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Rheology Enhancement for Remediated PX6 Melter Feed

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Introduction

IDMS PX6 was remediated by adding 30 wt% aluminum nitrate ($Al(NO_3)_3$) solution to the PX6 melter feed to achieve an amount of aluminum equivalent to 0.87 g. per 100 g. melter feed. This is equivalent to adding 1.64 g. of Al2O3 per 100 g. of melter feed. The remediation corrected the deficiency of aluminum in the feed, but as a side-effect reduced the pH and insoluble solids concentration, rendering the rheological properties of the feed unsuitable for maintaining frit suspension. The aluminum nitrate addition also rendered the feed highly oxidizing, with the parameter F-N (formate minus nitrate) currently estimated to be -1.9 in the remediated IDMS feed material.

We recommend a chemical addition of 1.89 ml 50 wt% caustic (NaOH) solution per kilogram of IDMS PX6 melter feed to enhance the rheological properties of the material for suspending frit. We also recommend that the IDMS melter feed tank contents be sampled after the caustic treatment to confirm the chemical composition will produce acceptable glass and to characterize the solids concentration, pH, and rheological properties of the material. This memorandum summarizes results of experimental work performed on the original IDMS PX6 melter feed, the remediated IDMS PX6 melter feed, and melter feeds produced in a laboratory simulation to duplicate the IDMS remediation as well as the experimental results on the caustic treatment to enhance the rheology. Characterization of the products of excess caustic addition and what steps to take if excess caustic is inadvertently added to the IDMS PX6 melter feed are also discussed.

Summary of Conclusions

The following are the main conclusions from this work:

1) The remediation of IDMS melter feed with 30 wt% aluminum nitrate solution caused the material to thin and the disappearance of a detectable yield stress.

2) Duplication of the remediation strategy in the laboratory produced the same shift in rheological properties of the IDMS PX6 feed.

3) Samples of the remediated IDMS PX6 feed and the material produced in the laboratory duplication of the aluminum nitrate remediation foam when shaken vigorously (high shear). The foam is relatively stable, taking about 30 minutes to disappear.

4) The rheological properties were restored by adding 1.89 ml 50 wt% caustic (NaOH) solution per kilogram of IDMS PX6 melter feed. This result was obtained in an initial test performed 9/12/94 and duplicated in a followup test performed 9/29/94. Analyses of glass samples prepared by vitrifying this sample in a crucible indicated the remediated IDMS PX6 melter feed will produce acceptable glass (within ± 5% of the PCCS targets). The caustic treatment did not change the tendency of the material to foam when shaken.

5) A slow formic acid denitration reaction is probably occurring in the remediated IDMS PX6 melter feed, as evidenced by a pungent odorous gas that vented when the sample container was opened to perform the duplicate caustic treatment.

6) Addition of 2.75 ml 50 wt% caustic (NaOH) solution per liter of IDMS PX6 melter feed caused the rheological properties to thicken excessively, indicating excessive caustic had been added. The yield stress of this material approached 250 dynes/cm^2.

7) The rheological properties after excess caustic addition were recoverable (thinned) by diluting the feed with water.

8) Addition of concentrated nitric acid produced shifts in the rheological properties of the IDMS PX6 feed similar to the remediation with aluminum nitrate solution.

Experimental

A sample of the original, unremediated IDMS PX6 melter feed was provided by W. G. Ramsey of the DWPT Glass Technology Group (GTG) for characterization and experimental use in duplicating the $Al(NO_3)_3$ remediation performed in the IDMS Melter Feed Tank. A sample of the remediated IDMS melter feed (ID-PX6-MFTR-7487) was provided by the DWPT Large Scale Experimentation Group (LSEG) for experimental use in developing methods to enhance the rheological properties. The materials were analyzed for pH and solids concentration. Rheological characterization of the materials was performed using a HAAKE Rotovisco RV20 rheometer. The RV20 utilizes the Searle method (concentric cylinders with inner cylinder rotating) to determine the rheological flow curve (shear stress versus shear rate plot) from torque measurements. Rheograms were obtained at 25 °C over a range of shear rates of from 0 - 350 sec^{-1} by increasing the shear rate from 0 to 350 sec^{-1} in 5 minutes, holding at 350 sec^{-1} for 0.1 minute, and decreasing the shear rate from 350 to 0 sec^{-1} in 5 minutes. The rheological

properties were modeled as Bingham fluids to allow comparisons between the various materials and with DWPF materials.

Results

Figure 1 depicts rheograms for three materials of interest: the unremediated IDMS PX6 melter feed (before aluminum nitrate treatment) sent to TNX by Ramsey, the remediated PX6 melter feed (post-aluminum nitrate treatment), and the remediated PX6 melter feed after the caustic treatment, which restored the rheological properties essentially to those of the unremediated starting material. More detailed results are as follows:

Unremediated IDMS PX6 Melter Feed: Figure 1 depicts the rheological flow curve obtained for the unremediated IDMS PX6 melter feed (before aluminum nitrate treatment) sent to TNX by Ramsey. The Bingham fluid parameters for the increasing shear rate curve are yield stress = 68.4 dynes/cm^2 and consistency = 21.7 cp. The unremediated feed was analyzed at 45.82 wt% total solids, 35.02 wt% insoluble solids, and pH = 8.27, all of which are typical of IDMS melter feeds produced with simulated sludge feed containing noble metals.

Remediated PX6 Melter Feed: Figure 1 depicts the rheological flow curve at 50 °C obtained 8/22/94 for sample ID-PX6-MFTR-7484, the remediated PX6 melter feed (post-aluminum nitrate treatment). The material behaves essentially like a Newtonian fluid, with no yield stress. The Bingham fluid parameters for the increasing shear rate curve reduce to viscosity = 10.5 cp and zero yield stress. These properties are not typical of IDMS melter feeds produced with noble metals in the simulated sludge feed.

Proper Caustic Adjustment of PX6 Melter Feed: Figure 1 depicts the rheological flow curve obtained for material produced by adding 0.8 ml of 50 wt% caustic to 422.4 g. of remediated ($Al(NO_3)_3$-treated) ID-PX6-MFTR-7487 melter feed on 9/12/94. The pH was determined to rise from 3.4 to 3.91 as a result of the caustic treatment. The Bingham fluid parameters are yield stress = 52.4 dynes/cm^2 and consistency = 40 cp. The caustic-treated feed was analyzed at 37.86 wt% total solids, 13.65 wt% insoluble solids, and pH = 3.94.

A followup test was performed 9/29/94 by adding 1.1 ml of 50 wt% caustic to 584.5 g. of remediated ($Al(NO_3)_3$-treated) ID-PX6-MFTR-7487 melter feed. A pungent gas vented from the container of remediated IDMS PX6 feed when it was opened to perform the duplicate caustic treatment. The gases were likely the result of a slow formic acid denitration reaction, which is also indicated from a reduction of the formate content of the to material from > 20,000 mg/L to about 2000 mg/L. The Bingham fluid parameters for the increasing shear rate curve were yield stress = 45.2 dynes/cm^2 and consistency = 43.8 cp, which agree with the parameters determined in the earlier test. The caustic-treated feed was analyzed at 47.58 wt% total solids and pH = 4.11. Analyses of glass samples prepared by vitrifying the remediated IDMS PX6 melter feed in a crucible are shown in Table 1. The results indicate the remediated IDMS PX6 melter feed will produce acceptable glass after the caustic treatment to modify the rheological properties. The primary frit elements (potassium, silicon, and boron) and primary waste oxides are within ± 5% of the PCCS targets.

Lab Simulation of IDMS PX6 Remediation: Figure 2 depicts the rheological flow curve at 25 °C of material produced in the laboratory to duplicate the remediation of the IDMS PX6 melter feed. The rheogram of the remediated IDMS PX6 feed is also shown, for comparison. The laboratory simulation was performed by adding 172 ml of the 30 wt%

aluminum nitrate solution used in the IDMS remediation to 500 ml of the unremediated IDMS PX6 feed sent to TNX by Ramsey. The material also behaves essentially like a Newtonian fluid, with no yield stress. The Bingham fluid parameters for the increasing shear rate curve reduce to viscosity = 8.85 cp and zero yield stress. The lab-remediated feed was analyzed at 38.02 wt% total solids, 15.35 wt% insoluble solids, and pH = 3.37.

Excess Caustic Adjustment of PX6 Melter Feed: Figure 3 depicts the rheological flow curve obtained for material produced by adding 0.55 ml of 50 wt% caustic to 200 ml of remediated ($Al(NO_3)_3$-treated) ID-PX6-MFTR-7487 melter feed. Immediately after the treatment, the pH was determined to be 4.68. The Bingham fluid parameters for the increasing shear rate curve are yield stress = 244 dynes/cm^2 and consistency = 25.5 cp. The excess caustic-treated feed was analyzed at 32.9 wt% total solids, 9.03 wt% insoluble solids, and pH = 4.17. The rheological parameters exceed the DWPF design bases.

Mitigating Excess Caustic Adjustment: Figure 3 also depicts the rheological flow curve obtained for material produced by adding 12.0 g. deionized water to 47.9 g. of the excess caustic-treated material prepared as described above. Immediately after the treatment, the pH was determined to be 4.68. The Bingham fluid parameters for the increasing shear rate curve are yield stress = 43.2 dynes/cm^2 and consistency = 50.6 cp. The diluted excess caustic-treated feed was analyzed at 26.7 wt% total solids, 8.17 wt% insoluble solids, and pH = 4.30.

Nitric Acid Remediation Tests: Figure 4 depicts rheograms of the unremediated IDMS PX6 melter feed after treatment with concentrated (70 wt%) nitric acid. Rheograms of the unremediated and remediated IDMS PX6 melter feeds are also shown for comparison. Addition of 20 ml of 70 wt% nitric acid to 678.3 g. of unremediated IDMS PX6 melter feed (29.5 ml/kg feed) reduced the rheological properties to yield stress = 25 dynes/cm^2 and consistency = 9 cp. In a followup test, addition of 43 ml of 70 wt% nitric acid to 693.0 g. of unremediated IDMS PX6 melter feed (62 ml/kg feed) reduced the rheological properties to zero yield stress and viscosity = 8.85 cp, indicating that nitric acid addition is capable of producing essentially the same shifts in the rheological characteristics as occurred in the aluminum nitrate remediation.

Quality Assurance

The experimental procedures and observations are recorded in laboratory notebooks WSRC-NB-93-35 assigned to J. C. Marek and WSRC-NB-90-131 assigned to R. E. Eibling. All samples were provided with a unique identifier to facilitate tracking and data basing of results. The accuracy of all analytical measurements was controlled with check standards that were controlled to within 5% of their nominal values. The analytical results are stored in the Laboratory Information Management System (LIMS) on the TNX VAX computer in 679-T.

Table 1. Analysis of Vitrified Sample After Caustic Treatment to Modify Rheology of Remediated IDMS PX6 Melter Feed

Element	Analytical Values, wt% ICP/MW	ICP/Na2O2	Average wt%	Target Values, wt%	% from Target
Al		2.708	2.708	2.765	-2.07
B		2.567	2.567	2.601	-1.30
Ba		0.069	0.069	0.069	0.06
Ca	0.596		0.596	0.591	0.83
Cr	0.068		0.068	0.089	-23.3
Cs					
Cu	0.194		0.194	0.177	9.41
Fe	6.650	6.730	6.690	6.768	-1.15
K	2.370		2.370	2.354	0.66
Li		2.193	2.193	2.354	-6.86
Mg	0.871	0.918	0.895	0.896	-0.22
Mn	1.320		1.320	1.300	1.51
Na	7.710		7.710	7.290	5.76
Ni	0.705		0.705	0.699	0.80
P	0.000		0.000	0.000	0.000
Pb	0.145		0.145	0.128	13.22
Si		23.50	23.50	24.46	-3.93
Sr	0.014		0.014	0.010	42.12
Ti	0.082	0.083	0.083	0.079	4.68
Zn	0.081		0.081	0.069	17.46
Zr	0.625		0.625	0.719	-13.09

Figure 1.
Rheograms of Unremediated, $Al(NO_3)_3$ Remediated, and Caustic-Treated Remediated IDMS PX6 Melter Feeds

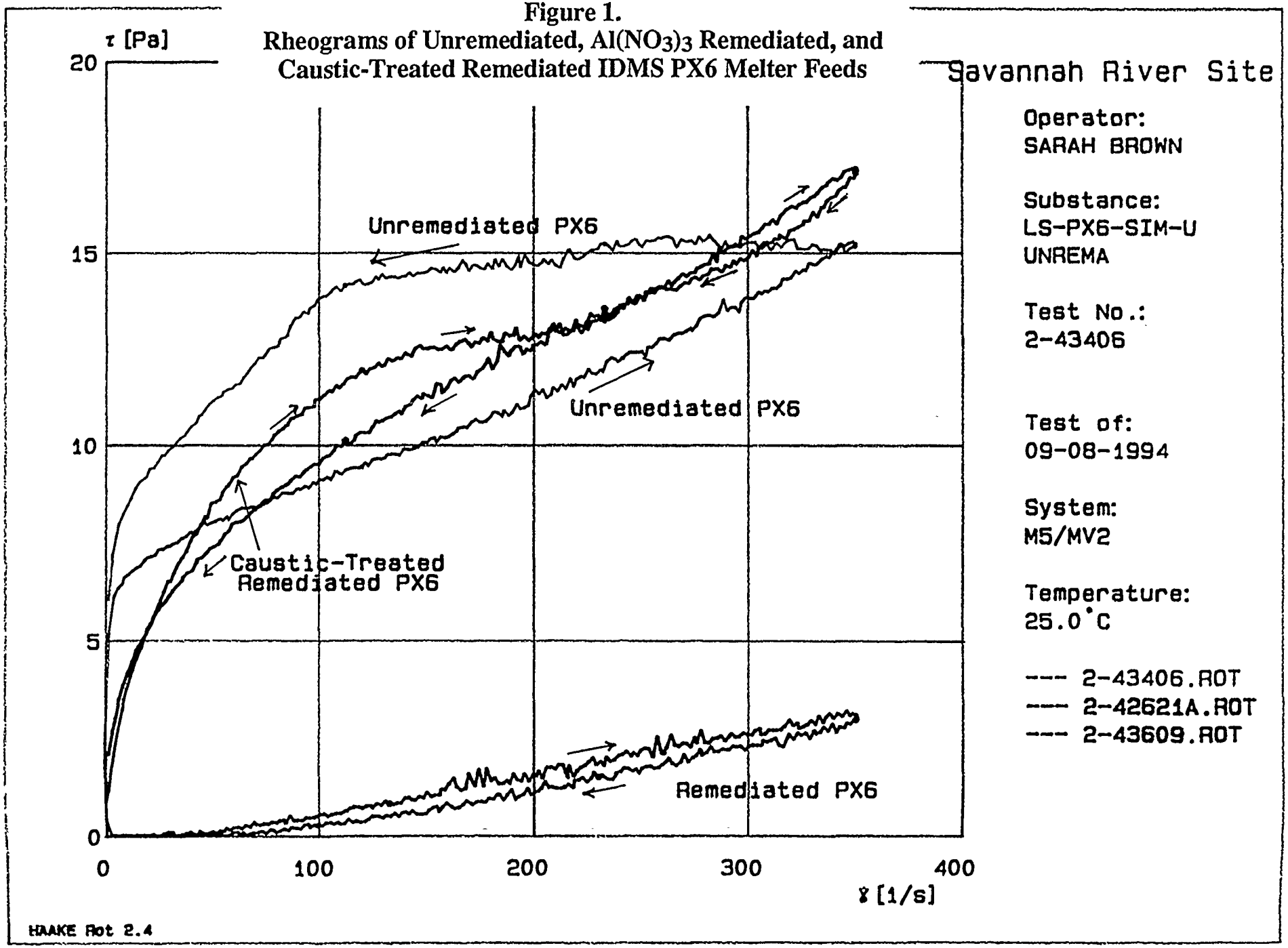

Figure 2.
Rheograms Comparing Remediated IDMS PX6 Melter Feed with Material Produced in Laboratory Simulation

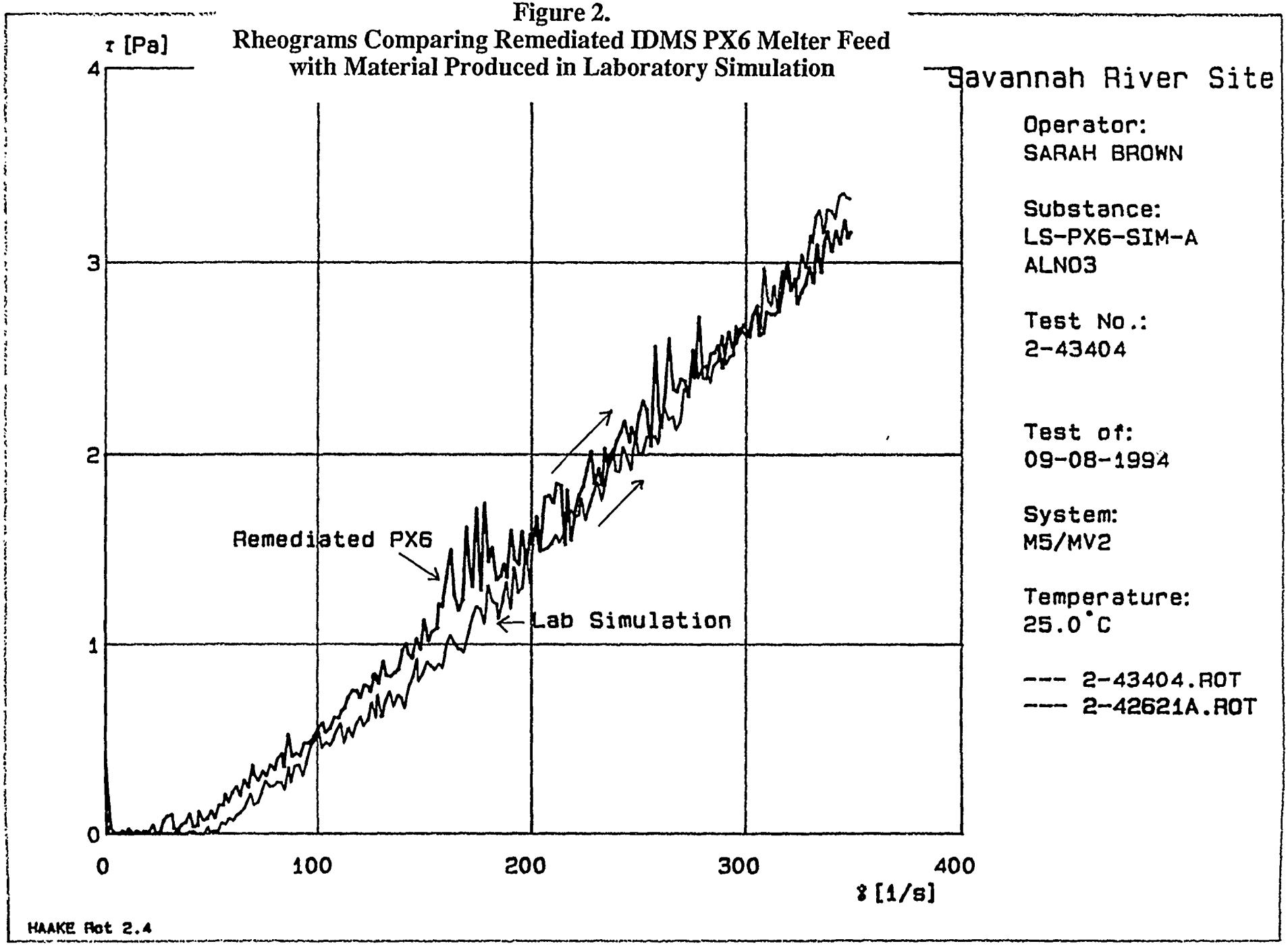

Figure 3.
Rheograms of Remediated IMDS PX6 Melter Feed
Treated with Excess Caustic and Subsequently Diluted with Water

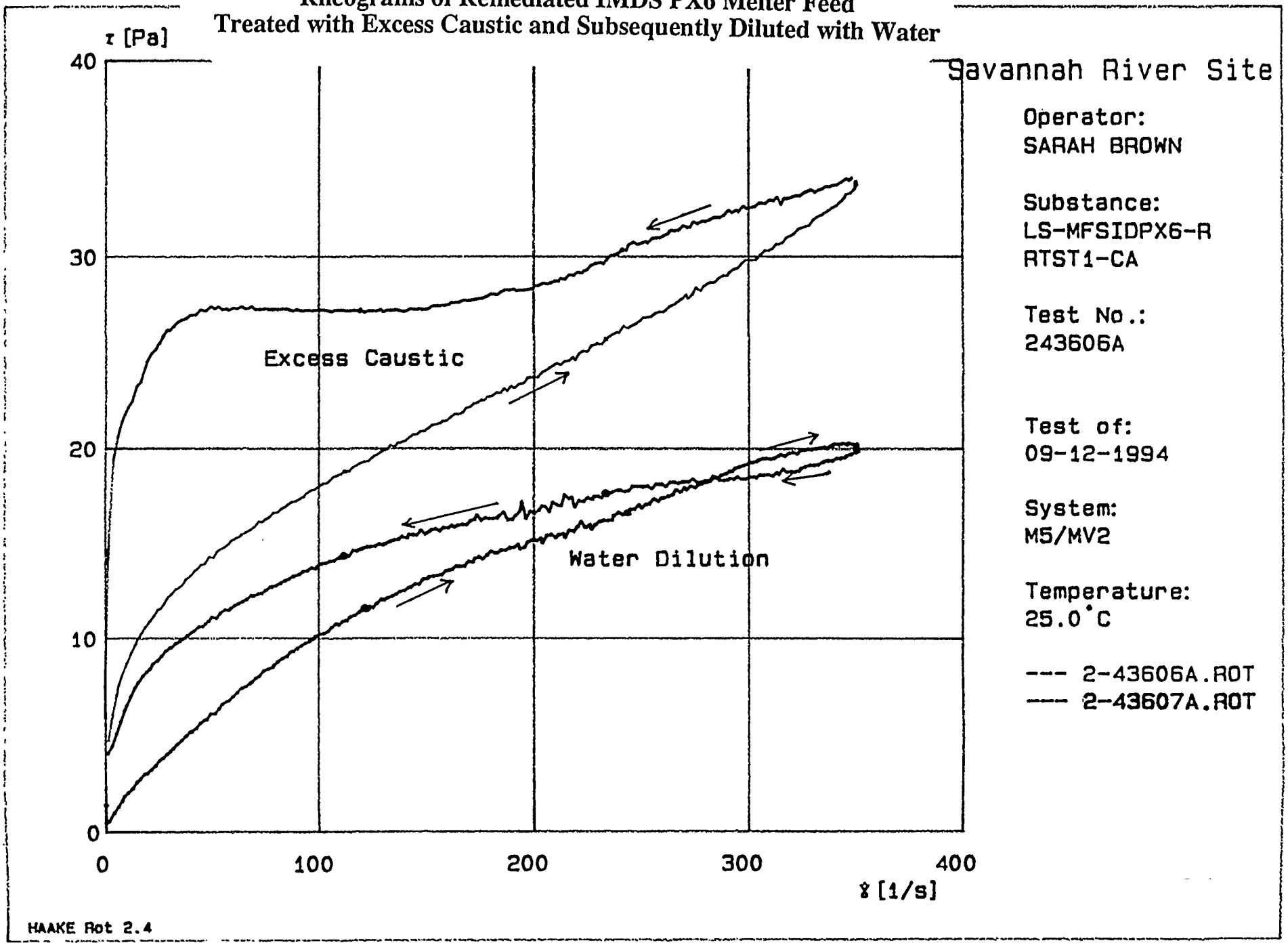

Figure 4.
Rheograms Comparing Nitric Acid Treatments with
Unremediated and $Al(NO_3)_3$ Remediated IDMS PX6 Melter Feeds