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Rheological Performance of Polymers in Heavy Brines for Workover and Completion

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Abstract

Solids free fluids are used for drilling, completion and workover operations. These fluids minimize formation damage and improve well productivity. Heavy brines are commonly used as completion fluids to maintain overbalance on the formation. Densities up to 19.2 lb/gal can be achieved using Potassium chloride (KCl), Calcium chloride ($CaCl_2$), Calcium bromide ($CaBr_2$), Sodium bromide (NaBr) and Zinc bromide ($ZnBr_2$) or a combination of two or more salts. Various water-soluble biopolymers and synthetic polymers are used as viscosifiers in these brines.

Biopolymers like Xanthan gum exhibit excellent shear and temperature resistance; however, they are prone to biodegradation and problems of injectivity. At very high salt concentrations complete hydration of Xanthan is not achieved[8]. Synthetic polymers like partially hydrolyzed polyacrylamide (PHPA) are prone to shear degradation. Copolymers of polyacrylamide and 2-Acrylamido-2-methylpropane sulfonic acid substituted polyacrylamide (AMPS) have better shear and temperature resistance than PHPA. An understanding of the effects of high temperature and salinity on the rheological properties of these fluids, as encountered in deep offshore wells is of great interest.

The present study examines the rheology of Xanthan gum, PHPA and an associative AMPS substituted copolymer of polyacrylamide in saturated $CaCl_2$ (divalent) and KCl (monovalent) salts at ambient (75 °F) and elevated temperature (250 °F). The fluid samples were static and dynamically aged to check their compatibility in brines. Fluid loss properties were also investigated to evaluate the formation damage potential of the samples. For field applications minimal hydration time is desired. An OFITE viscometer was used to measure hydration time of the fluids; while model Fann 35 viscometer was used to measure rheology of the samples. The rheology, fluid loss property and hydration time of the fluids are presented as a function of salt type, brine density, and temperature.

Introduction

Viscosified heavy brine completion fluid serves the dual purpose of maintaining hydrostatic pressure and improving the solid carrying capability. Different types of polymers are used to viscosify brines and their rheology is dependent on the nature and concentration of polymer, salt type and concentration, temperature, and pH.

Xanthan gum is a slightly anionic natural polysaccharide derived from the bacterium *Xanthomonas Campestirs*. It is extensively used as a viscosifier in the oil and gas industry. The molecular structure of Xanthan was studied by Jansson et al[7]. The Xanthan monomer is shown in **Fig. 1**. It displays good low shear viscosity, which is useful in suspending solids at low flowrates[8]. Xanthan in saturated brine hydrates rapidly at elevated temperature (120 ºC) and high shear. Milas and Rinaudo[16] showed that in presence of external salts Xanthan provides the highest viscosity between pH 7-8. Gelation in Xanthan in presence of polyvalent metal salts (Ca^{2+}, Ba^{2+} and Fe^{2+}) occurs only at very high pH (pH>10)[8].

Partially hydrolyzed polyacrylamide is prepared by hydrolysis of polyacrylamide with a strong base like potassium hydroxide. The monomer of PHPA is shown in **Fig. 2**. PHPA is highly susceptible to mechanical degradation (Maerker[11]). The effects of divalent cations on degree of hydrolysis have been studied extensively (Martin et al.[13]). At higher salinity, the polymer chain coils up leading to reduced viscosity. Degree of hydrolysis increases at low pH (Muller[17]).

The copolymer of acrylamide and AMPS used in the present study is a water soluble associating polymer. AMPS substituted polymer is more resistant to shear degradation due to the rigidity of sulfonate group (Noik et al.[21]). The structure of AMPS monomer is shown in **Fig. 3**. Associating polymer has hydrophobic groups attached to the polymeric chain. At high salinity, these groups associate with each other to minimize exposure to solvent. This increases their hydrodynamic size and thereby results in higher viscosity. Rheology of associating AMPS polymer is depended on the type of hydrophobic group (Taylor and Nasr-El-Din[31]). Furthermore, presence of hydrophilic sulfonated groups

increases the rigidity of the polymer chain and their shear stability. Viscosity of the solution is dependent on degree of sulfonation, molecular weight and salinity. Degree of sulfonation governs charge density on the polymer chain. The cations in brine shield the negative charges. As a result, the chain collapses and causes a decrease in viscosity.

Test Methodology

Three types of polymers were selected to compare the effects of salinity and temperature on their rheology. One biopolymer, Xanthan and two synthetic polymers PHPA and a copolymer of AMPS were chosen. PHPA used was in powdered form while Xanthan and AMPS polymer were liquid.

Polymer concentrations yielding similar viscosity in freshwater were considered. To determine these polymer concentrations, fluid samples were prepared in freshwater at different polymer loadings. The samples were aged at 75 °F for 48 hr and their viscosities were recorded. The average of the apparent viscosity values during aging was calculated. The fluid samples showing similar viscosities were selected for further analysis. **Figure 4** shows viscosity versus shear rate of the samples in freshwater. **Table 1** lists the apparent viscosity of each sample. Viscosity at high shear rates for all the polymers in freshwater are similar. Model 35 Fann viscometers (spring constant, N = 1 and 0.2) were used for rheology measurements. The measurements were performed at ambient temperature and pressure. The viscometer used was equipped with R1B1 bob and cup geometry. Scope of this paper is to emphasize the performance of polymers at high shear rates as experienced during pipe flow.

Fluid samples were prepared in different Potassium Chloride (KCl) and Calcium Chloride ($CaCl_2$) brine solutions and their viscosities were observed for 48 hr. Several batches of samples were prepared and the brine concentrations showing stable viscosities in all the polymers were selected. All the polymers showed stable viscosity in 9.2 lb/gal KCl and 11.2 lb/gal $CaCl_2$.

After finalizing the polymer and brine concentrations, samples of each polymer were prepared in freshwater, 9.2 lb/gal KCl and 11.2 lb/gal $CaCl_2$. The samples were hydrated for 24 hr, followed by 48 hr aging at ambient temperature (75 °F). Separate batch of samples were Hot Rolled (HR) for 12 hr using a model 173-00-RC OFITE 5-Roller Oven at 250 °F after 24 hr of hydration (**Fig. 5**). These hot rolled samples were then aged for 48 hr at ambient temperature.

Another batch of samples was prepared and the test was run on the OFITE low pressure wall mount filter press (**Fig 6**). Cumulative filtrate volume was recorded as a function of time and filter cake thickness was measured.

Theory

Following set of equations were used to characterize fluids.

Wall shear stress values were obtained from dial readings using the following equation.

$$\tau_w = 0.01066\, N\, \theta_i \tag{1}$$

where, τ_w is wall shear stress (lb_f/ft^2), N is spring factor and θ_i is the dial reading at ith rpm.

Wall shear rate was calculated from the speed of rotating sleeve using the following equation.

$$\gamma_w = 1.703 \times RPM \tag{2}$$

where, γ_w is wall shear rate (sec^{-1}).

Wall shear stress and wall shear rate data were analyzed to obtain power law parameters: flow behavior index, n and viscometer consistency index, K_v.

All fluids tested showed a shear-thinning behavior, which was adequately described by Ostwald–de Waele (Power law) model. An apparent viscosity, μ_a of power law non-Newtonian fluid is represented by the following expression,

$$\mu_a = 47880\, K_v \left(\gamma_w\right)^{n-1} \tag{3}$$

The viscosity of Calcium Chloride brine, μ_s at a given brine concentration and temperature was calculated using the following equation (Ortego and Vollmer[23]).

$$\mu_s = \left\{\exp\left[4.5 + 2.682 \times 10^{-5} \exp\left(\rho\right)\right]\right\} \times T \wedge \left(-0.014\,\rho^3 + 0.375\,\rho^2 - 3.109\,\rho + 7.278\right) \tag{4}$$

where, T is the fluid temperature ($°F$) and ρ is brine density (lb/gal).

Static Aged Experiments

The objective of this test was to ensure the rheological stability of fluid samples for a period of 48 hr. Samples were hydrated for 24 hr followed by 48 hr static aging. **Figure 7** shows the rheology of Xanthan in different base fluids. **Figures 8 and 9** show similar plots for PHPA and AMPS fluids. Apparent viscosities were calculated and compared for each polymer in different base fluids (**Fig. 10**). **Tables 2-4** list the apparent viscosities of all fluids tested. **Table 5** lists the apparent viscosity of fluids aged statically. **Table 6** lists the power law model fluid paremters n and K_v of the static aged samples.

Results and Discussion

Xanthan in freshwater maintains constant viscosity (**Fig. 7**) which is in agreement with Seright and Henrici[30]. In brine

solution, viscosity of Xanthan is higher than freshwater. Viscosity increase is significantly higher in $CaCl_2$ as compared to KCl. This is due to stabilization of the helical Xanthan structure in presence of cations (Lambert et al.[9]; Milas and Rinaudo[16]; Seright and Henrici[30]). High concentration of Ca^{2+} ions increases the anionic character. As a result more hydrogen bonds are formed leading to an increased viscosity[8]. The pH recorded for all samples was approximately 7 (Milas et al.[16]).

PHPA in freshwater maintains constant viscosity during static aging (**Fig. 8**). Addition of salt leads to a marked decrease in viscosity. Viscosity of PHPA in 11.2 lb/gal $CaCl_2$ at high shear rates is comparable to that of 11.2 lb/gal $CaCl_2$ brine as computed by **Eq. 4** (4.8 cP at 75 °F). Furthermore, some precipitation of polymer was observed (**Fig.11**). PHPA is anionic in nature due to presence of carboxylate ions formed by the hydrolysis of amide group. In freshwater the negative charges along polymer chain repel each other and extend the polymer chain. This causes rapid dissolution of polymer in water (Ward and Martin[32]). Cations attach to the negative charges on polymer chain and screen them from each other. This causes polymer chain to coil up, decreasing the viscosity. Moreover, in high Ca^{2+} concentration complexion of carboxylate groups takes place, resulting in the precipitation of polymer (Muller et al.[20]). For the current study all samples recorded a pH close to 7 (Muller[17]).

AMPS substituted copolymer in freshwater maintains its viscosity over the test duration (**Fig. 9**). Viscosity reduces upon addition of salt. However, unlike PHPA, viscosity of AMPS in $CaCl_2$ is higher than in KCl brine. Precipitation did not occur in any fluid sample. Associative copolymer of AMPS is anionic in nature due to the presence of sulfonate group. Cations from salt shield the negative charges and cause polymer chain to contract. So the viscosity of AMPS polymer in brine (both KCl and $CaCl_2$) is less than that in freshwater. At very high Ca^{2+} ion concentration, charge shielding brings the hydrophobic groups of AMPS polymer together, and intra-molecular interactions begin. This leads to an increase in viscosity for AMPS polymers in $CaCl_2$ (Rashidi et al.[25, 26], Taylor and Nasr-El-Din[31]).

Figure 10 compares the apparent viscosity of all fluids aged at 75 °F. As discussed earlier, highest viscosity was observed was for Xanthan fluids in $CaCl_2$ brine and the lowest in case of PHPA in $CaCl_2$ brine.

Dynamic Aged Experiments

Field application involves fluids being circulated at high bottom hole temperature. Dynamic aging simulates the effect of high temperature on rheology of the polymers. Fresh fluid samples were prepared and hydrated for 24 hr. Samples were then hot rolled for 12 hr at 250 °F and allowed to cool to ambient temperature before measuring the viscosity. Hot rolled samples are marked as "HR". Samples are then aged at ambient temperature for 48 hr. To remove any free oxygen from the aging cells oxygen scavenger (Na_2SO_3) was added at a concentration of 2 lbm/bbl.

Figures 12-14 show the rheology of all hot rolled fluids. **Figure 15** compares the apparent viscosity of all hot rolled fluids. **Tables 7-9** show the viscosity of hot-rolled samples of Xanthan, PHPA and AMPS fluids respectively. **Table 10** shows the apparent viscosity of different fluids. **Table 11** lists the power law model fluid parameters n and K_v of dynamically tested fluids.

Results and Discussion

The viscosity of the dynamic aged Xanthan fluid samples in freshwater is higher than the static aged samples. In KCl and $CaCl_2$, brines dynamic aged samples exhibit similar viscosity as static aged samples. Xanthan molecules have helical structure (Lambert et al.[9]; Milas and Rinuado[15]). On cooling, the helical structures form weak inter-molecular bonds, which explains the higher viscosities of the dynamic aged samples (Norton et al.[22]). Lambert et al.[9] proposed that in presence of cations Xanthan fluid shows better stability at high temperature than in freshwater. Furthermore, as Xanthan fluid sample is cooled down it reverts back to its original high viscosity (Norton et al.[22]).

Hot rolled PHPA sample in freshwater partially loses its viscosity. However dynamic aged PHPA fluid sample in brine shows slight increase in viscosity. PHPA in freshwater undergoes molecular weight degradation in presence of residual impurities. Degradation is accelerated at high temperature causing a decrease in viscosity (Muller[17]; Seright et al.[29]). Addition of oxygen scavenger consumes the dissolved oxygen which slows down free radical degradation of dynamic aged sample, as compared to the static aged PHPA (Muller[17]). It is important to note that addition of salt causes permanent viscosity reduction.

The viscosity of hot rolled AMPS fluid in freshwater is slightly lower. Dynamic aged fluid sample in KCl shows similar viscosity as compared to the static aged fluid sample. However, dynamic aged AMPS in $CaCl_2$ shows a significant decrease in apparent viscosity as compared to the static aged sample. AMPS sample in freshwater undergoes molecular weight degradation at high temperature and so a decrease in viscosity is observed (Muller[17]). AMPS polymer shows slightly better temperature resistance than PHPA. Significant reduction in viscosity for $CaCl_2$ may be due to the degradation of hydrophobic groups in the chain, which leads to coiling up of the polymer chain. Large viscosity loss in AMPS copolymer in $CaCl_2$ can also be due to hydrolysis of the sulfonate groups (Rashidi et al.[25]).

Figure 15 compares the apparent viscosity of all dynamically aged samples. Again, Xanthan in $CaCl_2$ displayed the highest viscosity, while PHPA in $CaCl_2$ has the lowest viscosity. AMPS copolymer fluid shows only marginal improvement over PHPA fluid.

API Filter Press Tests

Fluids used during completion are maintained to provide higher hydrostatic pressure than the formation fluid pressure. This overbalance leads to fluid leakoff into the formation resulting in formation damage. Formation of a filter cake that can be removed easily during production is desired. Different types of acid soluble ($CaCO_3$ and $MgCO_3$), water soluble (salts in saturated brines) and oil soluble (oil-soluble resin) solids called bridging agents are used to counter the fluid loss to formation[27]. Bridging agents form the solid network that aids in formation of filter cake, (Watson and Viste[33]). Apart from these, many metal cross linked gels (mainly cross-linked HEC) are used to control fluid loss. The advantages of each technique have been well documented (Himes and Dahl[3]).

Low pressure API filter press test was carried out on the fluid samples. **Figures 16-18** show the cumulative filtrate volume versus time plot for Xanthan, PHPA and AMPS respectively. The fluid loss characteristics of all samples were evaluated. **Tables 12-14** present cumulative filtrate volume versus time data for each fluid.

Results and Discussion

Xanthan fluid in freshwater displayed total spurt. Cumulative filtrate volume reduces drastically for Xanthan fluid in KCl and $CaCl_2$. Filter cakes are formed for Xanthan fluid samples in brine (**Figs. 19 and 20**). In absence of bridging agent the API cumulative filtrate volume of all polymers in fresh water was very high. However, for Xanthan fluid in saturated brine, there may be some precipitation of salt fines. These salt fines can act as bridging agents. Furthermore, formation of weak inter-molecular bonds of Xanthan molecules at high salinity (Norton et al.[22]) can generate a network structure, which facilitates the formation of filter cake.

Cumulative filtrate volume of PHPA fluid in $CaCl_2$ is the highest while in freshwater it is the lowest. In absence of bridging agent the cumulative filtrate volume is high. Polymer dissolves completely in freshwater and shows higher viscosity and therefore, greater resistance to flow. As discussed previously PHPA does not yield good viscosity in nearly saturated brine. As a result, both in KCl and $CaCl_2$, the cumulative filtrate volumes are higher than in freshwater. PHPA precipitates in presence of $CaCl_2$ and the resulting fluid behaves like brine. This causes a very high fluid loss for PHPA in $CaCl_2$ (**Fig. 17**).

AMPS fluid sample in freshwater shows the highest cumulative filtrate volume while in $CaCl_2$ exhibits the lowest cumulative filtrate volume (**Fig. 18**). AMPS copolymer shows lowest viscosity in KCl due to the coiling of polymer chain (Rashidi et al.[26]). More salt is dissolved thereby decreasing the amount of salt fines generated. This explains the larger cumulative filtrate volume recorded for AMPS in KCl. AMPS fluid in $CaCl_2$ shows higher viscosity which implies that more polymer dissolves in solution. As a result salt precipitates out and generates salt fines resulting in lower cumulative filtrate volume.

Hydration Tests

Hydration tests were carried out using an OFITE Model 900 viscometer (spring constant = 1) to study the ease of hydration of each polymer in different base fluids. It should be noted that the final viscosity from hydration test is not a good representation of the optimum viscosity achieved by the fluid. The tests only give an indication of the "time" it takes for the polymers to attain a constant viscosity. In field "on the fly mixing" is carried out in tanks equipped with agitators that provide shear to polymer. Moreover, pumping fluid through pipe at high flow rate aids in proper mixing of the polymer. In the laboratory, fluids were mixed using a small commercial blender (**Fig. 21**) at high shear rate for 30 sec and then the contents were transferred to cup of OFITE viscometer. Total time for fluid preparation and transfer was recorded and is reported in **Table 15**. Hydration test was run at 300 rpm (511 sec^{-1}) for 20-23 min at 75 ºF. **Figure 22** shows the plot of viscosity as a function of time. An approximate comparison can be made regarding the ease with which different polymers hydrate in various base fluids.

Results and Discussion

Xanthan in freshwater hydrates very rapidly and it shows significantly higher viscosity than observed during static aging (**Fig. 22)**. Since liquid Xanthan was used to prepare fluid samples, the rate of hydration is very high. High viscosity observed in hydration test may be due to insufficient shearing of the polymer. Therefore, for field application proper mixing of polymer is recommended. In presence of brine the fluid sample displays low viscosity. Xanthan is slightly anionic, so it takes longer time to hydrate especially, in presence of cations.

Powdered PHPA hydrates slowly in freshwater. PHPA is very sensitive towards cations and so displays lower viscosity in KCl as compared to water. Tests with $CaCl_2$ did not yield good result because the polymer did not hydrate properly. So, they have not been included in the analysis.

AMPS copolymer hydrates readily in freshwater and displays higher viscosity than observed in static aging. High hydration rate in freshwater is because of the use of liquid polymer. Furthermore, higher viscosity value during hydration test suggests that proper mixing is required to attain optimum viscosity. The viscosity in KCl is higher than for $CaCl_2$. AMPS sample viscosity continuously decreases in KCl while it increases in $CaCl_2$. The decreasing viscosity in KCl is due to the shielding of the negative charges on polymer chain which coils up the molecule. In $CaCl_2$ viscosity is increasing due to the association of the hydrophobic groups in polymer chain.

Conclusions

1. Three types of polymers (one biopolymer and two synthetic polymers) were selected for this study. Polymer concentrations that yielded similar viscosity were selected for comparison. Samples of these polymers were prepared at different KCl and $CaCl_2$ brines density. Brine density that showed stable viscosity was finalized.

2. Samples of Xanthan (60 lb/Mgal), PHPA (30 lb/Mgal) and copolymer of AMPS (40 lb/Mgal) were prepared in freshwater, 9.2 lb/gal KCl, and 11.2 lb/gal $CaCl_2$ and static and dynamic aged for 48 hr. All fluids displayed shear thinning behavior, which could be described by Ostwald-de Waele (Power Law) model.

3. Static aged Xanthan fluid samples displayed higher viscosity in brine due to the stabilization of their helical structure in presence of cations. Xanthan fluid viscosity was higher in $CaCl_2$ due to greater hydrogen bonding. Dynamic aged Xanthan fluid samples maintained their viscosity in brines. Dynamic aged Xanthan in freshwater displayed slightly higher viscosity than static aged due to inter-molecular bonding.

4. Static aged PHPA samples in brines showed a mark decrease in viscosity due to charge shielding of the carboxylate groups by cations. Polymer precipitated in $CaCl_2$ due to complexion. Dynamic aged PHPA in freshwater showed a decrease in viscosity due to molecular weight degradation. Addition of oxygen scavenger in dynamic aged PHPA in brine reduced the rate of molecular weight degradation as a result they displayed slightly higher viscosity than static aged sample.

5. Static aged AMPS fluids showed lower viscosity in brines because of charge shielding by cations. Viscosities in $CaCl_2$ (as opposed to PHPA) are higher due to the hydrophobic interactions. Dynamic aged AMPS polymer in water shows a decreased viscosity due to molecular weight degradation. Marked decrease in viscosity of dynamic aged AMPS samples in $CaCl_2$ is either due to the degradation of hydrophobic groups or due to hydrolysis of the sulfonate group.

6. Fluid loss properties of all samples were studied using a low pressure API filter press. In absence of bridging agent very high cumulative filtrate volumes were observed in all freshwater samples.

7. Xanthan samples in brines displayed lower cumulative filtrate volumes due to inter-molecular association of Xanthan molecules. Also salt fines are generated that act as bridging agents. PHPA recorded very large cumulative filtrate volumes in brines due to collapse of the polymer chain. AMPS displayed higher cumulative filtrate volumes in $CaCl_2$ due to salt precipitation caused by greater polymer dissolution.

8. Hydration tests were conducted to examine the ease of hydration of polymers in different base fluids. Liquid polymers hydrated rapidly in freshwater but they require proper mixing to obtain optimum viscosity.

9. Xanthan is slightly anionic so it takes longer to hydrate, both in freshwater and brines. PHPA and AMPS hydrate slowly in presence of cations.

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Nomenclature

K_v = Viscometer consistency index, ($lb_f s^n/ft^2$)
n = Flow behavior index, dimensionless
N = Spring factor (equals 1.0 for number 1 spring and 0.2 for 1/5 spring)
T = Temperature, (°F)

Greek Symbols

γ_w = Wall shear rate, (s^{-1})
θ_i = Fann 35 viscometer reading at i^{th} rpm, dimensionless
μ_a = Apparent viscosity, (cP)
μ_s = Solvent viscosity, (cP)
ρ = Brine density, (lb/gal)
τ_w = Wall shear stress, (lb_f/ft^2)

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Table 1 Apparent viscosity of polymers in freshwater - Static Aging at 75 °F

Polymer	60 lbm/Mgal Xanthan - freshwater	30 lbm/Mgal PHPA - freshwater	40 lbm/Mgal AMPS - freshwater
Shear rate (sec^{-1})	Apparent Viscosity (cP)		
5.1	1419	638	703
10.2	806	410	450
170.3	81	69	73
340.6	**46**	**44**	**47**
510.9	**33**	**34**	**36**
1021.8	**19**	**22**	**23**

Table 2 Apparent viscosity of Xanthan fluids - Static Aging at 75 °F

Fluid	60 lbm/Mgal Xanthan - freshwater			60 lbm/Mgal Xanthan - 9.2 ppg KCl			60 lbm/Mgal Xanthan - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr
5.1	1369	1366	1521	2339	2335	2292	2171	2080	1987
10.2	777	775	865	1316	1315	1304	1400	1340	1288
170.3	78	78	87	127	128	132	236	225	222
340.6	44	44	50	72	72	75	152	145	144
510.9	32	32	36	51	51	54	118	112	112
1021.8	18	18	20	29	29	31	76	72	72

Table 3 Apparent viscosity of PHPA fluids - Static Aging at 75 °F

Fluid	30 lbm/Mgal PHPA - freshwater			30 lbm/Mgal PHPA - 9.2 ppg KCl			30 lbm/Mgal PHPA - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr
5.1	679	590	645	26	49	49	21	21	21
10.2	431	385	415	21	39	40	17	17	17
170.3	68	68	70	9	14	17	7	8	8
340.6	43	44	45	7	11	14	6	6	6
510.9	33	34	35	6	10	12	5	6	6
1021.8	21	22	22	5	7	10	4	5	5

Table 4 Apparent viscosity of AMPS fluids - Static Aging at 75 °F

Fluid	40 lbm/Mgal AMPS - freshwater			40 lbm/Mgal AMPS - 9.2 ppg KCl			40 lbm/Mgal AMPS - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr	Hydration	24 hr	48 hr
5.1	686	686	737	49	66	71	50	48	47
10.2	440	441	469	39	52	55	44	44	44
170.3	72	73	74	16	19	20	27	30	33
340.6	46	47	47	13	15	16	24	27	30
510.9	36	36	36	11	13	14	22	25	29
1021.8	23	23	23	9	10	11	20	23	27

Table 5 Apparent viscosity of all fluids - Static Aging at 75 °F

Fluid	Freshwater			9.2 ppg KCl			11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Xanthan	PHPA	AMPS	Xanthan	PHPA	AMPS	Xanthan	PHPA	AMPS
5.1	1419	638	703	2322	41	62	2079	21	48
10.2	806	410	450	1311	33	49	1343	17	44
170.3	81	69	73	129	13	18	228	8	30
340.6	46	44	47	73	11	14	147	6	27
510.9	33	34	36	52	10	12	114	6	25
1021.8	19	22	23	29	8	10	74	5	23

Table 6 n and K_v of Static Aged Samples

Fluid	Hydration		24 hr		48 hr	
	n	K_v	*n*	K_v	*n*	K_v
Xanthan in freshwater	0.182	0.109	0.182	0.108	0.186	0.120
Xanthan in KCl	0.170	0.189	0.171	0.188	0.186	0.180
Xanthan in $CaCl_2$	0.367	0.127	0.365	0.122	0.375	0.115
PHPA in freshwater	0.345	0.041	0.383	0.034	0.365	0.038
PHPA in KCl	0.695	0.0009	0.644	0.002	0.705	0.002
PHPA in $CaCl_2$	0.708	0.0007	0.711	0.0007	0.715	0.0007
AMPS in freshwater	0.357	0.041	0.361	0.041	0.345	0.045
AMPS in KCl	0.682	0.002	0.628	0.003	0.611	0.003
AMPS in $CaCl_2$	0.824	0.0014	0.859	0.0013	0.895	0.0012

Table 7 Apparent viscosity of Xanthan fluids - Dynamic Aging at 75 °F

Fluid	60 lbm/Mgal Xanthan - freshwater			60 lbm/Mgal Xanthan - 9.2 ppg KCl			60 lbm/Mgal Xanthan - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr
5.1	2418	2411	2606	2770	2893	3085	2272	2395	2333
10.2	1334	1342	1449	1522	1593	1691	1439	1531	1516
170.3	120	125	134	134	141	148	225	249	263
340.6	66	69	74	74	78	81	143	159	171
510.9	47	49	53	52	55	57	109	122	133
1021.8	26	27	29	28	30	31	69	78	86

Table 8 Apparent viscosity of PHPA fluids - Dynamic Aging at 75 °F

Fluid	30 lbm/Mgal PHPA - freshwater			30 lbm/Mgal PHPA - 9.2 ppg KCl			30 lbm/Mgal PHPA - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr
5.1	267	256	232	49	49	53	15	15	15
10.2	182	177	164	39	39	42	13	13	13
170.3	38	39	40	15	16	16	8	8	8
340.6	26	27	28	12	12	13	7	7	8
510.9	21	22	23	11	11	11	6	7	7
1021.8	14	15	16	8	9	9	5	6	6

Table 9 Apparent viscosity of AMPS fluids - Dynamic Aging at 75 °F

Fluid	40 lbm/Mgal AMPS - freshwater			40 lbm/Mgal AMPS - 9.2 ppg KCl			40 lbm/Mgal AMPS - 11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr	Cooled	24 hr	48 hr
5.1	325	292	292	72	77	82	20	20	25
10.2	222	204	205	55	59	62	18	18	22
170.3	47	47	49	18	19	20	11	11	13
340.6	32	33	34	14	15	15	10	10	11
510.9	26	26	28	12	13	13	9	9	11
1021.8	18	18	19	9	10	10	8	8	9

Table 10 Apparent viscosity of all fluids - Dynamic Aging at 75 °F

Fluid	Freshwater			9.2 ppg KCl			11.2 ppg $CaCl_2$		
Shear rate (sec^{-1})	Apparent Viscosity (cP)								
	Xanthan	PHPA	AMPS	Xanthan	PHPA	AMPS	Xanthan	PHPA	AMPS
5.1	2478	252	303	2916	50	77	2334	15	22
10.2	1375	174	210	1602	40	59	1495	13	19
170.3	126	39	48	141	16	19	246	8	12
340.6	70	27	33	77	12	15	158	7	10
510.9	50	22	27	55	11	12	121	7	10
1021.8	27	15	18	30	9	9	78	6	9

Table 11 n and K_v of Dynamic Aged Samples

Fluid	Cooled		24 hr		48 hr	
	n	K_v	*n*	K_v	*n*	K_v
Xanthan in freshwater	0.143	0.204	0.155	0.200	0.153	0.217
Xanthan in KCl	0.136	0.237	0.139	0.246	0.133	0.265
Xanthan in $CaCl_2$	0.331	0.172	0.378	0.147	0.383	0.140
PHPA in freshwater	0.445	0.014	0.466	0.013	0.495	0.011
PHPA in KCl	0.665	0.002	0.675	0.002	0.663	0.002
PHPA in $CaCl_2$	0.805	0.0004	0.834	0.0004	0.839	0.0004
AMPS in freshwater	0.449	0.017	0.478	0.014	0.489	0.014
AMPS in KCl	0.605	0.003	0.606	0.003	0.599	0.003
AMPS in $CaCl_2$	0.829	0.0006	0.831	0.0006	0.815	0.0007

Table 12 Fluid loss properties of Xanthan fluids

Xanthan in freshwater		Xanthan in 9.2 ppg KCl		Xanthan in 11.2 ppg $CaCl_2$	
Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)
0	0	0	0	0	8
0.5	48	1.5	6	1.5	13
1	79	5	8	5	14
1.5	114	7.5	9	7.5	15
2	142	10	10	10	16
2.5	164	15	12	15	17
3	187	20	13	20	18
3.5	208	25	14	25	19
4	232	30	15	30	21
Filter Cake Thickness	1/32"	3/32"		5/32"	
Spurt Loss (ml)	-	-		8	

Table 13 Fluid loss properties of PHPA fluids

PHPA in freshwater		PHPA in 9.2 ppg KCl		PHPA in 11.2 ppg $CaCl_2$	
Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)
0	0	0	0	0	0
0.5	7	1.5	18	1.5	11
1	9	5	44	5	31
1.5	13	7.5	62	7.5	43
2	16	10	78	10	54
5	30	15	106	15	74
7.5	42	20	131	20	89
10	52	25	154	25	103
15	69	30	178	30	117
20	82				
25	92				
30	101				
Filter Cake Thickness	1/32"	1/32"		1/32"	
Spurt Loss (ml)	-	-		-	

Table 14 Fluid loss properties of AMPS fluids

AMPS in freshwater		AMPS in 9.2 ppg KCl		AMPS in 11.2 ppg $CaCl_2$	
Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)	Time (min)	Cumulative filtrate volume (ml)
0	0	0	0	0	0
0.5	9	1.5	12	1.5	8
1	13	5	35	5	18
1.5	16	7.5	52	7.5	24
2	20	10	70	10	29
3	27	15	95	15	41
4	34	20	119	20	50
5	40	25	138	25	60
7.5	58	30	153	30	68
10	74				
12	88				
15	106				
20	136				
25	166				
30	196				
Filter Cake Thickness	1/32"	1/32"		1/32"	
Spurt Loss (ml)	-	-		-	

Table 15 Fluid preparation plus transfer time for hydration test

Fluid	Total time (Mixing + Transfer) in sec
Xanthan in freshwater	45
Xanthan in KCl	45
Xanthan in $CaCl_2$	48
PHPA in freshwater	46
PHPA in KCl	46
PHPA in $CaCl_2$	46
AMPS in freshwater	46
AMPS in KCl	46
AMPS in $CaCl_2$	45

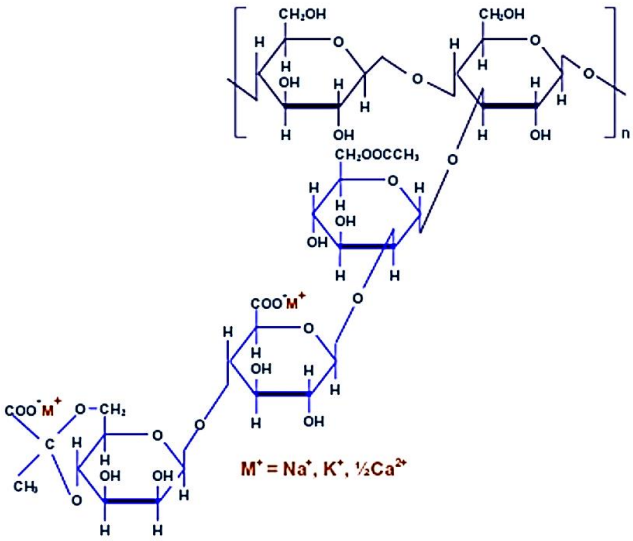

Figure 1 Xanthan monomer (Wolbers[35])

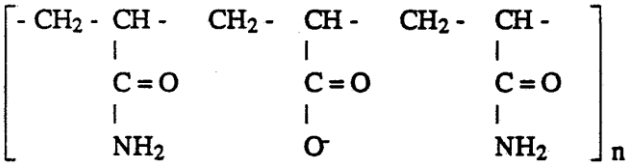

Figure 2 PHPA monomer (Luetzelschwab[10])

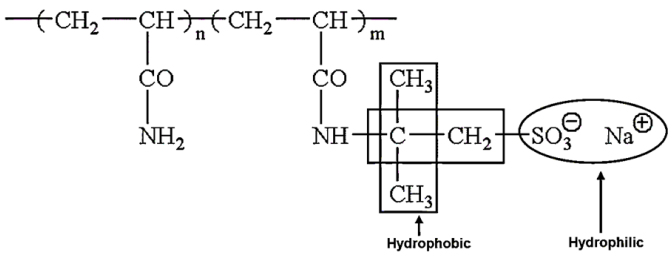

Figure 3 AMPS monomer (Boles[1])

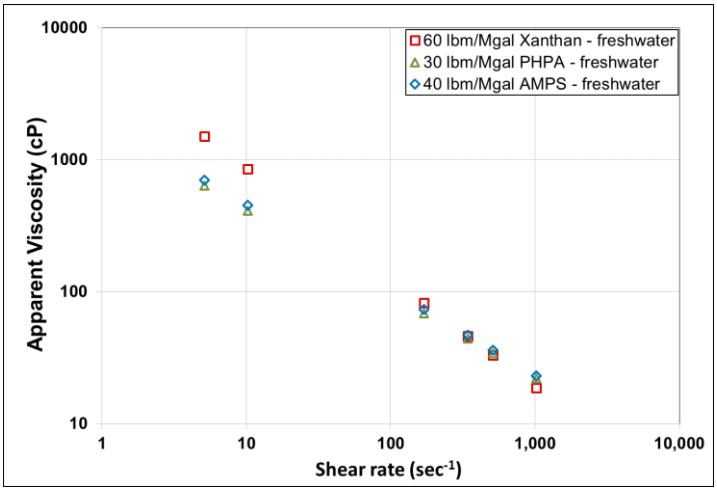

Figure 4 Apparent viscosity of polymers in freshwater

Figure 5 173-00-RC OFITE 5-Roller Oven

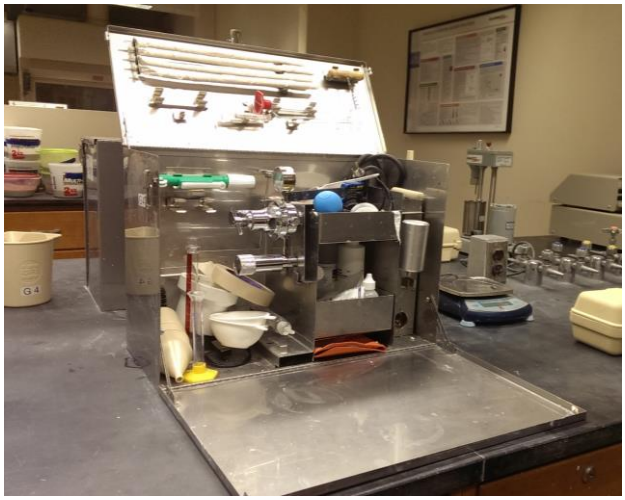

Figure 6 OFITE Low pressure Wall Mount Filter press

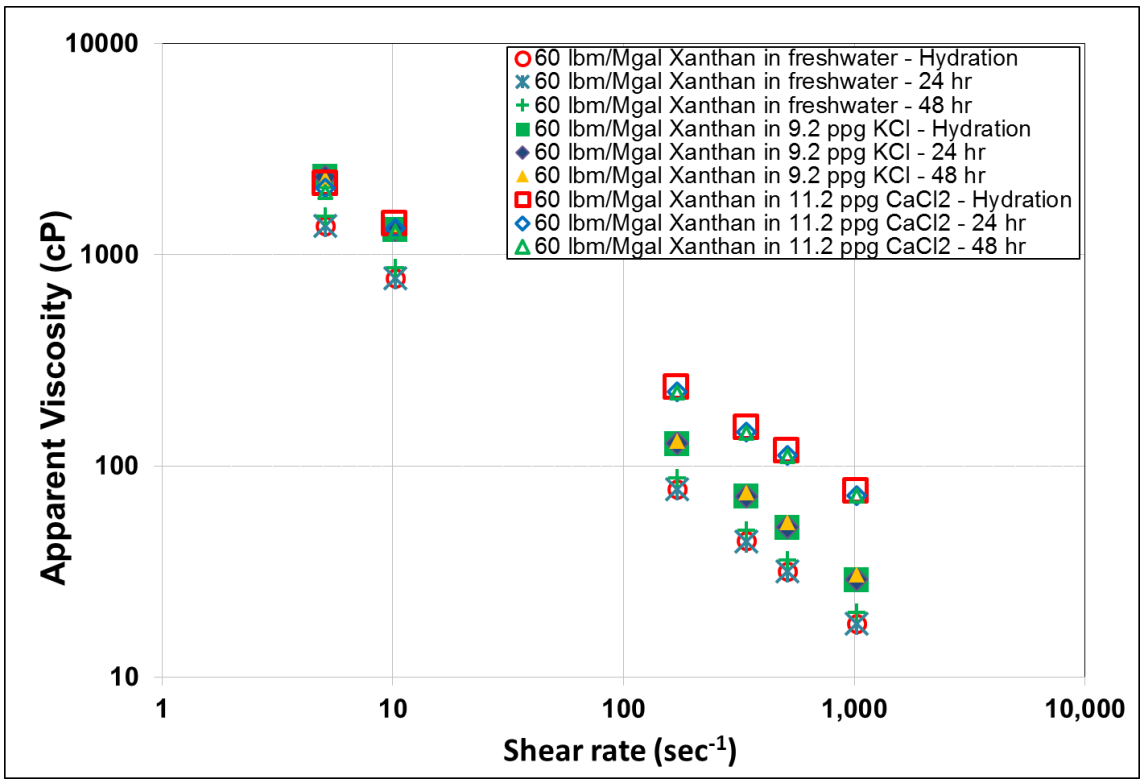

Figure 7 Apparent viscosity of Xanthan fluids - Static Aging at 75 °F

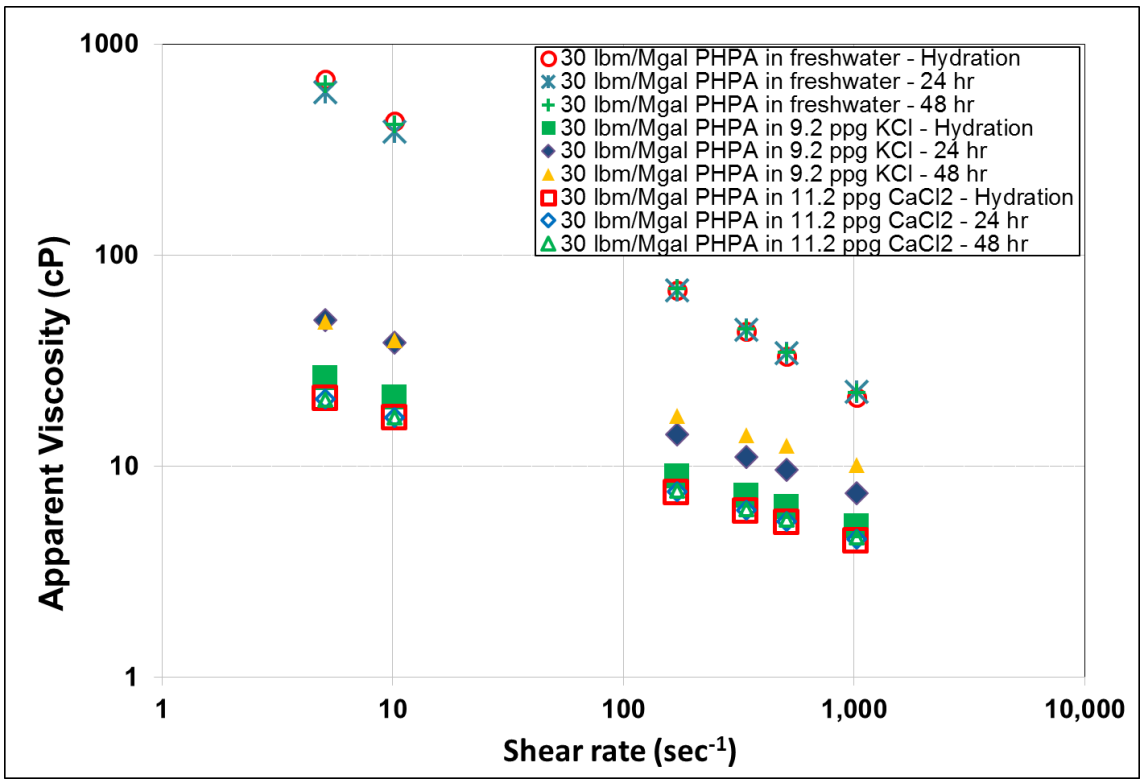

Figure 8 Apparent viscosity of PHPA fluids - Static Aging at 75 °F

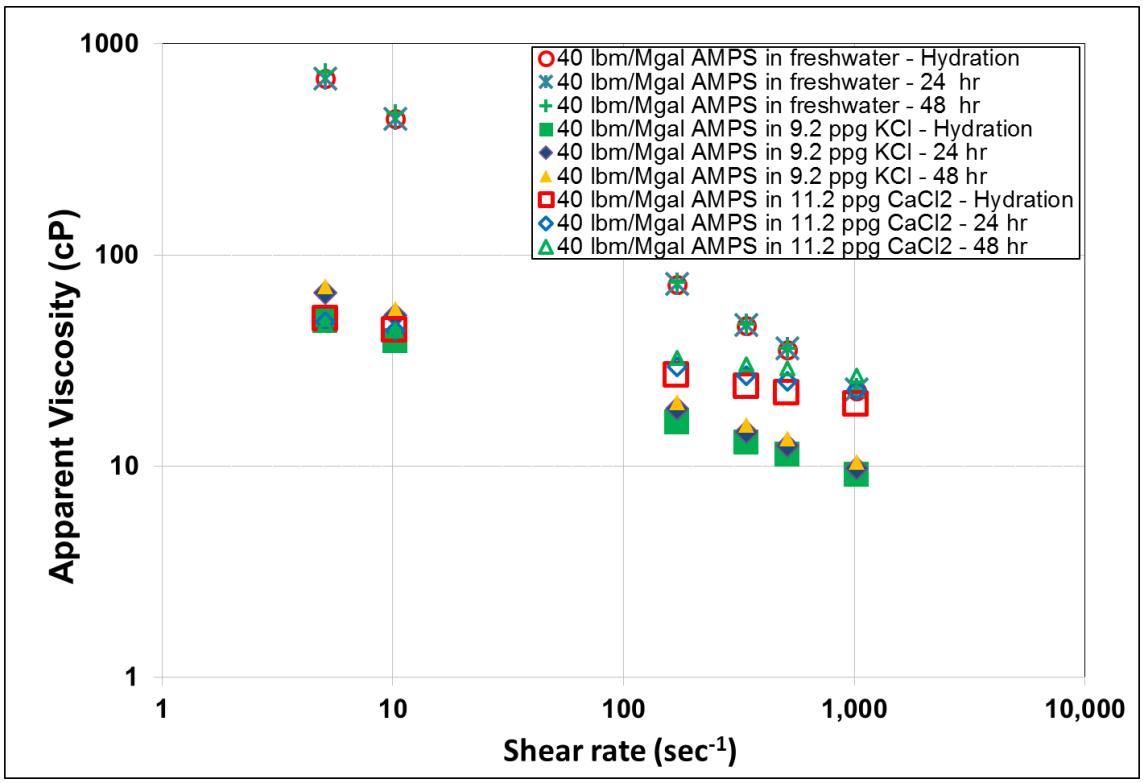

Figure 9 Apparent viscosity of AMPS fluids - Static Aging at 75 °F

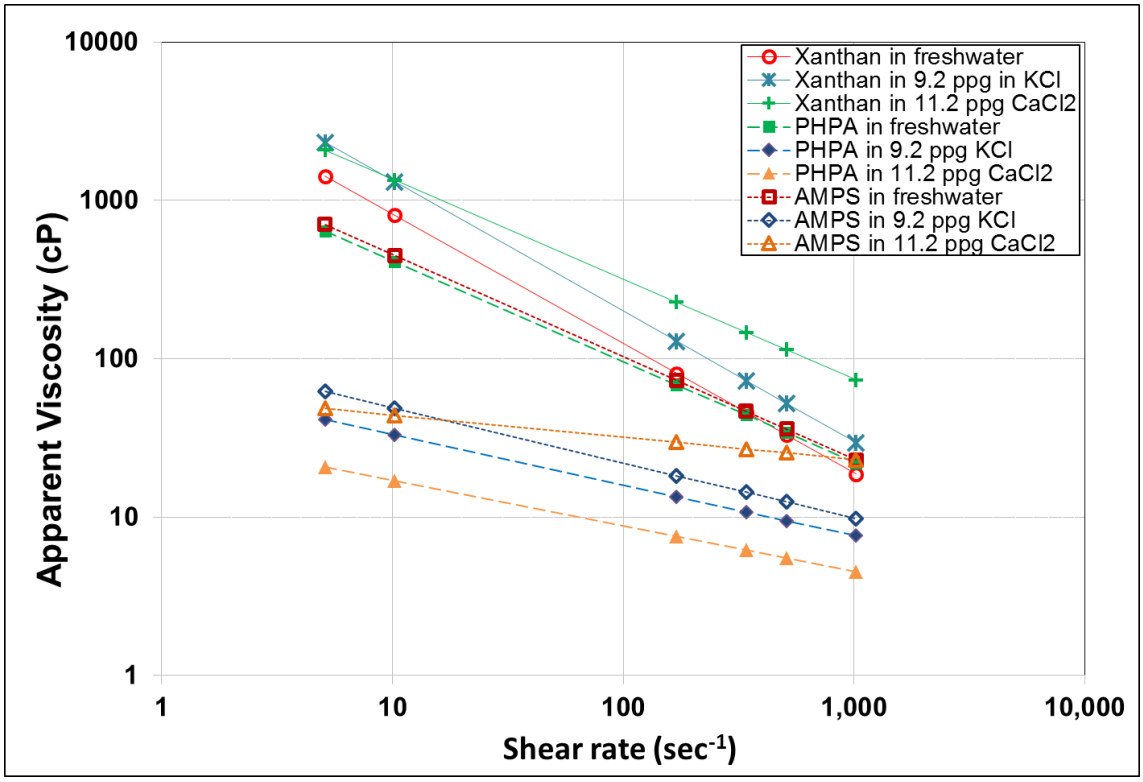

Figure 10 Apparent viscosity of all fluids - Static Aging at 75 °F

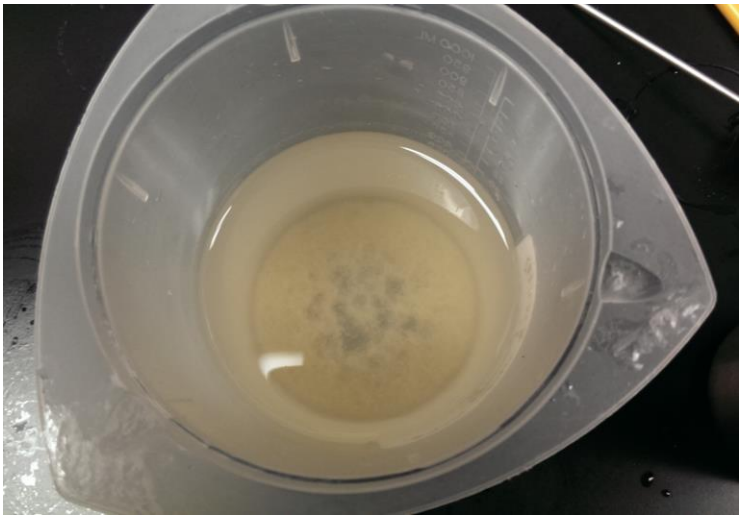

Figure 11 Precipitation of PHPA in 11.2 lb/gal $CaCl_2$

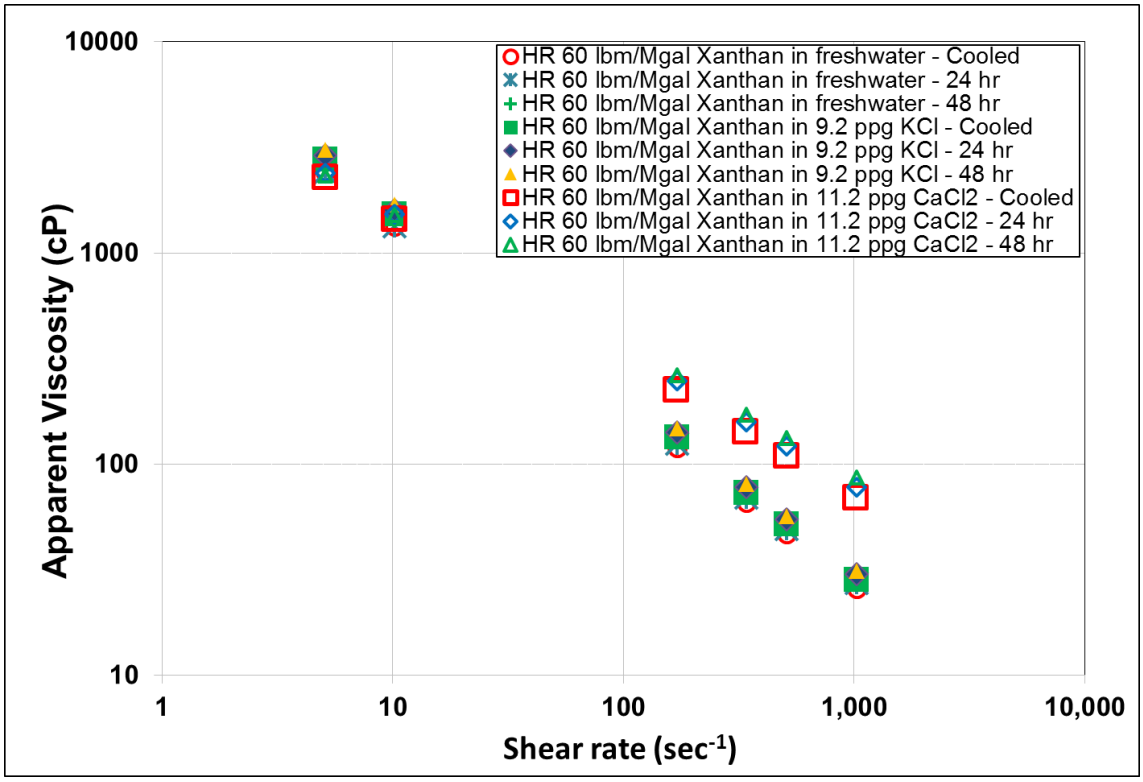

Figure 12 Apparent viscosity of Xanthan fluids - Dynamic Aging at 75 °F

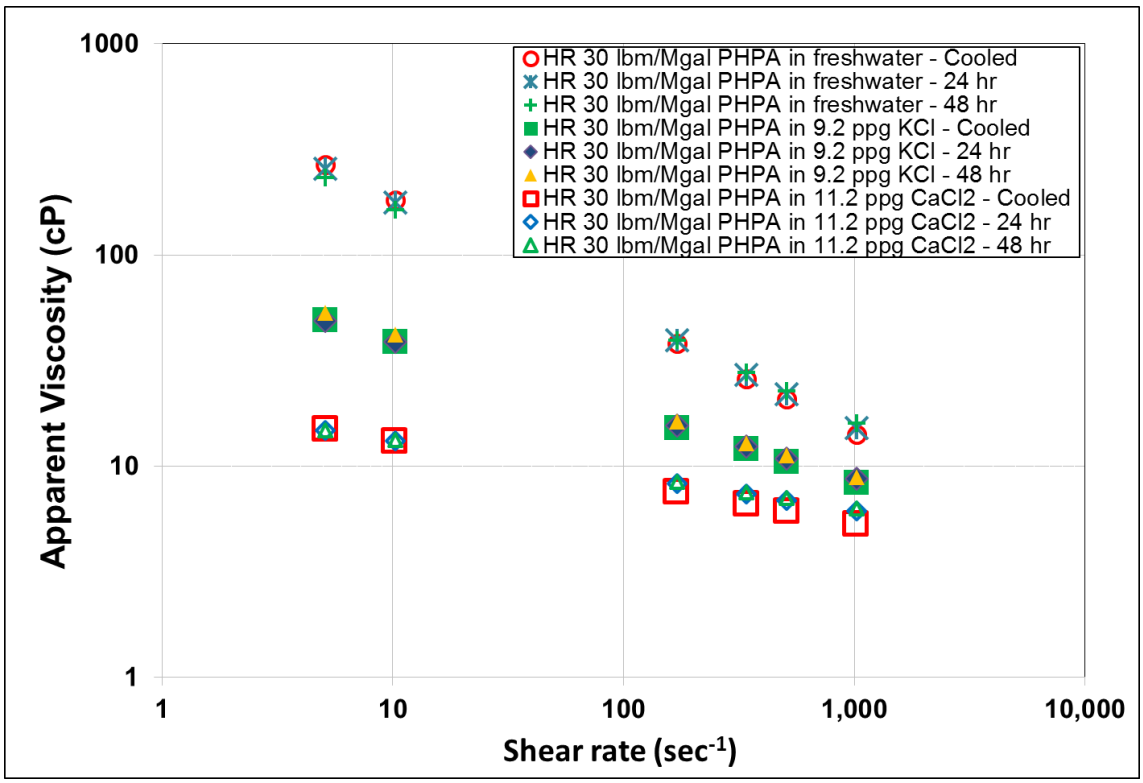

Figure 13 Apparent viscosity of PHPA fluids - Dynamic Aging at 75 °F

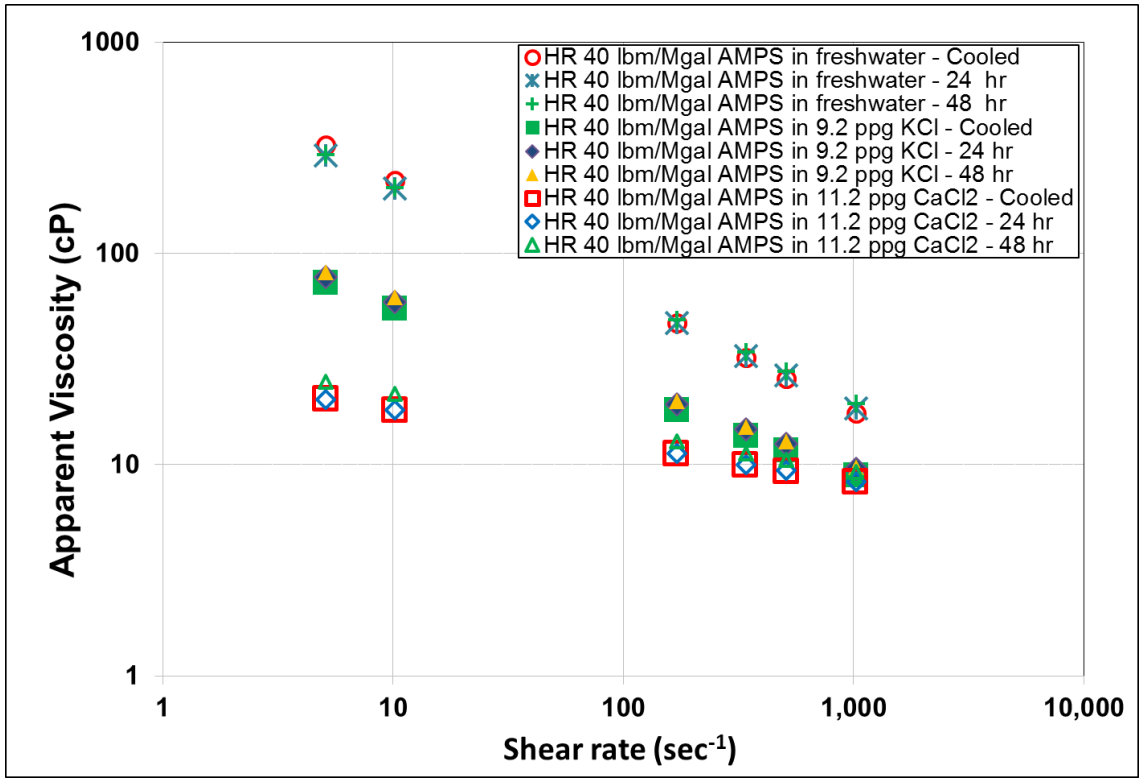

Figure 14 Apparent viscosity of AMPS fluids - Dynamic Aging at 75 °F

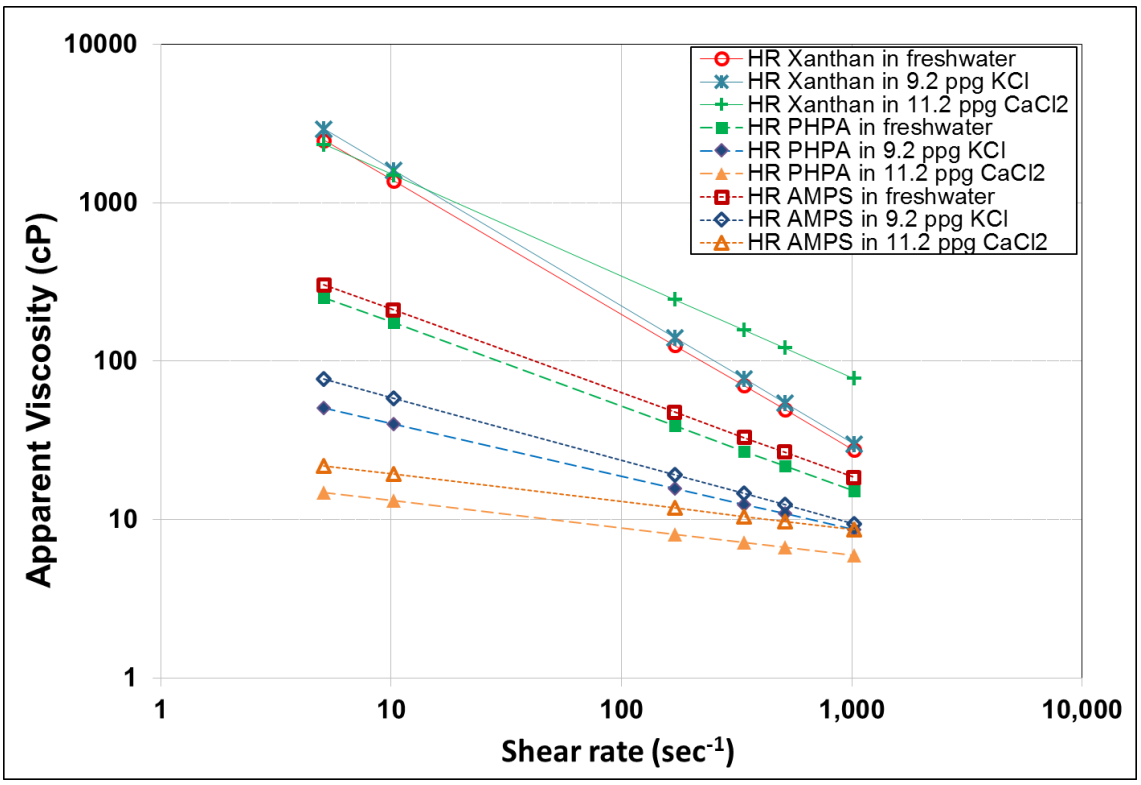

Figure 15 Apparent viscosity of all fluids - Dynamic Aging at 75 °F

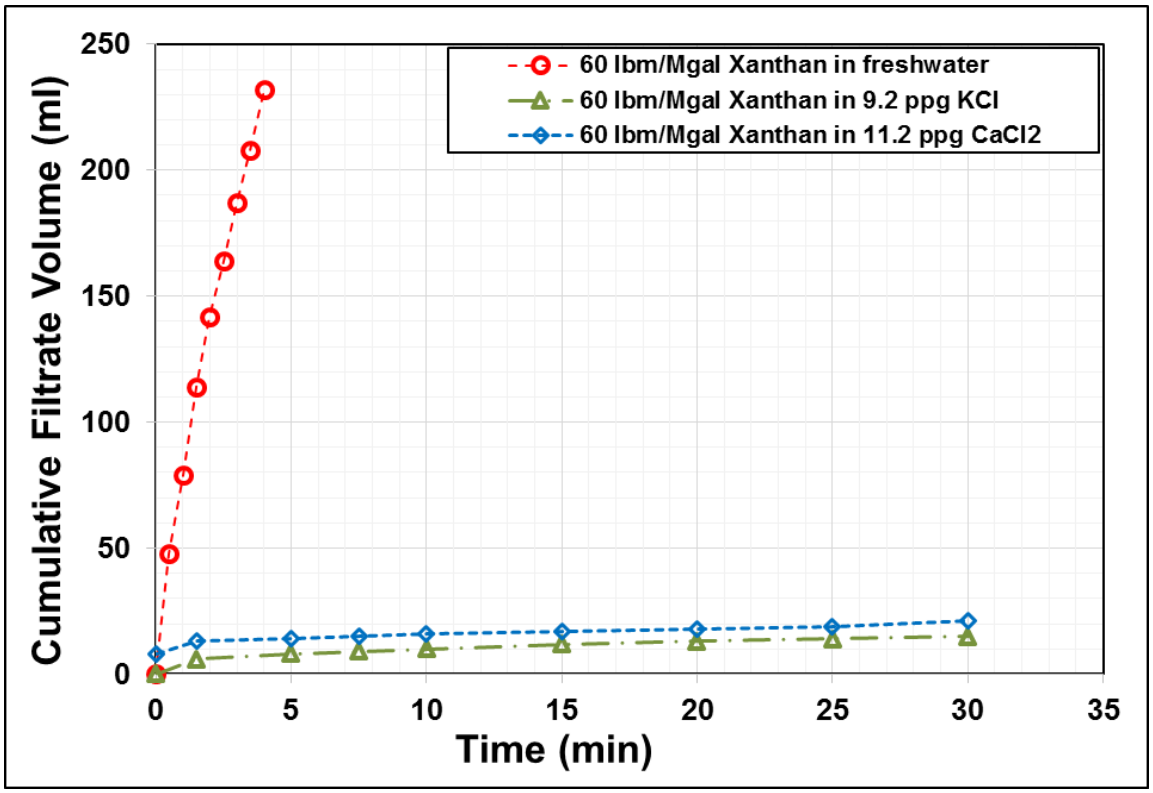

Figure 16 Filtrate volume versus time for Xanthan fluids

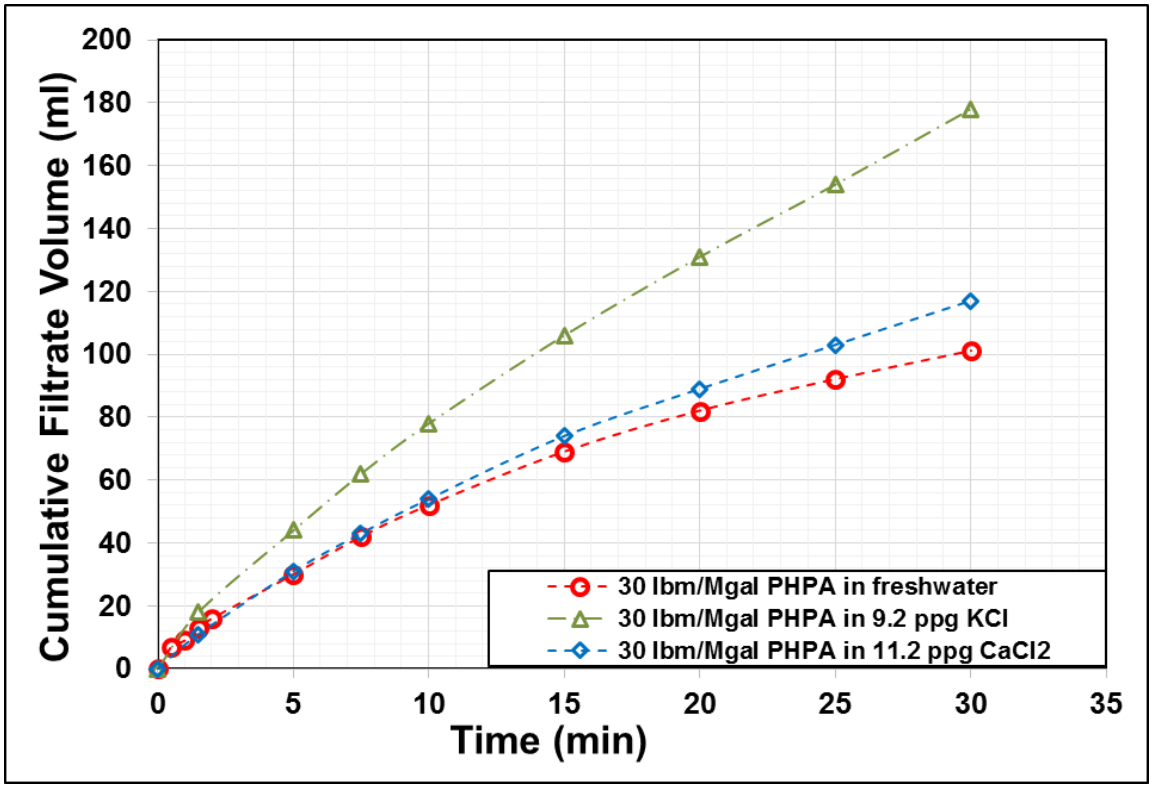

Figure 17 Filtrate volume versus time for PHPA fluids

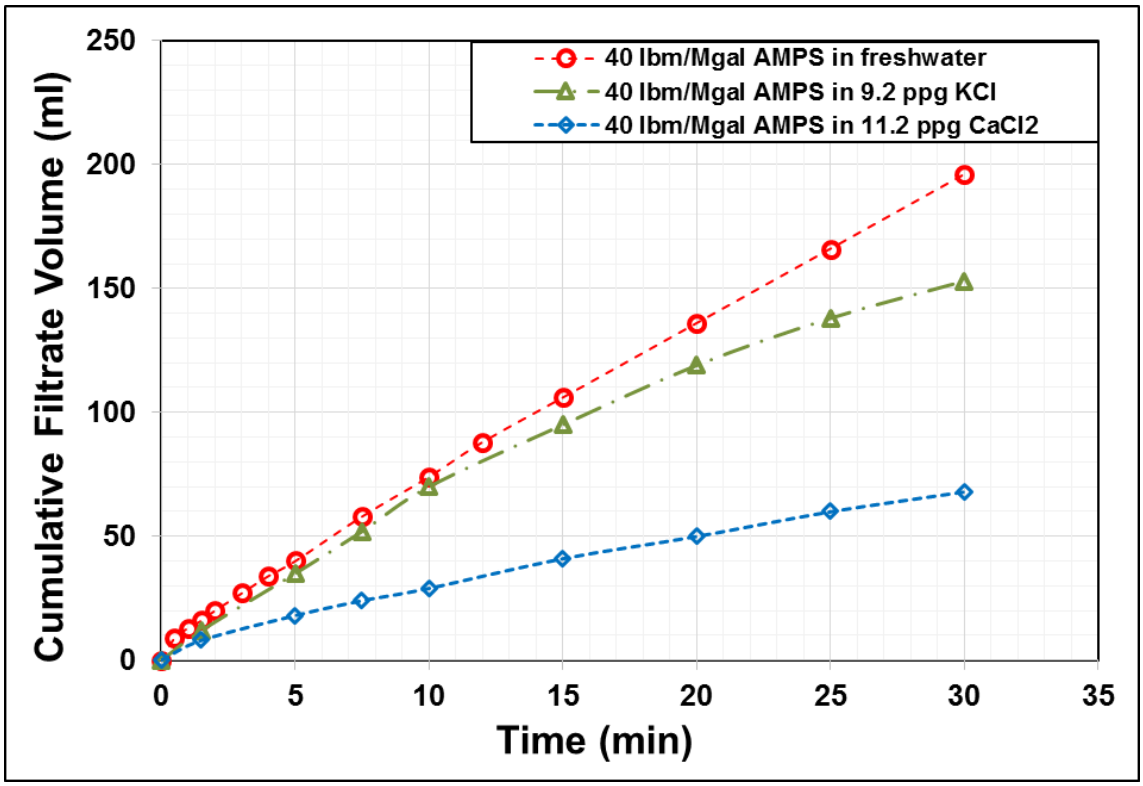

Figure 18 Filtrate volume versus time for AMPS fluids

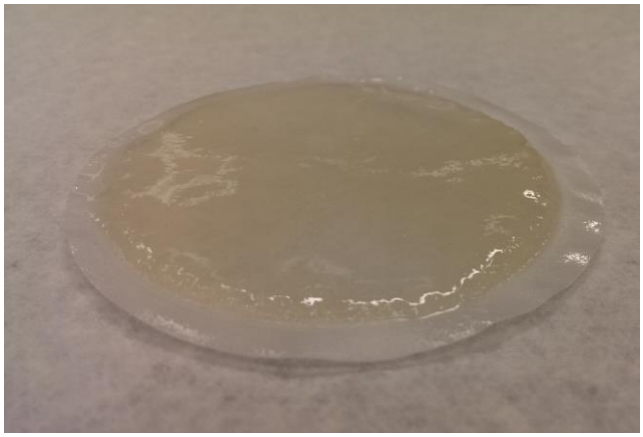

Figure 19 Filter Cake for Xanthan in 11.2 lb/gal $CaCl_2$

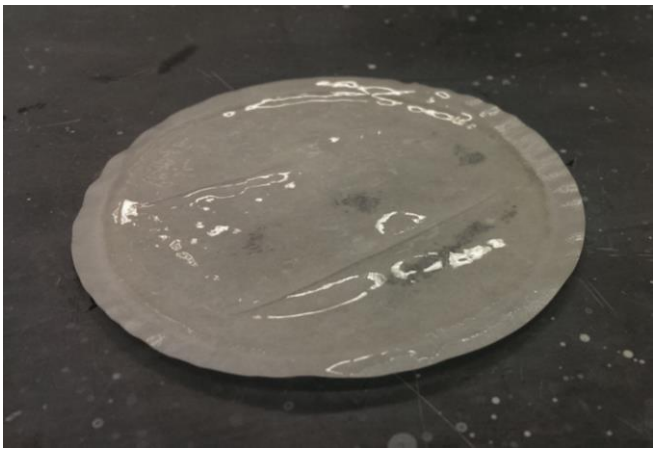

Figure 20 Filter Cake for Xanthan in 9.2 lb/gal KCl

Figure 21 Commercial Blender used for mixing fluids for hydration test

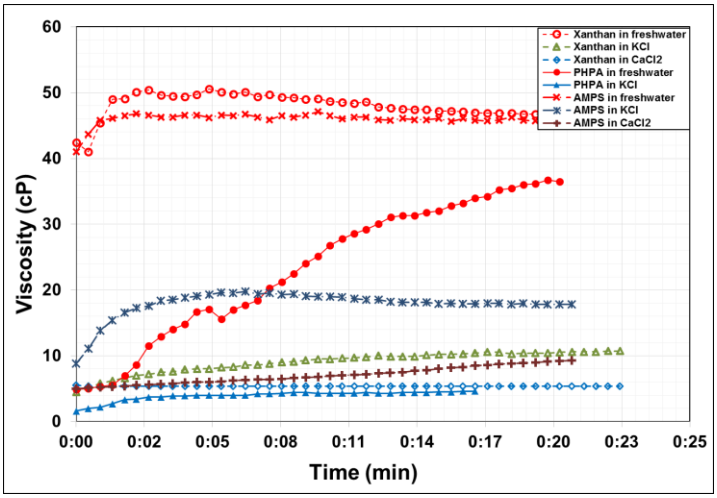

Figure 22 Rate of hydration with time