludge plus FRIT) and HLW sludge
  - Hanford, HLW sludge

[7] Pareizs, J.M., "Review of Rheology Modifiers for Hanford Waste", SRNL-STI-2013-00493, September 2013

Rheology – Modifiers – SRS/Hanford simulated waste streams

- Modifiers were tested to assess their ability to reduce the Bingham Plastic yield stress
  - Reduce water content
  - Increase throughput when using melter, more energy applied to solids rather than to boiling.
- Modifiers have been used in other industries, such as concrete and oil.
- Modifiers include antifoams.
- SRS moving towards glycolic acid flowsheet, well in excess of what was tested.
- Water is a modifier, but is excluded, given water management issues.
- 31 different modifiers tested:
  - 500 to 16,000 PPM

ADVA Cast 555	Dolapix PC75
ADVA Flex	Duramax 3005
Alcosperse 149	EDAPLAN 470
Alcosperse 240	Glycolic Acid Solution
Alcosperse 408	Phenylboric Acid
Alcosperse 725	Polyacrylic Acid - 1800 MW
Antifoam 747	Polyacrylic Acid - 2000 MW
Citric Acid	Polyacrylic Acid - 5000 MW
CTAB	Pomosperse AL36
Cytec P35	Recover®
Cytec P70	Sodium Metasilicate
Darvan C	Sodium Polyphosphate
Disperse-Ayd W-22	Sodium Polyphosphate tetrabasic
Disperse-Ayd W-28	Sugar
Dolapix A88	Taylor Antifoam 747
Dolapix CE64	

Rheology – Modifiers – SRS/Hanford simulated waste streams

- Results where reduction was greater than 10%

Modifier	Description	DWPF Simulated SRAT Product	DWPF Simulated Melter Feed	Hanford Simulated Waste	PPM applied	Yield Stress reduction
ADVA Cast 555	organic mixture a	Not Evaluated	X	Not evaluated	1,000 to 16,000	> 50%, 10,000 ppm
ADVA Flex	proprietary polycarboxylate	Not Evaluated	X	Not evaluate	1,000 to 16,000	> 50%, 10,000 ppm
Alcosperse 149	sodium polyacrylate	Not Evaluated	Not Evaluated	X	1000	8 test, one <2%, seven 14 to 37%
Alcosperse 240	proprietary polyacrylate	Not Evaluated	Not Evaluated	X		
Alcosperse 408	proprietary polyacrylate	Not Evaluated	Not Evaluated	X		
Alcosperse 725	proprietary polyacrylate	Not Evaluated	Not Evaluated	X		
Citric Acid	citric acid	Not Evaluated	X	X	1,000 to 16,000	SRS: 4,000 to 16,000 ppm, Hanford: >30% on 1000 ppm, >70% on 5000 ppm
Cytec P35	proprietary polyacrylate	Not Evaluated	Not Evaluated	X	1,000	4 to 30%
Cytec P70	proprietary polyacrylate	Not Evaluated	Not Evaluated	X		
Disperse-Ayd W-28	proprietary polyacrylate	X	X	Yield stress increased	500 to 9,000	SRS: > 10%, Hanford, see comment
Dolapix A88	organic mixture	Not Evaluated	X	Not evaluated	800 to 10,000	Only 2 of the 10 showed decrease >10%
Dolapix CE64	proprietary polyacrylate	X	X	X	600 to 16,000	2/3rd of sample >10%
Dolapix PC75	synthetic polyelectrolyte	Not Evaluated	X	Not evaluated	1,000 to 16,000	8 of 12 samples >10%
Duramax 3005	polyglycol	Not Evaluated	Not Evaluated	X	1,000	>10%
Glycolic Acid Solution	glycolic acid	Not Evaluated	X	Not Evaluated	1,000 to 14,000	14 of 52 tests >10%
Polyacrylic Acid	polyacrylic acid	Not Evaluated	X	X	900 to 14,000	SRS: 161 of 188 show reduction, Hanford: >50% on 5000 ppm
Pomosperse AL36	proprietary polyacrylate	Not Evaluated	Not Evaluated	X	1000	> 9%
Recover®	organic mixture b	Not Evaluated	X	Not Evaluated	1,000 to 16,000	33 of 76 test > 10%
Sodium Metasilicate	crystallized silicate	Not Evaluated	X	Not Evaluated	1,000 to 10,000	3 of 4 tests > 10%
Sodium Polyphosphate	phosphate polymer	Not Evaluated	X	X	1,000 to 10,000	SRS: not effective, Hanford: 2 of 3 > 10%
Sugar	glucose	Not Evaluated	X	Not Evaluated	1,000 to 10,000	2 of 4 > 10%

Rheology – Modifiers – SRS/Hanford simulated waste streams

- SRS testing glycolic flowsheet.
- Recommended modifiers for future studies for Hanford sludges
  - Citric acid
  - Polyacrylic acid
- Modifiers impact that will need to be assessed:
  - Blending of glass former chemicals with sludge
  - Glass Redox
  - Recycle stream
  - Hydrogen generation
  - Testing on radioactive samples