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Impact and Interaction of Polymers, NACL and Cellulose Particles on the Rheological Properties of Drilling Fluids under Conditions of Thermal and Mechanical Wear

Karl Ronny Klungtvedt[1], Arild Saasen[2]

[1]European Mud Company, NO-4033 Stavanger, Norway
[2]University of Stavanger, NO-4036 Stavanger, Norway

ABSTRACT

Water-based drilling fluids are often prepared by combining polymers for viscosity and filtration control and salts for inhibition and density into a freshwater or seawater base fluid. For certain drilling operations, the desired drilling fluid density may limit the potential concentrations of salts, whereas high temperature stability may still be required. In the following the interaction effects between polymers, salts and cellulose based particles on fluid viscosity and fluid loss, and any implications for optimising recipes for low density water-based drilling fluids are presented.

The viscosity impact of xanthan gum and crosslinked starch were highly dependent on the presence of salts and cellulose particles when exposed to hot-rolling at 90°C. It was found that either cellulose particles or salts were needed for the xanthan gum and crosslinked starch to retain the viscosity impact after exposure to high temperatures and mechanical wear. In contrast, the viscosity impact of polyanionic cellulose showed less viscosity interaction effects in the presence of salts and cellulose particles. A statistically significant relationship between the calculated yield stress of the fluid and the API fluid loss was identified, indicating that a higher yield strength may lead to lower fluid loss. In the tests conducted with freshwater, the addition of a selected cellulose particle blend led to more stable fluid rheology, higher fluid yield strength and lower fluid loss.

In general, the introduction of mechanical wear during the hot-rolling process was found to reduce the viscosity impact of the polymers in addition to the thermal degradation, thus indicating that the rheological stability of the fluid is dependent on grinding or shearing during circulation in the wellbore.

INTRODUCTION

Drilling of depleted hydrocarbon reservoirs and geothermal wells in some cases have common challenges. For depleted reservoirs, the drilling fluid density is normally kept at a minimum in order to reduce the differential pressure during drilling, and thereby prevent effects such as induced fracturing and lost circulation. High shear rate rheology has been found to impact fluid loss into natural fractures, as a higher viscosity reduces the flow into the fractures[1].

Geothermal wells are conventionally drilled with water-based drilling fluids and are exposed to high temperatures, giving a high risk of polymer degradation and drilling fluid instability[2]. An increased understanding of how the temperature stability of polymers vary with the presence of other chemicals in the drilling fluid is thus of great importance. Xanthan gum is an anionic polysaccharide typically used as a viscosifier in water-based drilling fluids. Its temperature stability is dependent on the other chemicals in the drilling fluid, but 120°C is often considered at as limit beyond which it starts to degrade[3]. Polyanionic cellulose (PAC) is another anionic polymer, but in contrast to xanthan gum it is primarily used as a filtration control agent and secondary as a viscosifier. Another commonly used filtration control agent is starch, which is a polysaccharide. These polymers interact through electrostatic forces, hydrogen bonds and entanglement in aqueous solutions, thereby impacting the fluid viscosity.

Conventional bridging materials such as calcium carbonate and graphite are generally regarded to be inert, and thus have little interaction effect with xanthan gum, poly anionic cellulose and starch. Ground cellulose, on the other hand is known to form hydrogen bonds and van der Waals bonds in aqueous solutions[4]. In the following it is discussed how this interaction could impact the thermal stability of polymers conventionally used in water-based drilling fluids with regards to retaining fluid viscosity.

The main objective is to show the thermal stability of selected drilling fluid additives in aqueous solutions to identify combinations of products which may yield a more stable fluid viscosity profile in conditions where salts may not be desirable to use due to fluid density impact. Hereunder to show:

- potential interaction between commonly used drilling fluid polymers on effect on thermal stability
- potential interaction between commonly used drilling fluid polymers and a selected cellulose particle blend and effect on thermal stability

RHEOLOGICAL MODEL USED FOR ANALYSING AND COMPARING THE DIFFERENT FLUID COMPOSITIONS

For comparing the rheological properties of the different fluids, the Herschel-Bulkley model, initially modified by Nelson and Ewoldt[5] and later modified by Saasen and Ytrehus[6], was used. The modified version presented in equation (1.0) isolates the descriptive parameters into a yield stress (τ_y), a surplus shear stress (τ_s) at a characteristic shear rate ($\dot{\gamma}_s$), and a curvature index (n). There three parameters are not dependent and can thus be used for comparing the properties of different fluids.

$$\tau = \tau_y + \tau_s \left(\frac{\dot{\gamma}}{\dot{\gamma}_s}\right)^n \tag{1}$$

The viscosity measurements were conducted using an Ofite Model 900 Viscometer, which permits readings at shear rates from to 1.70 (1/s) to 1021 (1/s). The yield stress was calculated as 2 times the shear stress at 1.7 (1/s) minus the shear stress at 3.4 (1/s). The characteristic shear rate was selected to be 170.2 (1/s), so n values can be calculated for specific shear rates by comparing the shear stress at that shear rate with the shear stress at the characteristic shear rate. All tests in the study were conducted at a reference temperature of 49°C.

MATERIALS USED FOR TESTING AND TEST PROCEDURES

The tests were conducted using materials conventionally used in water-based drilling fluid, and at concentrations that could typically be used for drilling purposes. The difference between the tests is then either in the form of which materials are included in the specific recipe, or the treatment of the fluid before testing. Tests are conducted before hot-rolling and after hot-rolling and with/without the inclusion of a threaded steel rod to simulate exposure to mechanical wear as per Klungtvedt and Saasen[10]. Table 1 lists the materials used for testing and the recipe structure.

TABLE 1: Materials used in the testing

Product name	Description	Function	Concentrations used for 350ml sample	Code used in tests
Barazan	Xanthan gum	Viscosity	1.5 g for relevant samples	X
N-Dril HT Plus	Cross linked starch	Filtration control	6.0 g for relevant samples	N
Dextride E	Modified starch	Filtration control	6.0 g for relevant samples	D
PAC-L	Poly anionic cellulose (PAC)	Viscosity and filtration control	5.0 g for relevant samples	P
AURACOAT UF	Cellulose particle blend	Filtration control and bridging material	5.0 g for relevant samples	A
NaCl	NaCl salt	Density, inhibition, and polymer stabilization	95.0 g for relevant samples	S
Calcium Carbonate	Sieved $CaCO_3$ with particle size <50µm	Density and bridging material	20.0 g for relevant samples	C
Soda Ash	Na_2CO_3	Treat Ca^{2+} contamination	0.02 g	
Caustic Soda	NaOH	Alkalinity control	0.25 g	
Magnesium Oxide	MgO	Alkalinity control, pH buffer	1.0 g	
Water	H_2O	Base fluid	As required	

Each test is named using the following convention. “Number”, “Product Code” with the annex “-R” if a degradation rod was included in the hot-rolling process. following the code shown in **Table 1** for the materials used for testing. As an example, Fluid 9 containing Xanthan Gum, PAC-L and NaCl is denoted “9XPS”. The full recipes are listed in the appendix, **Table 1** and the full fluid description according to the modified Herschel-Bulkley model is presented in Equation 1. Fluid compositions 1-6 were designed to analyse the viscosity impact of the individual additives X, N, D, P and A separately, before analysing interaction effects.

RESULTS AND DISCUSSIONS

Xanthan gum

Fig.s 1 and 2 shows the flow curves of the xanthan gum solution, X, before and after hot-rolling at temperatures of 90°C and 20°C, respectively. From **Fig. 1**, it is clear that the viscosity profile is shear thinning before hot-rolling, and that the overall viscosity falls significantly after hot-rolling. The yield stress, τ_y, values fell with 88-95% and the surplus stress, τ_s,values fell with 50-64%. Whilst the curvature, n, values increased from 0.34-0.37 before hot-rolling to 0.42-0.66 after hot rolling. Figure 2 shows the flow curves for the same fluid recipe, using a rolling temperature of 20°C. In this case, the viscosity of the fluid is largely unchanged, however, the τ_y values fell with 19% for the test without the degradation rod and 28% for the test with the degradation rod. The τ_s values and the n values showed no significant changes. When tested in isolation, it is clear that the viscosity impact of xanthan gum is highly sensitive to thermal degradation at a temperature of 90°C.

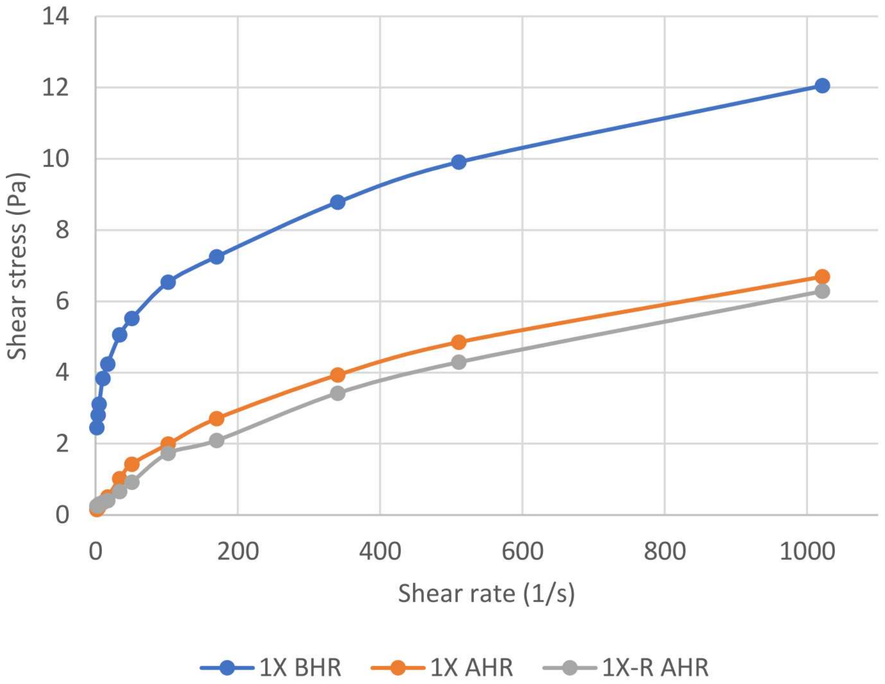

FIGURE 1: Flow curves of fluid 1X with xanthan gum measured before and after hot-rolling at 90°C

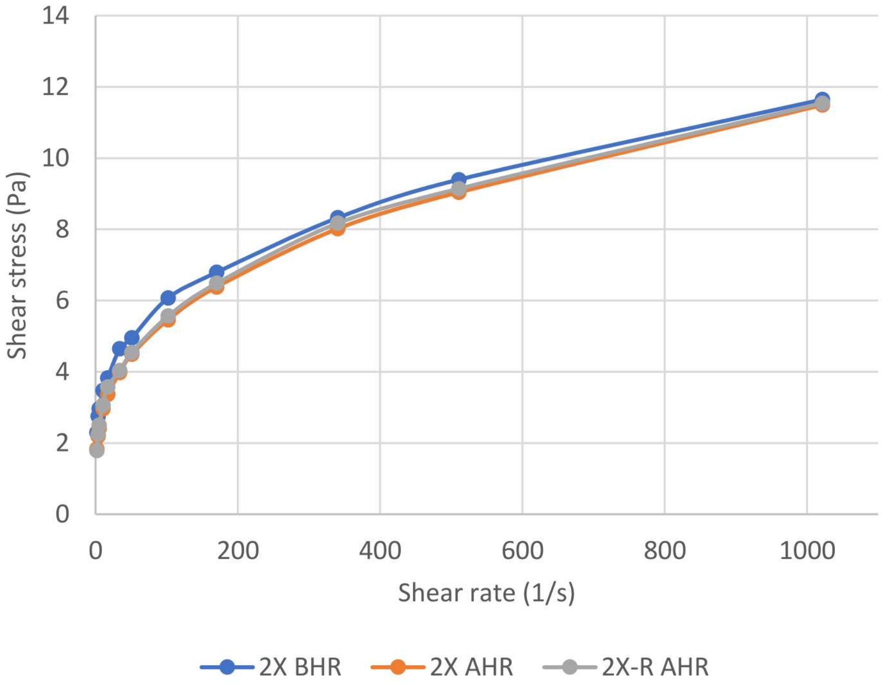

FIGURE 2: Flow curves of fluid 1X with xanthan gum measured before and after hot-rolling at 20°C

Starch

Fig.s 3 and 4 show the flow curves of the fluid with the crosslinked starch N and the modified starch D. The fluids with modified starch N experience 60% reduction in τ_y values for both samples after hot-rolling at 90°, 41-63% reduction in τ_s values and an increase in n values from 0.29-0.47 to 0.55-1.00. The thermal exposure is thus significantly reducing the viscous impact of the starch. The flow curves for the fluid with the modified starch D, show that the viscous impact is low when comparing the fluid before and after hot-rolling. It should also be noted that the shear stress readings of less than 1 Pa are less precise, due to the limited precision of the viscometer.

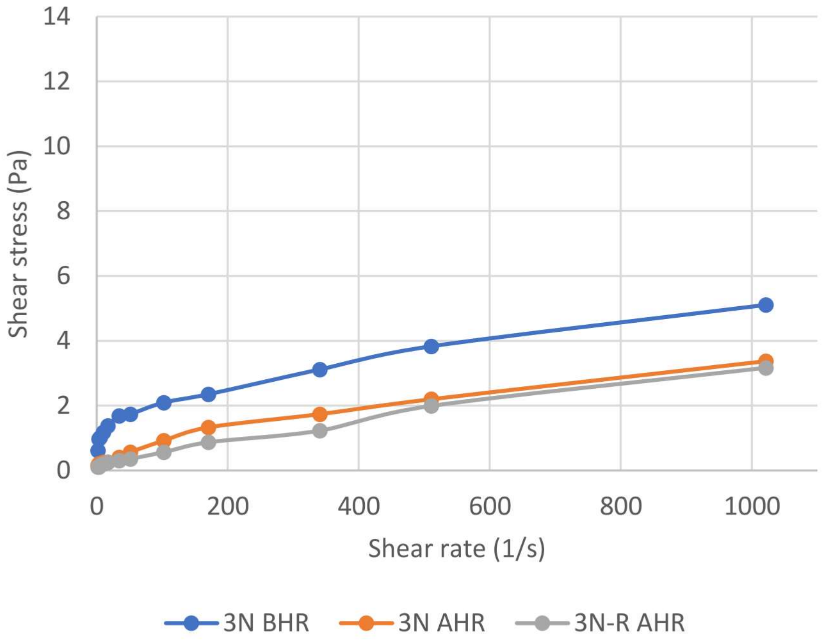

FIGURE 3: Flow curves of fluid 3N with cross linked starch measured before and after hot rolling at 90°C

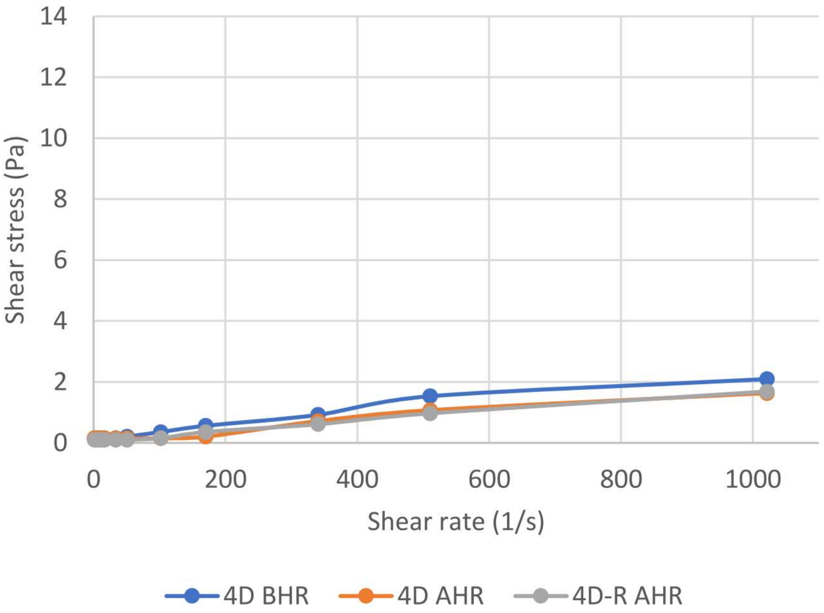

FIGURE 4: Flow curves of fluid 4D with modified starch measured before and after hot rolling at 90°C

Poly-anionic cellulose and cellulose particles

Fig. 5 represents the flow curves for a poly-anionic cellulose product. Using the modified Herschel-Bulkley model, the n values range from 0.91-0.97 before hot-rolling and 0.79-0.96 after hot-rolling. The fluids appear to behave close to a Newtonian liquid, with no significant yield strength. The reduction in τ_s values is around 7-10% after hot-rolling, thus indicating high thermal stability at 90°C. The flow curves of the fluid with the cellulose particle blend, shows low viscous impact of the particle addition and no change in viscosity after hot-rolling. The shear stress at 1021 1/s was less than 1 Pa.

FIGURE 5: Flow curves of fluid 5P with PAC measured before and after hot rolling at 90°C

Material interaction effects on fluid viscosity parameters

When tested in isolation for viscosity impact, it was clear that the thermal degradation of xanthan gum was significant. **Fig. 6** presents a comparison of the flow curves of xanthan gum on its own, fluid 1X and xanthan gum together with the cellulose particle blend in fluid 7XA. The viscosity impact of adding the cellulose particle blend to the xanthan gum fluid has a marginal effect on the fluid before hot-rolling, but a significant impact after hot-rolling. The improvement in stability is very significant for the τ_s values, where the reduction after hot-rolling is ranging from 28-29% for fluid 7XA, relative to the reduction of 50-64% for fluid 1X. Also, the curvature index, *n*, retains lower values of 0.45-0.49 for fluid 7XA versus 0.42-0.66 for fluid 1X, after hot-rolling. Although there are no significant changes in measured yield stress, it is clear that the interaction between the xanthan gum and the cellulose particle blend creates a more stable fluid viscosity with regards to thermal degradation.

A similar degradation as observed for fluid viscosified with xanthan gum was observed for the fluid viscosified with crosslinked starch, N. A significant loss of viscosity after hot-rolling was obtained. **Fig. 7** presents the flow curves of fluid 3N together with fluid 8NA, to visualise any viscosity impact of interaction between the starch and the cellulose particle blend. A notable improvement in resistance towards thermal degradation can be seen, as the flow curves for fluid

8NA are near identical before and after hot-rolling. The analysis using the modified Herschel-Bulkley model shows an increase in yield stress for the combined fluid, as well as no significant alteration of the other fluid parameters. So, whereas the inclusion of the cellulose particle blend improved the stability of the surplus stress and the flow index, when combined with xanthan gum, it improved the stability of all three viscosity parameters when combined with crosslinked starch.

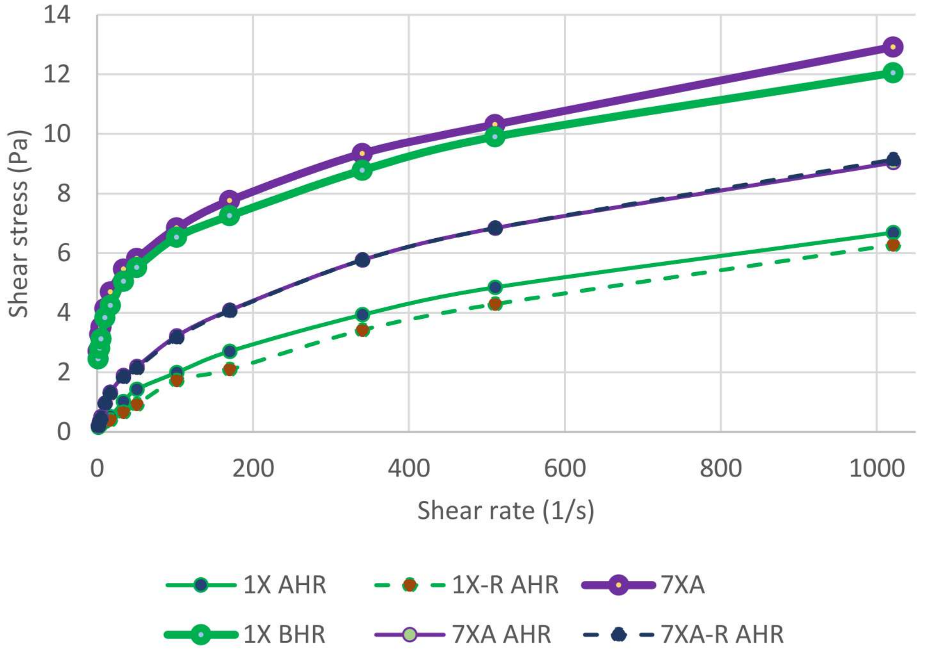

FIGURE 6: Flow curves of fluid with only xanthan gum added, 1X, and the fluid with xanthan gum and cellulose particles, 7XA

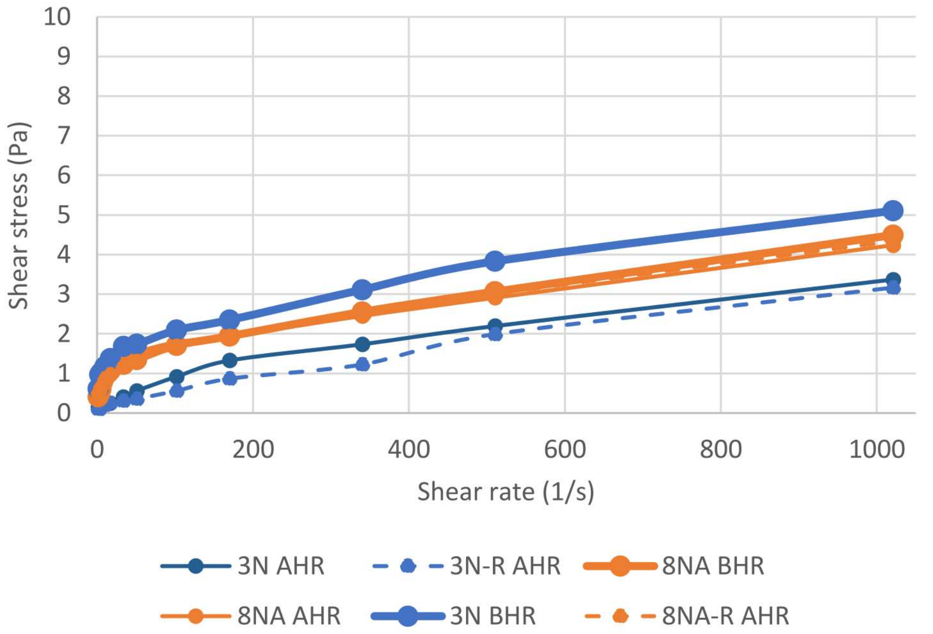

FIGURE 7: Flow curves of fluid with only cross linked starch added, 3N, and the fluid with cross linked starch and cellulose particles, 8NA

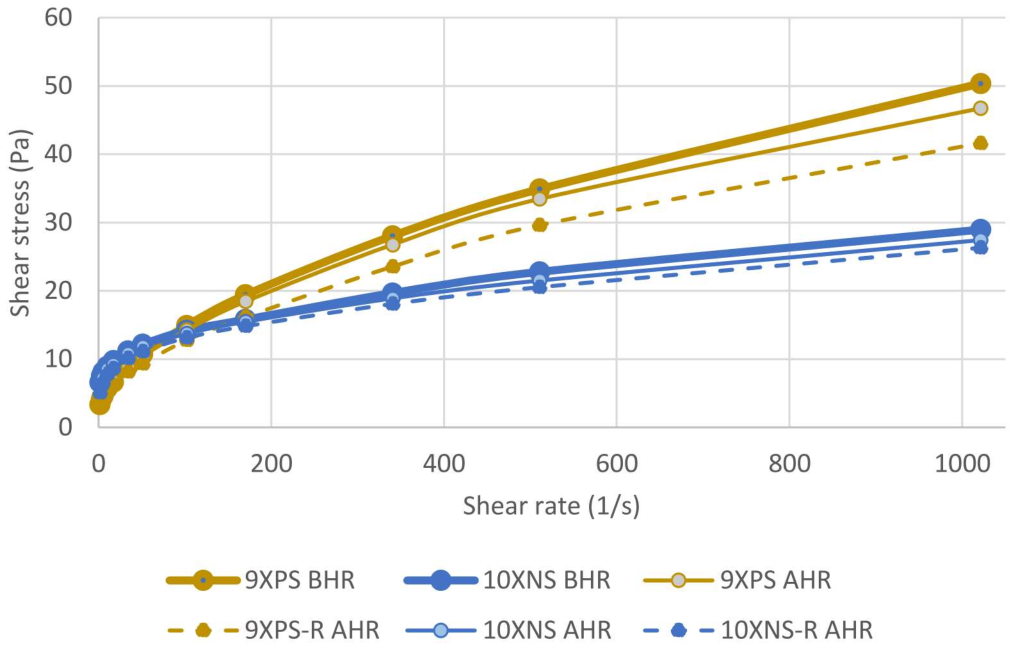

FIGURE 8: Flow curves of fluid with xanthan gum, PAC and salt added, 9XPS, and the fluid with xanthan gum, cross linked starch and salt, 10XNS

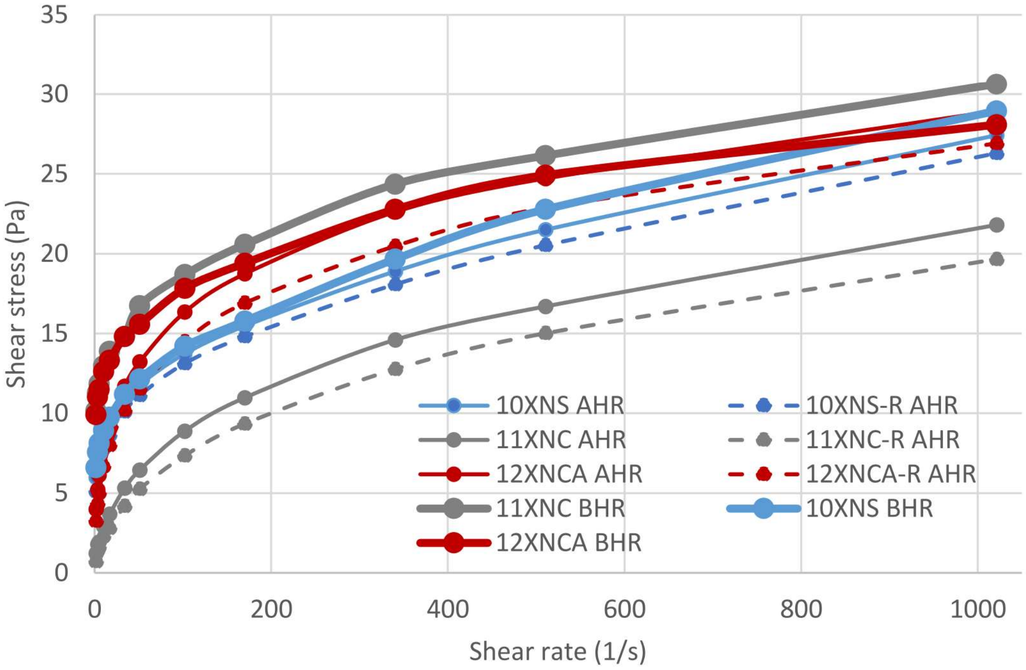

FIGURE 9: Flow curves of fluid with xanthan gum, cross linked starch and salt, 10XNS, fluid with xanthan gum, cross linked starch and carbonate, 11XNC, and the fluid with xanthan gum, cross linked starch, carbonate and cellulose particles, 12XNCA

Salts are commonly added to drilling fluids for increasing fluid density, improving inhibition and other effects. Tests were conducted with an inclusion of 95g of NaCl per 350ml sample, for fluids with a combination of xanthan gum and poly-anionic cellulose, fluid 9XPS, and combinations of xanthan gum and crosslinked starch, fluid 10XNS. The flow curves are presented in **Fig. 8**. For both fluids, the viscosity profile obtained before hot-rolling is substantially retained after hot-rolling. For fluid 9XPS, a 7-20% reduction in τ_s values were recorded, with the highest reduction in surplus stress occurring with for the fluid with mechanical wear. For fluid 10XNS, the reduction in yield stress ranged from 8-27% after hot-rolling, also with the highest degradation occurring after exposure to mechanical wear. Thus, for the fluids with NaCl, it can be summarized that the salt did have a stabilising effect for polymers, that individually showed tendency for thermal degradation, although the individual mixtures showed reduction in either yield stress or surplus stress. Another effect of the inclusion of the salt was an increase in the fluid density to 1.17 g/cm^3, whereas the polymer fluids alone had a density of near 1.0 g/cm^3. For certain drilling operations, such as e.g. the drilling of a depleted reservoir, the increase in density may have detrimental effects.

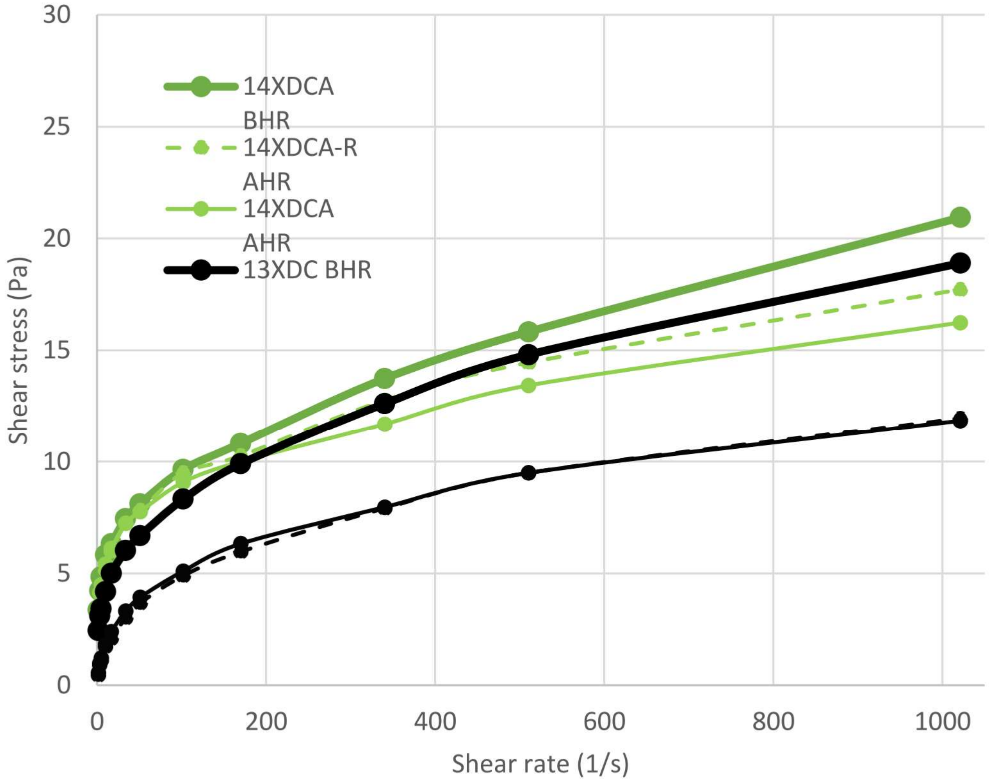

FIGURE 10: Flow curves of fluid with xanthan gum, modified starch and calcium carbonate, 13XDC, and fluid with xanthan gum, modified starch, Calcium carbonate and cellulose particles, 14XDCA

When drilling reservoir sections, it is common to include calcium carbonate as a bridging material. The particle size is then selected to effectively bridge the formation pores to reduce fluid loss, whilst also aiming to limit formation damage. The sample of calcium carbonate used for the tests was sieved to very that the particles were < 50 µm, which typically would be relevant for drilling a sandstone or carbonate reservoir with low to medium permeability. **Fig. 10** presents the flow curves for fluid 10XNS together with 11XNC, where salt has been replaced by calcium carbonate and fluid 12XNCA, where salt has been replaced by calcium carbonate and the cellulose particle blend. The flow curves of these fluids are presented in **Fig. 10**. Relative to fluid 10XNS, both fluid 11XNC and fluid 12 XNCA. When comparing the three fluids, it is clear that the fluid with high concentration of salt, 10XNS, has the highest stability in viscosity. In contrast, fluid 11XNC has a 93-100% reduction in yield stress and 11-19% reduction in surplus stress, indicating that the calcium carbonate does not have any significant effect on stabilizing the viscosity of the polymer fluid. For fluid 12 XNCA, the reduction in yield stress significant, but lower reduction than for fluid 11XNC, at 69-75%. The surplus stress is, however, increased by around 38-50%, thereby providing an overall effect of reducing thermal degradation of viscosity.

Fluids 13XDC and 14XDCA are relatively comparable with fluids 11XNC and 12XNCA, where the only difference being the use of a modified starch instead of a crosslinked starch. The flow curves of fluids 13XDC and 14XDCA are presented in **Fig. 10**. Relatively similar to fluid 11XNC with crosslinked starch, the flow curves of fluid 13XDC show significant signs of viscosity degradation after hot-rolling. The yield stress fell with 91-100% and the surplus stress fell with 24-26%, hence reducing the overall fluid viscosity considerably. As for the fluid with crosslinked starch, the additional inclusion of the cellulose particle blend substantially improved the thermal stability of the fluid viscosity. For fluid 14XDCA, the reduction in yield stress was as low as 16-18% and the reduction in surplus stress as low as 1-5%. In the tests for fluids 1X, 2X, 3N, 4D, 7XA, 11XNC, the reduction in shear stress was accompanied by an increase in the curvature index, *n*, thus indicating that the fluid viscosity profile was shifting towards being closer to a Newtonian fluid after thermal degradation. For fluids 8NA, 9XPS, 10XNS and 13 XNC, the changes in curvature index, *n*, were small after hot-rolling. In contrast, the curvature index fell by 19-41% for fluid 14XDCA and by 6-17% for fluid 12XNCA, thus indicating that the fluids became more shear-thinning after hot-rolling.

Comparison of fluid loss and fluid viscosity changes

The fluids containing xanthan gum together with either poly-anionic cellulose or starch were tested for fluid loss using an API filter-press at room temperature at 100 psi differential pressure and 2.5 μm openings filter paper. The objective was to identify if and how the hot-rolling process impacted the filtration control functionality of the polymers. Some of the fluids contained bridging particles in the form of Calcium carbonate and/or cellulose particle blend. Due to the size of the bridging particles, it could be expected that these would have small to no impact on filtration through a low-permeability filter. Any fluid loss impact from adding these bridging agents may thus be a consequence of interaction with the polymers and/or thermal stabilisation of the polymers during hot-rolling.

Fig. 11 presents a comparison of the API fluid loss and the calculated yield stress of the different fluids. The fluid loss data are also correlated with the various fluid viscosity parameters in **Table 2**. For these simple fluid loss tests, there are two main variables which control the fluid loss. The first is the effectiveness of the different additives in creating a low-permeability filter-cake and the second is the viscosity of the fluid filtrate. For most tests on 2.5 μm filter-paper, the fluid filtrate viscosity is often very similar to the viscosity of the base fluid[7]. For fluids 9XPS and 10XNS, the base fluid is a NaCl brine with density between 1.17 and 1.18 and a viscosity in the region of 1.7, whereas the base fluid for the other samples was freshwater with a viscosity around 1.0 mPa*s[8].

Using 11XNC as a reference fluid with a fluid loss of 6.9-7.4 ml, the fluid loss is lower for both of 9XPS and 10XNS. The lower fluid loss can in general be explained by the higher base fluid viscosity of the latter two fluids. When comparing 12XNCA with 11XNC, the fluid loss was reduced to 6-6.3 ml for the fluid with cellulose particle blend. Also, the fluid with cellulose particle blend had a significantly higher yield strength than fluid 11XNC. The same changes are observed when analysing fluids 13XDC and 14XDCA; with the addition of the cellulose particle blend, the yield strength is improved, and the fluid loss is reduced.

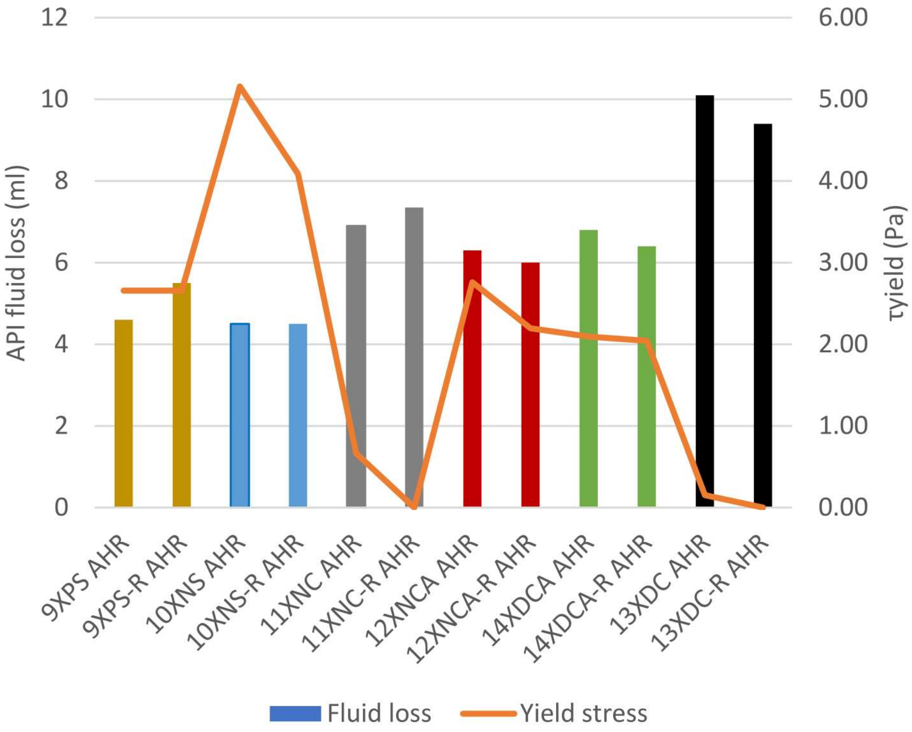

FIGURE 11: Flow curves of fluid with xanthan gum, PAC and salt added, 9XPS, and the fluid with xanthan gum, cross linked starch and salt, 10XNS

The correlation data in **Table 2** show a negative correlation of 0.85 between the calculated yield stress and the measured fluid loss. Using a t-test for this simple dataset, the critical value for a 95% confidence interval is +/-2.306, whereas the calculate t-value is -2.405, thus indicating that the correlation is statistically significant. The other correlations are not significant using the same 95% confidence interval.

The statistical significance is not a proof of causality, however, there may be explanations which support the case for claiming causality. The fluid loss tests were conducted against a low-permeability filter-paper and the fluid loss rates were low for all the tests. There were no spurt-loss occurrences during these tests. Therefore, in such cases where the fluid loss rate follows a linear regression when plotted against the square root of time[9] and the rate of fluid loss is low, the low shear rate viscosity or fluid yield strength will naturally oppose the flow of fluid into the filter-cake. If the fluid loss tests showed a significant spurt-loss, this spurt-loss would have happened in a condition when the fluid shear rate was high[1], and potentially a significant correlation with the surplus stress may be found. There is hence also a logical explanation why there may be a causal relationship between a higher low shear rate viscosity or yield strength and a low fluid loss rate during steady filtration. It should be considered that the tested fluids are low-solids fluids, so that the correlation may only be relevant for fluids of relatively similar solids content.

A further analysis was conducted by comparing the changes in rheological parameters for the tests with and without the degradation rod. **Table 3** shows an overview of the average changes calculated as the value of the test with degradation rod minus the value without the degradation rod. A negative value thus describes a negative impact on the numerical value of the parameter following inclusion of the degradation rod. All average values were negative, thus indicating that there is a marked impact of including the degradation rod into the hot-rolling process. The physical impact of using the degradation rod may be a higher separation of the different polymeric particles in the fluids, thereby leading to reduced viscosity. Another observation is that the reduction in yield stress and surplus stress was higher for the tests without the cellulose particle blend, A, than tests with the cellulose particle blend.

TABLE 2: Fluid loss and viscosity parameter correlations

	9XPS AHR	9XPS -R AHR	10XNS AHR	10XNS R AHR	11XNC AHR	11XNC -R AHR	12XNC A AHR	12XNCA -R AHR	14XDC A AHR	14XDCA -R AHR	13XDC AHR	13XDC -R AHR	Measured against fluid loss	
Fluid loss (ml)	4.6	5.5	4.5	4.5	6.9	7.35	6.3	6	6.8	6.4	10.1	9.4	COVAR S	CORR
τ_{yield}	2.66	2.66	5.16	4.09	0.66	0.00	2.76	2.20	2.09	2.04	0.15	0.00	-2.48	-0.85
$\tau_{surplus}$	15.78	13.48	10.32	10.72	10.32	9.35	15.98	14.71	7.92	8.22	6.18	5.98	-4.24	-0.67
n 1021	0.57	0.59	0.43	0.41	0.40	0.42	0.28	0.29	0.32	0.36	0.36	0.39	-0.07	-0.37
n 51.07	0.60	0.56	0.36	0.33	0.44	0.47	0.32	0.35	0.24	0.19	0.43	0.39	-0.02	-0.07

TABLE 3: Changes in rheological parameters with inclusion of degradation rod

	All tests	Tests without A	Tests with A
τ_{yield}	-0.18	-0.22	-0.11
$\tau_{surplus}$	-0.38	-0.42	-0.29

CONCLUSIONS

An assessment was conducted to identifying potential interaction effects when applying different polymers and a cellulosic particle blend in low-solids, low-density water-based drilling fluid. Such fluids may be relevant for drilling of depleted hydrocarbon reservoirs or when drilling geothermal wells. The overall thermal stability of different polymers an aqueous solutions were studied, and some clear effects were observed:

- There is a significant correlation between the yield stress, τ_y, and fluid loss, where a higher yield stress is correlated with a lower fluid loss.
- Presence of the selected cellulose particle blend improves the thermal stability of the tested combinations of modified starch, crosslinked starch and xanthan gum.
- Lower value of curvature indices, *n*, appeared after thermal degradation of fluids with xanthan gum, starch and the cellulose particle blend.
- The tests with degradation rod yielded, on average, lower yield stress and surplus stress, thus indicating that the inclusion of mechanical wear reduces the viscosity of the tested fluids.
- It was also observed that the reduction in viscosity was lower for the tests with the cellulose particle blend, thereby indicating that the presence of the cellulosic particles may have reduced the mechanical wear on the polymers.

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