

Impact of Rheological Modifiers on Various Slurries Supporting DOE Waste Processing - 10099

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ABSTRACT

Controlling the stability and rheological properties of slurries has been an important but challenging issue in nuclear waste treatment, one that previous research has yet to sufficiently address. At the Hanford and Savannah River sites, operation of the waste treatment facilities at increased solids loading reduces the evaporative load on the melter systems and thereby increases waste processing rates. However, at these higher solids loadings, increased slurry rheology becomes a significant processing issue. The current study evaluates the use of several rheological modifiers to alleviate increased slurry rheology at high waste solids concentrations. Rheological modifiers change particle interactions in slurry. For colloidal slurries, modifiers mainly alter the electrostatic and steric interactions between particles, leading to a change in slurry rheology. Weak organic acid type rheological modifiers strengthen electrostatic repulsion whereas nonionic/polymer surfactant type rheological modifiers introduce a steric repulsion. We investigated various rheological modifiers using high-level waste (HLW) nuclear waste simulants characterized typically by high ionic strength and a wide range of pH from 4 to 13. Using rheological analysis, it was found that citric acid and polyacrylic acid would be good rheological modifiers for the HLW simulants tested, effectively reducing the yield stress by 40% or more. Physical insights into the mechanisms driving stabilization by these rheological modifiers will be discussed.

INTRODUCTION

In the U.S. Department of Energy nuclear waste processing plants, such as the Hanford Tank Waste Treatment and Immobilization Plant (WTP) at Hanford and the Defense Waste Processing Facility (DWPF) at the Savannah River site (SRS), plant throughput is enhanced by increasing the insoluble solids concentration of nuclear waste slurries, reducing the evaporative load on the joule-heated melters [1]. However, increasing the amount of insoluble solids results in a significant increase in rheological properties that challenges mechanical designs for mixing and transporting the waste slurries within the plants. Controlling the stability and rheological properties of waste slurries plays a crucial role in supporting the throughput increase. Higher throughputs reduce the mission life of the facilities and therefore reduce the cleanup mission costs; for example, an increase from 48.8 to 52.1 wt% (a 3.3 wt% increase) in the solid content of nuclear waste slurries would reduce the operating life of these plants by one year for both facilities, resulting in roughly one billion dollars in lifecycle cost savings. Given the challenging properties of these complex waste slurries, reduced rheological properties are also potentially important for sustainable operations of both WTP and DWPF.

Controlling the stability and rheological properties of nuclear waste slurries is extremely challenging given the complexities of the wastes, which have high pH (>12), high electrolyte content, high insoluble solids concentration (> 25 wt%), a broad chemical speciation, and a broad particle size distribution (0.3 to ~ 300 μm). The attractive van der Waals interaction is likely to dominate over repulsive electrostatic interaction under these severe conditions so that one may often need to introduce a small amount of chemical additives called rheological modifiers to control the stability and rheological properties of the slurry. In general, rheological modifiers for slurries are expected to change particle interactions such as colloidal interactions (i.e., electrostatic and steric interactions) and hydrodynamic interactions, leading to a change in dispersion and rheological properties. For colloidal slurries, changes in colloidal interactions become very effective, owing to the enormous surface areas of the particles, but the hydrodynamic interactions between the particles become significant for non-colloidal slurries [2].

In previous studies, different rheological modifiers have been tested on various HLW simulants. The first study was performed for the West Valley Demonstration Project (WVDP), which processed waste generated from the Plutonium URanium EXtraction (PUREX) and THORium EXtraction (THOREX)

separations processes [3]. The simulant consisted primarily of iron hydroxide and silicon dioxide solids dispersed in a basic suspending phase (due to the addition of sodium hydroxide). Addition of 1000 ppm sodium metasilicate and polyglycols reduced the apparent viscosity by at least 85% at a shear rate of 256 sec^{-1} . Nitric acid was also tested and was shown to be more effective than sodium metasilicate and polyglycols. A second set of studies investigated both simulated SRS melter feed and WTP AZ-102 washed sludge [4]. The melter feed is slightly acidic because the basic sludge is processed with a nitric/formic acid process. This waste stream contains both the sludge particles and glass frit particles. While Durmax D-3005 (Rohm & Haas) increased the yield stress at 1000 ppm for the SRS melter feed, it decreased the yield stress by 18% for the WTP AZ-102 washed sludge. A third set of simulant studies investigated both processed sludge and melter feeds at SRS, both of which are acidic [5]. Unlike the previous study, Durmax D-3005 was found to be ineffective on both waste streams. Dolyapix CE64 and a series of Ayd W (proprietary polyacrylates) were effective, decreasing the yield stress from 9 to 85%. This study also investigated the impact of water addition to reduce the yield stress and concluded that much more water, by mass, was required to have any effect on rheology as compared to the effective rheological modifiers.

However, most of these studies did not show systematic results for the effects of rheological modifiers. More importantly, none of them provided detailed interpretations and physical insights on the mechanisms of rheological modification, which is not informative for further investigations and studies. From the previous studies, one may categorize rheological modifiers into two different types: weak acids and nonionic/polymer surfactants. For the current study, we selected a large number of rheological modifiers of each type and investigated their efficiency with rheological measurements in detail, starting with characterizations of Hanford AZ-101 pretreated HLW simulant. Comparing the two types of rheological modifiers, it will be shown that weak acid-type rheological modifiers are more effective at reducing the yield stress of waste simulant slurries. Based on the test results with the Hanford AZ-101 pretreated HLW simulant, two weak acids and a variety of nonionic/polymeric rheological modifiers were studied for melter feed simulants representative of the actual radioactive waste streams at SRS.

EXPERIMENTS

The studies were conducted with non-radioactive chemical simulants, given high radiation levels associated with actual nuclear waste slurries. PNNL (Pacific Northwest National Laboratory) focused on a Fe_2O_3 -rich nuclear waste simulant, obtained from Optima Chemical (Georgia, USA), that is representative of AZ-101 pretreated HLW. This simulant is based on the chemical composition of actual AZ-101 sludge waste at Hanford and demonstrates typical characteristics of a PUREX nuclear waste simulant, and thus can be considered as representative of such waste streams. It has a broad particle size distribution with a large amount of colloidal size particles (see Figure 1) and is highly caustic ($\text{pH} \sim 12.3$). The solids content is $\sim 25 \text{ wt}\%$ and is high relative to waste treatment applications. Solids content was measured by a Melter Toledo Halogen Moisture Analyzer (Model HR83), as described elsewhere [6]. It was known that the suspended particles are metal oxides/hydroxides (mainly, Fe_2O_3). The suspending phase contains a large amount of various electrolytes ($\sim 0.5\text{M}$) [7], which poses a challenge associated with charge screening, combined with a sufficiently large amount of particles.

SRNL (Savannah River National Laboratory) tested melter feed simulants developed to support processing the macro sludge batches at DWPF, as summarized in Table 1. The sludges used to make the melter feeds were considered high in either iron or alumina or a combination of both. Five different melter feeds were processed with nitric and formic acid, and then blended with FRIT (crushed glass between 70 and 200 mesh and designed specifically for each HLW stream). One of melter feeds tested was a precipitated sludge with metal oxides added while all other melter feeds tested were co-precipitated sludges. The melter feeds were either acidic or neutral unlike the AZ-101 pretreated HLW simulant. The non-radioactive simulants are chemically representative of the actual radioactive waste streams. Details of the SRNL melter feed simulants are provided elsewhere [8].

For tests exploring the impact of weak acid-type rheological modifiers on waste simulant slurry rheology, PNNL tested various acids. These were polyacrylic acid ($M_w \sim 1800$), citric acid, phosphoric acid, ethylenediaminetetraacetic acid, oxalic acid, nitrilotriacetic acid, gluconic acid, glycolic acid, iminodiacetic acid, and L-tartaric acid. For nonionic/polymer surfactant-type rheological modifiers, Pluronic L64, F38, F98 (BASF), and polyethylene oxides with four different molecular masses (400, 8000, 100000, and 400000 g/mol) were used. Polyethylene oxide with 8000 g/mol was obtained from Dow Chemicals. Rheological modifiers used in previous studies, sodium lignosulphonate ($M_w \sim 52000$), sodium metasilicate,

and Duramax D-3005 (Rohm & Haas), were tested for comparison. Note that Duramax D-3005 is known as an ammonium salt of acrylic polymer. All chemicals were purchased from Sigma-Aldrich unless otherwise indicated. Three different concentrations, 1000, 3000, and 5000 ppm (or μg per a gram of slurry), were typically added. Rheological modifiers used for tests at PNNL are summarized in Table 1.

Table 1. Summary of the PNNL and SRNL Tests

Laboratory	Tested simulants	Tested rheological modifiers	Notes
PNNL	AZ-101 pretreated high-level waste	<ul style="list-style-type: none"> - Weak acids (polyacrylic acid, citric acid, phosphoric acid, ethylenediaminetetraacetic acid, oxalic acid, nitrilotriacetic acid, gluconic acid, glycolic acid, iminodiacetic acid, L-tartaric acid) - Nonionic/polymer surfactants (Pluronic L64, F38, F98, polyethylene oxides) - Salts (sodium lignosulphonate, sodium metasilicate, Duramax D-3005) 	- Polyacrylic acid and citric acid are two common rheological modifiers used for all tests performed at both PNNL and SRNL.
SRNL	<ul style="list-style-type: none"> RuRhHg melter feed SB5-12/13 melter feed 09-SB5-23 melter feed 09-SB5-24 melter feed SB6-1,2,3,4 melter feed 	<ul style="list-style-type: none"> - Weak acids (polyacrylic acid, citric acid, phenylboronic acid) - Sodium pyrophosphate tetrabasic - Sugar - Dolapix A88, CE64, and PC75 - Antifoam 747 - W. R. Grace ADVA Cast 555, ADVA Flex, Recover 	

In addition to polyacrylic acid ($M_w \sim 1800$), citric acid, and sodium metasilicate, SRNL tested other rheological modifiers (see Table 1). These were sodium pyrophosphate tetrabasic, sugar, phenylboronic acid, Dolapix A88 (1-propanol, 2-amino-2-methyl), Dolapix CE64 (ethylene glycol), Dolapix PC75 (synthetic polyelectrolyte), antifoam 747 (polyether siloxane), W. R. Grace ADVA Cast 555 (2-propenoic acid, polymer with methyloxirane polymer with oxirane, sodium salt, acetic acid, polycarboxylate), W. R. Grace ADVA Flex (polycarboxylate), and W. R. Grace Recover (sodium gluconate and sucrose). Note that the Dolapix and W.R. Grace modifiers were liquids whereas the others were dry solids. The liquid modifiers were not corrected for the active components in the fluid and are presented based on the liquid addition. Modifier addition rates for the solid modifiers were typically 1000, 3500, 7000, and 10000 ppm and for the liquid modifiers 1000, 6000, 11000, and 16000 ppm. A majority of the modifiers tested at SRNL are organic in nature and can be considered as reductants in melter operations.

Rheological measurements were obtained using the concentric cylinder geometry on either a Haake RS-600 or an Anton Paar MCR 301. Tests employed a shear rate range of 0 to 1000 sec^{-1} (upward and downward runs) and a temperature of 25°C. For each rheological characterization, the shear rate was increased over 5 minutes, held for 1 minute and then decreased over 5 minutes. The amount of the slurry required per measurement ranged between 40 to 50 grams for both rheometers. The rheological data obtained were analyzed using the Bingham Plastic rheological model (i.e., $\tau = \tau_y + \eta_p \dot{\gamma}$), resulting in a Bingham Plastic yield stress (τ_y) and consistency or plastic viscosity (η_p). Here, τ and $\dot{\gamma}$ denote shear stress and shear rate, respectively. Rheological data at very low shear rates (e.g., $< 20 \text{ sec}^{-1}$) were not included in the analysis to avoid overweighting the Bingham plastic curve fit calculations. In addition, we did not include rheological data at intermediate and high shear rates (typically, above 300 to 500 sec^{-1}) since most of the slurries showed shear-thinning behaviors, which made it difficult to evaluate reasonable yield stresses. Most of the slurries tested showed reasonably high yield stresses (at least $\sim 15 \text{ Pa}$) and did not show flow instability, such as those indicative of Taylor vortices, minor settling, or the release of entrained gas. A control sample was used as the basis for the relative change in yield stress. A parameter to evaluate the efficiency of rheological modifiers is the “relative change in yield stress,” which is defined as the

difference in yield stress between the test and control samples divided by the yield stress of the control sample. A negative value of this parameter corresponds to a decrease in yield stress due to a rheological modifier, while a positive value corresponds to an increase. Thus, a large negative value defines a good rheological modifier for this application. Note that SRNL followed the same rheological protocol for analyzing their feeds, with the exception that the flow curves were obtained between 0 to 300 sec^{-1} , consistent with the range of shear rates DWPF melter feed are expected to observe [9].

Additionally, zeta potential for the AZ-101 control sample was measured by ZetaProbe (Colloidal Dynamics). The pH of the slurries was measured using the Orion Benchtop pH meter 420Aplus (PNNL) and the IQ Scientific Instruments 1Q150NP pH meter (SRNL).

RESULTS AND DISCUSSION

Characterization of AZ-101 Pretreated HLW Simulant Slurry

At PNNL, we first analyzed the particle size distribution (using a Malvern Mastersizer 2000) of the control sample, the AZ-101 pretreated HLW simulant. The size distribution was obtained by averaging over five identical measurements to minimize possible errors. As shown in Figure 1, the particle size distribution (as a volume %) exhibited a bimodal distribution, ranging from 0.5 to 200 μm . The surface area-weighted mean and volume-weighted mean diameters were 2.8 and 11.6 μm , respectively. The 50th and 90th percentile diameters, d_{50} and d_{90} , were about 5 μm and 66 μm , respectively. Note that about 70% of particles were from 1 to 10 μm , which verifies that the AZ-101 pretreated HLW simulant can be considered as colloidal slurry. This implies that a change in colloidal interactions plays a critical role in rheological properties of the slurry.

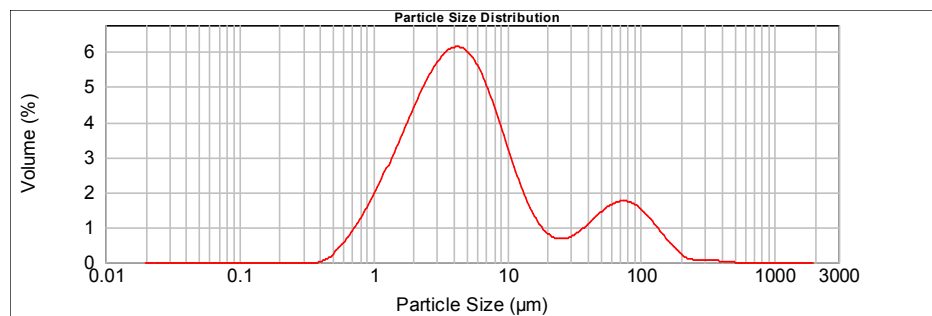


Figure 1. Particle size distribution of the AZ-101 pretreated HLW simulant

The pH measurement shows that the AZ-101 pretreated HLW simulant is highly caustic (pH~12.3). Under this condition, one may expect that the surface charges of the particles are negative since the point of zero charge (PZC) is typically less than pH~9 for most metal oxides/hydroxides [10,11]. Since aluminum hydroxide, $\text{Al}(\text{OH})_3$, is known to be well-dissolved under strong basic conditions at 25°C [12], Fe_2O_3 can be considered as a major suspended solid in the AZ-101 pretreated HLW simulant. The PZC of Fe_2O_3 is known to be pH~8.5 [10], so that, combined with sufficient charge screening from high salt concentrations, a zeta potential of the AZ-101 pretreated HLW simulant is expected to be weakly negative. This is consistent with the measured zeta potential of the AZ-101 pretreated HLW simulant of about -4.3 mV, which is weak compared to typical values ($\sim \pm O(10)$ mV) of zeta potential for colloidal suspensions.

Figure 2 shows a typical rheogram for the AZ-101 pretreated HLW simulant using the Haake RS-600. As is expected for concentrated waste simulant slurries, it shows a high yield stress (~ 45 Pa) owing to the high concentration of colloidal particles. The shear rate range for the data analysis is typically set to 40 to 200 sec^{-1} to avoid overweighting the Bingham plastic curve fit calculation at both very low and intermediate/high shear rates. As described, this yield stress value was used as a control value to evaluate the efficiency of rheological modifiers via a “relative change in yield stress.” Note that unique control sample yield stresses were measured for the SRNL simulants so that a similar method was used for the SRNL tests.

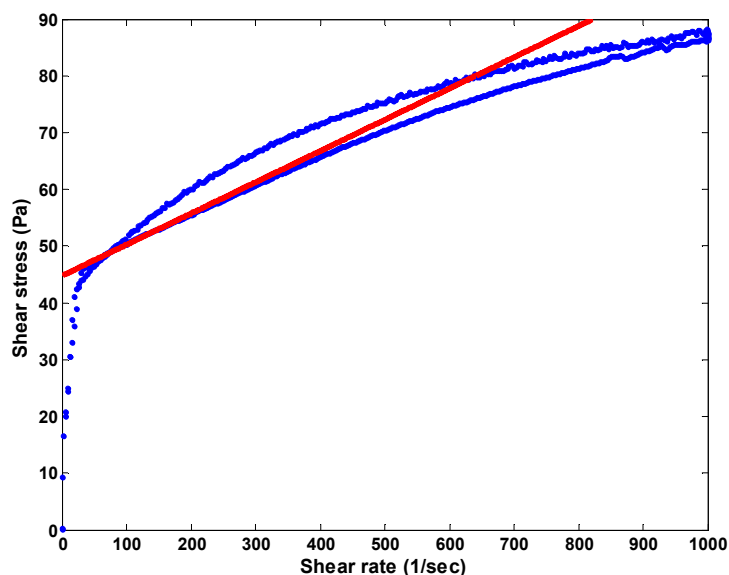


Figure 2. A typical rheological measurement for the AZ-101 pretreated HLW simulant slurry. Blue circles are experimental data; the upper one is down-ramp data, and the lower one is up-ramp data. The red line is the Bingham plastic curve fit based on the up-ramp data.

Nonionic/Polymer Surfactant-Type Rheological Modifiers (AZ-101 Pretreated HLW Simulant Slurry)

As described, the zeta potential of the AZ-101 pretreated HLW simulant is weak, which implies that an electrostatic repulsion alone would have little effect on stabilizing the slurry and controlling its rheological properties. One possible way to stabilize is to incorporate an additional repulsive steric layer to mitigate a dominant van der Waals attraction under the severe environment of the slurry. The repulsive steric layer can be typically introduced by nonionic/polymer surfactants, such as either di-block or tri-block-type nonionic surfactants. For nonionic/polymer surfactants, a hydrophilic chain of nonionic surfactant must provide a steric repulsion to avoid close approach between particles in an aqueous solution.

We first studied Pluronic surfactants, which are representative tri-block-type nonionic surfactants. Pluronic surfactant is a polyethylene oxide (PEO)-polypropylene oxide (PPO)-PEO tri-block copolymer where PPO and PEO function as hydrophobic and hydrophilic blocks, respectively. We expect that one PEO block adsorbs on the surface of the particles, and the other PEO block, along with the PPO block, provides a steric repulsion in an aqueous solution. Four different Pluronic surfactants were examined: L64, F38, F98, and F127. “L” and “F” denote sample appearance, liquid and flake, respectively. In the numerical designation of the Pluronic surfactants, the first digit (or the first two digits for F127) multiplied by 300 corresponds to an approximate molar mass of PPO, and 10 times of the last digit is a weight % of the PEO block. For example, L64 indicates that the approximate molar mass of the PPO is 1800 g/mol with 40 weight % of the PEO block.

Figure 3 shows the relative change in yield stress for three concentrations (1000, 3000, and 5000 ppm) of Pluronic L64, F38, F98, and F127. Results with F38 show a moderate and consistent decrease in yield stress, whereas the addition of L64 caused the yield stress to increase. The adsorption of nonionic/polymer surfactants is required to provide an additional repulsive steric layer on the particles. Particles here are mainly hydrophilic since they are metal oxides/hydroxides so that more PEO blocks would help to adsorb larger amounts of the Pluronic surfactant on the particles. F38 is much more hydrophilic, which is deduced from both the wt % of hydrophilic PEO block (40 wt% PEO for L64 and 80 wt% PEO for F38) and the hydrophilic-lipophilic balance (HLB) value (12 to 18 and >24 for L64 and F38, respectively) [13]. Thus, F38 is expected to be much more effective than L64 at reducing yield stress.

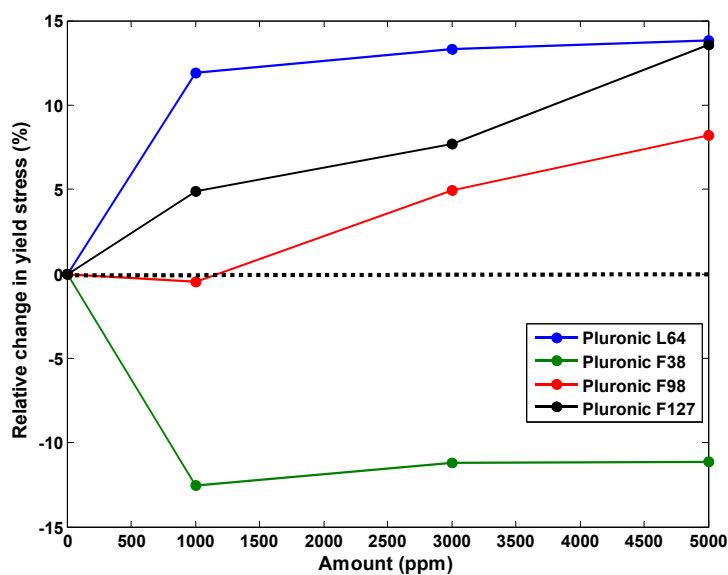


Figure 3. Percent change in yield stress for Pluronic series (PEO-PPO-PEO) surfactants. Four different Pluronic surfactants are used: L64, F38, F98, and F127. Note that the area below the dotted line is a favorable region for the rheological modification.

F98 and F127 have a reasonably high wt % of PEO, similar to that of F38, but both show approximately increases in yield stress with increasing concentration. Comparing F38 with F98, a main difference is the approximate molar mass of the PPO block (900 g/mol for F38 and 2700 g/mol for F98), which indicates that F98 has a longer chain length. It is known that the adsorption of non-selective polymers can decrease the stability of suspensions through bridging between particles [14,15]. Since the PEO block does not function by selectivity in the adsorption on the metal hydroxide/oxide surface, a larger overall size of Pluronic surfactants may correspond to a higher probability of bridging between the particles (i.e., two PEO groups in PEO-PPO-PEO adsorbed on the surfaces of nearby particles). Therefore, F98 and F127 may exhibit more bridges between particles, while F38 shows a moderate decrease (~12%) in yield stress. It also demonstrates that there might be an optimal molecular mass of PPO to minimize the yield stress.

To show a connection between the molecular mass and the possible bridging, we investigated PEO as a rheological modifier, using four different molecular masses. PEO is known to adsorb on mica surfaces (i.e., similar to metal hydroxide/oxide surfaces in our case) and create a steric layer [15] so that it can also be considered as a nonionic/polymer surfactant-type rheological modifier for the AZ-101 pretreated HLW simulant. Figure 4 shows the relative changes in yield stress for three different concentrations (1000, 3000, and 5000 ppm) for each PEO molecular mass (400, 8000, 100000, and 400000 g/mol). As clearly shown, the yields stress increases as the molecular mass of PEO increases. In this case, PEO with the lowest molecular mass exhibits moderate decreases in yield stress, comparable to that of F38 shown in Figure 3. Figure 4 suggests that the adverse effect from the bridges between particles is associated with the increase in molecular mass in nonionic/polymer surfactant-type rheological modifiers.

Weak Acid-Type Rheological Modifiers (AZ-101 Pretreated HLW Simulant Slurry)

A length scale at which the electrostatic interaction dominates over Brownian motion scales as κ^{-1} , the Debye length, whereas the steric interaction would be dominant on the order of R_g , the radius of gyration of nonionic/polymer surfactant [14,15]. Based on the electrolyte concentrations of the AZ-101 pretreated HLW simulant, one may estimate that the Debye length is about 11 nm at 25°C. Average molecular weights of Pluronic F38 and F98 are 4800 and 13000, respectively. Recognizing that R_g of adsorbed polyethylene oxide ($M_w \sim 4 \times 10^4$ g/mol) on mica surface in water (i.e., good solvent) is about 6.5 nm as a guideline [16], one may deduce that the radii of gyration of F38 and F98 nonionic/polymer surfactants are less than about

6 nm. Therefore, R_g is comparable to or smaller than κ^{-1} , which may imply that strengthening the electrostatic repulsion would be more effective for rheology modification.

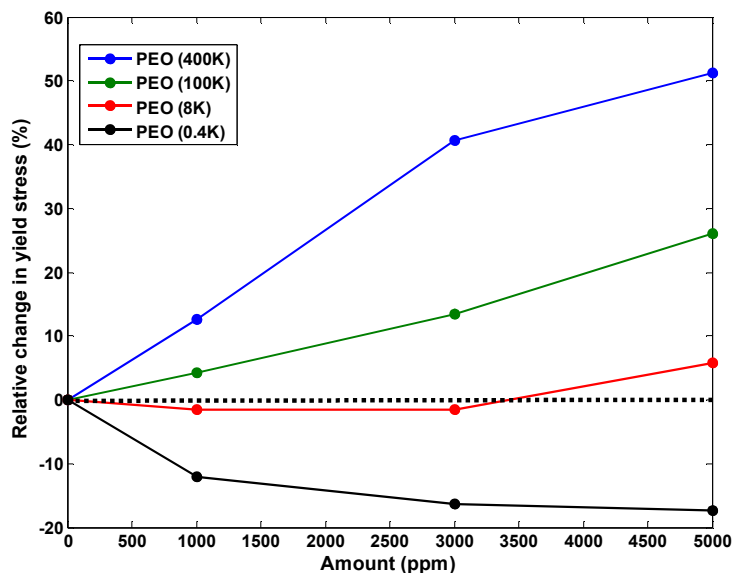


Figure 4. Percent change in yield stress for PEO with four different molecular masses: 400, 8000, 100 000, and 400 000 g/mol. Note that the area below the dotted line is a favorable region for the rheological modification.

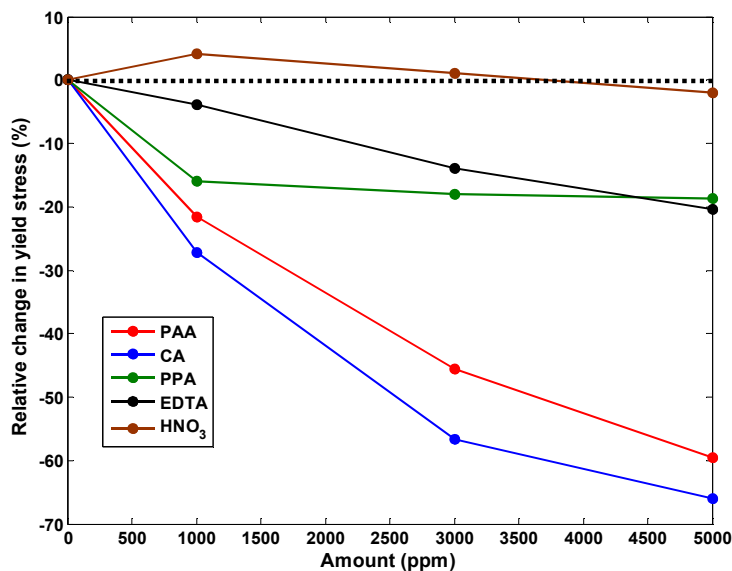


Figure 5. Percent change in yield stress for four different weak acids: polyacrylic acid (PAA), citric acid (CA), phosphoric acid (PPA), and ethylenediaminetetraacetic acid (EDTA). Nitric acid (HNO₃), a well-known strong acid, is tested to compare with weak organic acids.

Figure 5 shows the relative changes in yield stress for three concentrations (1000, 3000, and 5000 ppm) of four weak acids, polyacrylic acid (PAA), citric acid (CA), phosphoric acid (PPA), and ethylenediaminetetraacetic acid (EDTA). Note that polyacrylic acid is a polyelectrolyte whose molecular mass is about 1800 g/mol. Because of its relatively small molecular mass, we assume that steric interaction is not significant. As indicated in Figure 5, all the weak acids show a decrease in yield stress of ~20% or more at 5000 ppm. Surprisingly, CA and PAA show very significant decreases in yield stress (about 67%

and 60% at 5000 ppm, respectively). The efficiency as a rheological modifier does not seem to depend on the number of acid groups; while EDTA and CA have similar number of acid groups in unit mass, CA outperforms EDTA. For comparison, we performed separate experiments using rheological modifiers tested in previous studies. These included sodium lignosulphonate, sodium metasilicate, and Duramax D-3005. Sodium lignosulphonate and Duramax D-3005 at 5000 ppm decreased the yield stress by 40% and 22%, respectively, but both are significantly less efficient than CA and PAA. Sodium metasilicate increased the yield stress by 5%.

Under the caustic pH conditions, one expects that the significant decrease in yield stress may be caused by a neutralization reaction. In fact, pH values of the slurries drop from 12.3 to 11.3 after adding the weak acids evaluated in Figure 5. However, as seen in the figure, nitric acid, a well-known strong acid, shows a negligible decrease in yield stress compared to both CA and PAA, whereas its pH variation is nearly identical. Our separate experiment with water addition (5000 ppm) demonstrated less than 5% decrease in yield stress. Thus, it is confirmed that decreases in yield stress by CA and PAA are due to a change in electrostatic interactions (i.e., strengthening the electrostatic repulsions between particles) rather than a direct pH or a dilution effect.

Motivated by significant decreases in yield stress, we investigated more weak acids, including oxalic acid (OA), nitrilotriacetic acid (NTA), gluconic acid (GA), glycolic acid (GIA), iminodiacetic acid (IDA), and L-tartaric acid (L-TTA). Figure 6 shows the relative changes in yield stress for three concentrations (1000, 3000, and 5000 ppm) of the various weak acids. Note that the data for PAA, CA, PPA, and EDTA are also presented for better comparison. As indicated in Figure 6, all weak acids decreased the yield stress of the AZ-101 pretreated HLW simulant by more than ~15% at 5000 ppm. CA, PAA, and GA are efficient rheological modifiers, exhibiting at least 50% decrease in yield stress at 5000 ppm. Among the various weak acids examined, CA seems to be the most effective rheological modifier for the AZ-101 pretreated HLW simulant. Compared to the results with nonionic/polymer surfactant-type rheological modifiers (see Figures 3 and 4), it is clear that weak acid-type rheological modifiers are much more effective in reducing the yield stress of the AZ-101 pretreated HLW simulant.

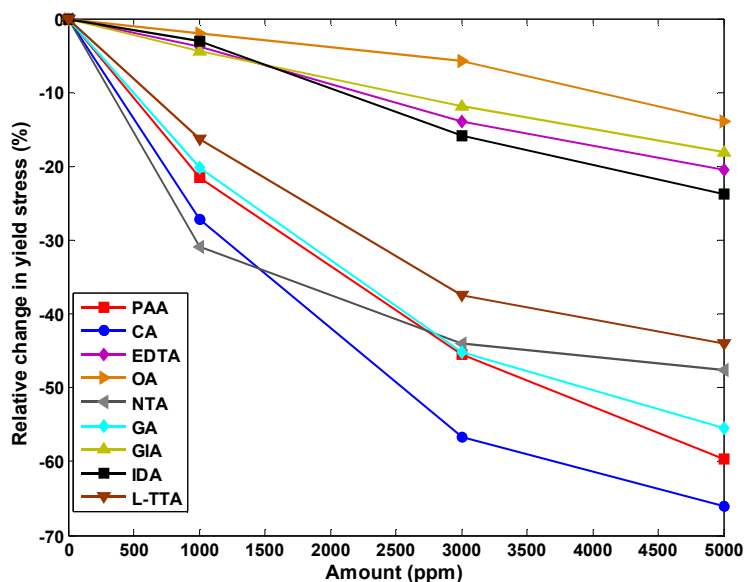


Figure 6. Percent change in yield stress for various weak acids: polyacrylic acid (PAA), citric acid (CA), phosphoric acid (PPA), ethylenediaminetetraacetic acid (EDTA), oxalic acid (OA), nitrilotriacetic acid (NTA), gluconic acid (GA), glycolic acid (GIA), iminodiacetic acid (IDA), and L-tartaric acid (L-TTA).

A “qualitative” mechanism for weak acid-type rheological modifiers can be explained by i) the capturing of cations in aqueous bulk solution and ii) adsorption on the surface of particles from the specific interaction between carboxylic groups in weak acid-type rheological modifiers and hydroxyl groups in the Fe_2O_3 particles, as described in [6]. In our case, $pH > PZC$ even after addition of the acids, so that charges on both the particle surface and weak acids have the same polarity. This triggers a competition between the

electrostatic repulsion and the specific interaction (i.e., attraction). For adsorption of the weak acids to occur, the energy penalty imposed by the electrostatic repulsion must be overcome, and thus, the specific interaction would necessarily be a major driving force. This competition between electrostatic repulsion and the specific interaction is clearly shown in the adsorption of PAA on silica particles at neutral pH [17]. While appreciable adsorption of PAA is detected for alumina particles (PZC is about pH=9) at neutral pH, no adsorption occurs for silica particles, surprisingly. The PZC of silica is pH~2.5 so that negative surface charges continuously build up as the pH increases from 2.5 [10,11]. Thus, one can expect that a large energetic penalty originating from the electrostatic repulsion at neutral pH may prevent adsorption on silica particles. Because of the minimal adsorption on surfaces at pH>PZC, one can also assume that appreciable amounts of cations in aqueous bulk solution can be captured by non-adsorbing PAA and CA species, since PAA and CA are typically fully dissociated at pH>PZC.

SRNL Results

The melter feed simulants (ranging between 45.7 and 59.8 wt% solids) were investigated with selected rheological modifiers, based on the experimental results at PNNL. In addition, more rheological modifiers from other industries were tested. A common suite of modifiers, Recover, PAA, and CA, were applied to all the melter feeds. As our tests progressed, additional rheology modifiers were identified and decisions were made to drop some existing rheology modifiers from the tests. The decision to drop rheology modifiers was based on previous performance, specifically their impacts on the Bingham yield stress.

The first simulant tested with rheology modifiers was the RuRhHg simulant (51.5 wt% solids), which was developed to determine the impact of noble metals on the DWPF process. Figure 7 shows that PAA, CE64, and ADVA Flex were very effective in decreasing the yield stress. This RuRhHg simulant was decanted to 59.8 wt% total solids and was tested with various rheological modifiers. The test results with the decanted RuRhHg simulant are shown in Figure 8. In this case, modifiers that were most effective in reducing the yield stress were those previously stated for the more dilute RuRhHg simulant and, additionally, ADVA Cast 555. Modifiers PAA and CE64 were also effective in reducing the plastic viscosity. Solids content did not seem to have significant impact on the effectiveness of the modifiers. Sugar and sodium metasilicate had little impact on the rheological properties.

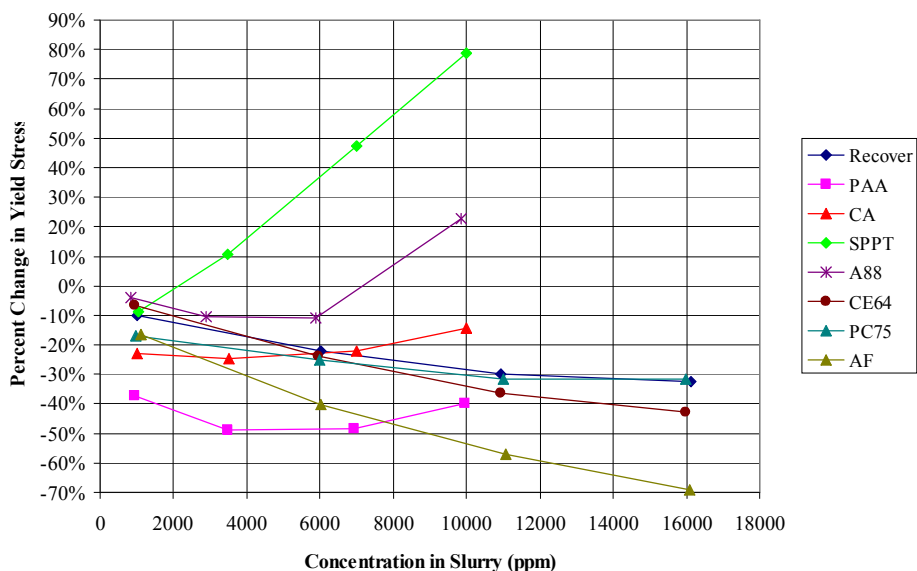


Figure 7. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), sodium pyrophosphate tetrabasic (SPPT), Dolapix A88, Dolapix CE64, Dolapix PC75 and Grace ADVA Flex (AF) modifiers with 51.5 wt% RuRhHg Melter Feed Simulant.

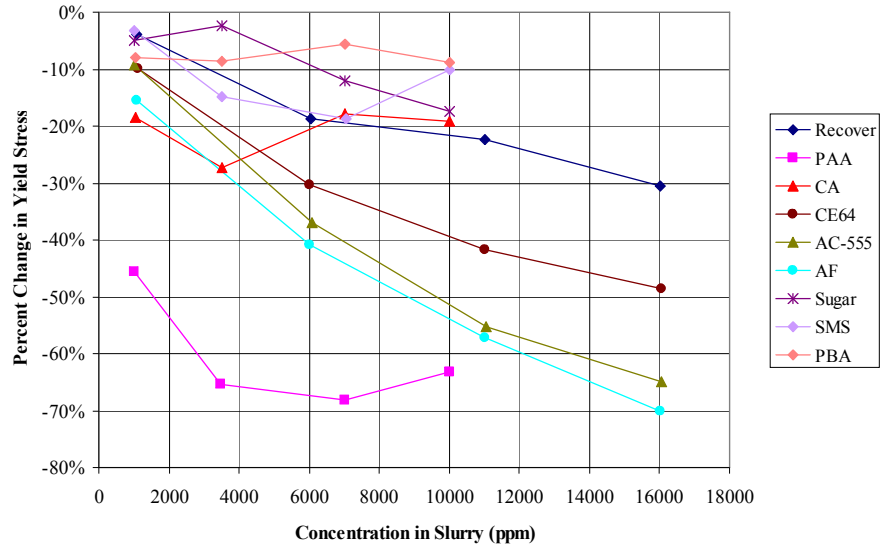


Figure 8. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), Dolapix CE64, Grace ADVA Cast-555 (AC-555), Grace ADVA Flex (AF), Sugar, Sodium Meta-silicate (SMS), and Phenylboronic Acid (PBA) modifiers with 59.8 wt% RuRhHg Melter Feed Simulant.

The next melter feed simulant was SB5-12/13, which was used to support processing of sludge batch 5, a sludge that was processed through aluminum dissolution prior to making melter feed. The effects of the rheology modifiers are shown in Figure 9. Rheology modifiers Recover, PAA, CA and ADVA Cast 555 were effective in reducing the yield stress. Rheology modifier PAA was also effective in reducing the plastic viscosity.

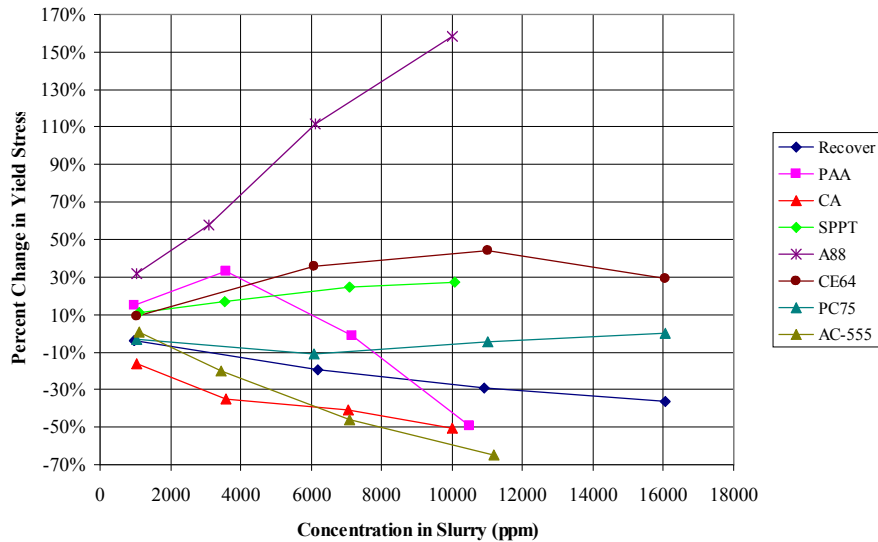


Figure 9. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), Dolapix A88, Dolapix CE64, Dolapix PC75, and Grace ADVA Cast 555 modifiers with 46.8 wt% SB5-12/13 Melter Feed Simulant.

09-SB5-23 and 09-SB5-24 melter feed simulants were also tested. They were designed to support sludge batch 5 processing and were specifically intended for investigating the effect pH had on processing parameters. All rheology modifiers tested were reasonably effective in reducing the yield stress for both melter feeds, as shown in Figures 10 (09-SB5-23 melter feed simulant, pH 7.4) and 11 (09-SB5-24 melter feed simulant, pH 5.1). While all rheology modifiers reduced the yield stress for both simulants, the starting

pH of the melter feed impacts the effectiveness of the rheology modifier, as determined by percentage change in the measured property; the more acidic the starting melter feed, the less effective the rheology modifier. This is possibly related to dissociation of the carboxylate or carboxylic acid group (for most rheological modifiers), since dissociation of these functional groups is known to decrease as pH decreases. Note also that the starting yield stress of 09-SB5-23 was 24.4 Pa and it was only 5.2 Pa for 09-SB5-24, showing that a starting pH affects rheological properties significantly. CA and PAA are considered as weak acids, and they reduced the pH of both melter feeds by essentially the same percentage.

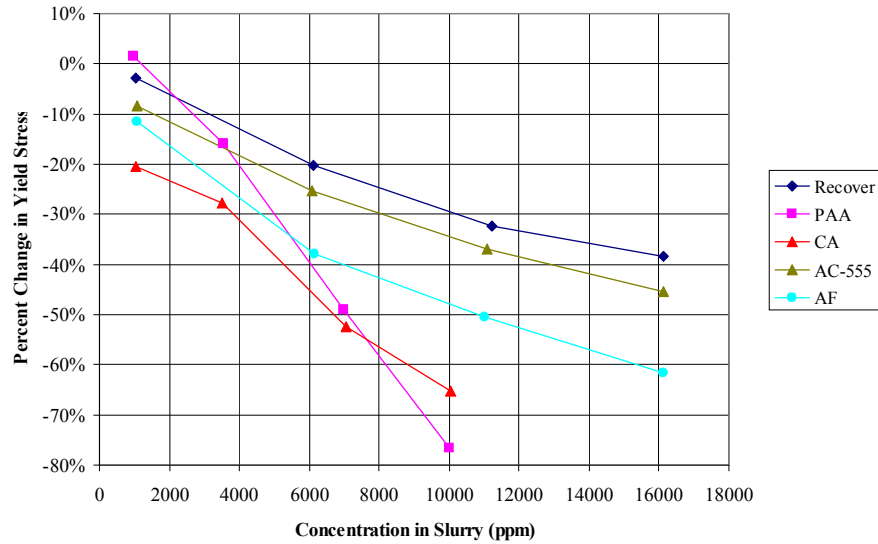


Figure 10. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), Grace ADVA Cast-555 (AC-555), and Grace ADVA Flex (AF) modifiers with 50.2 wt% and pH 7.4 Melter Feed Simulant 09-SB5-23.

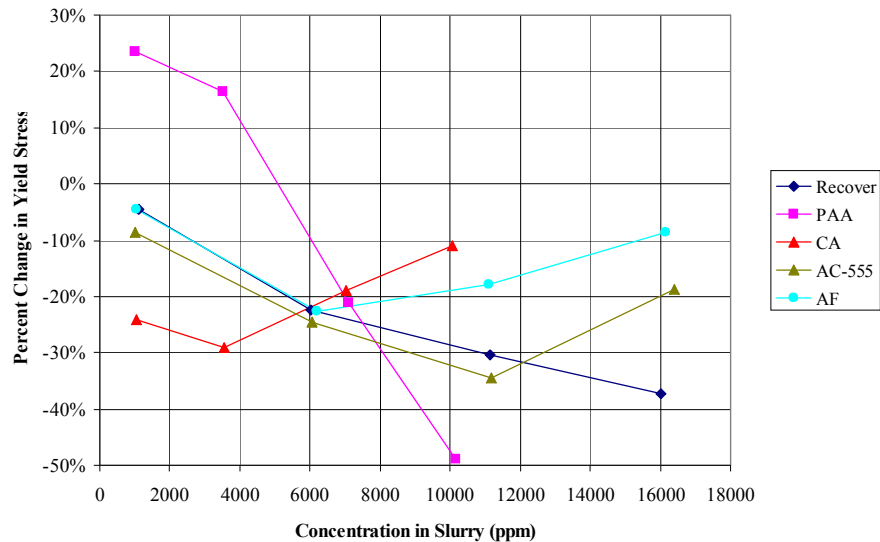


Figure 11. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), Grace ADVA Cast-555, and Grace ADVA Flex modifiers with 49.0 wt% and pH 5.1 Melter Feed Simulant 09-SB5-24.

The final melter feed simulant was SB6-1,2,3,4. This simulant was used to support initial scoping studies for processing sludge batch 6. As shown in Figure 12, rheology modifiers Recover, Dolapix PC75, CA, and PAA were very effective in reducing the yield stress. PAA was also effective in reducing the plastic viscosity.

SRNL tests with five different melter feed simulants indicate that CA and PAA as well as the Grace ADVA class rheology modifiers were effective. The Grace ADVA class modifiers contain polycarboxylates (of proprietary composition). Both CA and PAA reduced the pH by at least 10% on all the melter feeds at the higher concentrations. This was not observed with the GRACE ADVA modifiers, where the pH was reduced at most 5%. Although waste simulants tested at SRNL are different from the Hanford AZ-101 pretreated HLW simulant (e.g., pH), weak acid-type modifiers are nonetheless shown to be very effective in decreasing the yield stress (and plastic viscosity). This suggests that carboxylic acid groups could be a key factor in selecting rheological modifiers for nuclear wastes.

It was observed in the RuRhHg simulant tests that the effective rheology modifier is a definite benefit to processing at higher wt% solids. The yield stresses for the RuRhHg simulant (51.5 wt%) and the decanted RuRhHg simulant (59.8 wt%) are about 13.4 Pa and 62 Pa, respectively. 16000 ppm (2742 ppm active) ADVA Cast 555 decreased the yield stress of the decanted RuRhHg simulant to 21.7 Pa (i.e., 65% decrease) as shown in Figure 8. This significant reduction in yield stress clearly shows that this waste stream could be processed at approximately 8 wt% higher solids concentration with nearly the same rheological conditions as the original RuRhHg simulant. This gives rise to both cost and schedule savings.



Figure 12. Percent change in yield stress for Recover, polyacrylic acid (PAA), citric acid (CA), sodium pyrophosphate tetrabasic (SPPT), Dolapix A88, Dolapix CE64, Dolapix PC75, and Taylor Anti Foam 747 modifiers with 45.7 wt% SB6-1,2,3,4 Melter Feed Simulant.

CONCLUSIONS

Controlling rheological properties of slurries is pivotal in many industrial applications for efficient, economic, and safe processing. Using rheological modifiers is one of the most effective ways to accomplish this, especially given the complex/broad chemical and physical properties observed in nuclear waste slurries. We first investigated various rheological modifiers with the AZ-101 pretreated HLW simulants, testing two different types of rheological modifiers: a weak acid type and nonionic/ polymer surfactant type. Comparing the two types of rheological modifiers, PNNL found that CA and PAA were among the most effective modifiers for AZ-101 pretreated HLW. Then, these weak acids and some other rheological modifiers were applied for five SRS melter feed simulants. CA and PAA also turned out to be very effective for the various waste simulants tested at SRNL. They reduced yield stress by about 70% for the AZ-101 pretreated HLW simulant and up to 70% at higher concentrations for the SRS melter feeds.

We postulated that the adsorption on the particle surface is a key feature in weak acid-type rheological modifiers. Compared to CA, an attractive van der Waals interaction between PAA and a particle is expected to promote more adsorption of PAA on the particle, which may suggest that PAA with a larger molecular mass would be more efficient than that with a smaller molecular mass (i.e., molecular weight effect). In addition, as the molecular mass of PAA increases, the steric interaction becomes non-negligible. Also, the steric interaction would be coupled with ionic strength and pH. Such additional considerations of

PAA will help to gain more detailed physical insights on a working mechanism for polycarboxylic acid type rheological modifiers.

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