# Article

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Synthesis and Property Appraisal of Acrylamide-based Copolymer with Sulphonate Pendant for Viscosification and Filtration Loss Control in Aqueous Bentonite-based Mud

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#### Abstract

Polyacrylamide has been widely used as an additive for drilling mud because of its attractive viscosity but loses much of its effectiveness when exposed to adverse formation environmental conditions. Potassium 2-acrylamido-2-methylpropane sulfonate-acrylamide- n-butyl propenoate (KAMPSAMP) polymer was produced via free-radical and its structure confirmed through Fourier Transform Infrared Red (FTIR) and <sup>1</sup>H NMR spectral analyses. Salinity and thermal effects on the apparent viscosity (AV), plastic viscosity (PV), yield point (YP) and fluid loss of polymer-incorporated aqueous-based mud were examined. It was evident that the polymer favourably modified the properties of aqueous bentonite-based mud, exhibiting improved thermal stability of the salt-free mud compared to polymer-free blank mud. At the same conditions, it also maintained excellent drilling fluid loss control compared to the blank. For salted (5wt/v% NaCl) mud, a similar trend was observed, as improved rheological properties and API filtration loss control after hot-aging at elevated temperatures when juxtaposed with the polymer-free salted-blank. Furthermore, the copolymer provided more than seven-fold fluid loss control with reference to the blank when exposed to elevated temperature-high pressure filtration conditions. The rheology of mud consistently correlated with Herschel-Bulkley model rather than Power law model and Bingham Plastic model.

Keywords: KAMPSAMP polymer; Aqueous drilling mud; Fluid properties; Filtration loss; Fluid rheology.

#### 1. Introduction

Drilling is a very important aspect of any earth excavation practice, particularly for oil and gas prospecting <sup>[1]</sup>. Rotary drilling processes of oil and gas wells rely on drilling fluids for the important functions they play such as suspending and carrying of cuttings, cleaning of the wellbore, balancing of formation pressure, and cooling drill bits, among others <sup>[2-4]</sup>.

Drilling fluids can broadly be classified into water-based muds (WBMs), oil-based muds (OBMs), synthetic based fluids (SBFs) or gas-based fluids (GBFs) <sup>[5-7]</sup>. Despite some advantages such as minimum formation damage and faster rate of drilling using GBFs, they conspicuously exert lower column pressure gradient and are unsuitable for drilling water-bearing formations since wetted cuttings usually stick together and cannot easily be transported by the gas stream. Synthetic base fluids, on the other hand, combine the technical advantages of OBMs but are relatively more costly than WBMs or some OBMs depending formulations <sup>[8]</sup>. Oil-based muds, although considered the best choice for drilling problematic formations because of good lubricity, better thermal stability and non- hydration of shale clays <sup>[9-10]</sup>. None-theless, they are very expensive, their viscosities vary with temperature, non-ecofriendly and therefore engender disposal problems. Water based drilling fluids are liable to trigger more

damage to formation, cuttings fragmentation, clay hydration and hole instability <sup>[11]</sup>. Despite these drawbacks, they are more preferable and if properly formulated will perform efficiently <sup>[12]</sup>. The prevalent applications stem primarily from economic consideration and eco-compatibility relative to OBMs and SBMs <sup>[13-16]</sup>.

Mud rheological and filtration properties are a measure of their quality and should be very attractive to maintain good performance during drilling operations under varying conditions. Substantial changes in fluid properties usually create wellbore problems. Unfavourable formation conditions, especially, at elevated temperature and saline environment predispose clay hydration, degradation of additives and high fluid losses and adversely impact the performance on water-based fluids <sup>[17]</sup>. Bentonite clay, an important additive in the mud, has high surface area to volume ratio and usually forms low permeable filter cakes. Nevertheless, at elevated temperatures, bentonite muds are susceptible to flocculation which causes an surge in filter cake permeability. Failure of filtration control ingredients causes a drastic increase in the fluid loss resulting in thicker filter cake, excessive drag, high-pressure surges, pipe stuck, and increases in shale sloughing <sup>[18-19]</sup>. Addition of water-soluble polymers to the muds generally viscosify the base fluids, plug holes in the filter cake and encapsulate drilled solids resulting in reduced filtrate losses. The polymers also provide shale inhibition and prevent flocculation of the active clay particles <sup>[20]</sup>. Natural polymers are considered less stable than synthetic polymers at high temperatures <sup>[21]</sup>. It is imperative to explore synthetic polymers as mud additives for drilling operations where the mud is subjected to high temperature environments. Partially hydrolyzed polyacrylamide, basically a homopolymer, albeit broadly applied under normal conditions in the petroleum industry, suffers some setbacks when exposed to high temperature and salinity [22-24]. Copolymerisation of acrylamide with functional monomers therefore accords the opportunity to integrate the functions of at least two homopolymers in a copolymer with improved properties <sup>[25]</sup>. This work synthesized a KAMPSAMP polymer, comprising potassium 2- acrylamido-2-methyl propane sulfonate, acrylamide and n-butyl propenoate which blends the thermal resistance of the sulphonate-monomer with the attractive viscosity-building property of acrylamide.

# 2. Experimental

# 2.1. Materials and synthesis of KAMPSAMP polymer

Materials used were acrylamide (AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), N-butyl propenoate (NBP), dipotassium [(sulfonatoperoxy)sulfonyl]oxidanide ( $K_2S_2O_8$ ), so-dium pyrosulphite ( $Na_2S_2O_5$ ), sodium chloride (NaCl) and potassium hydroxide (KOH).

The water soluble KAMPSAMP polymer which consists of acrylamide, 2-acrylamido-2methylpropanesulfonic acid and N-butyl propenoate was synthesised via free radical polymerization in 90:10 v/v salted deionized water/ethanol solvent system using  $K_2S_2O_8$ /  $Na_2S_2O_5$ redox initiation. The reaction (Scheme 1) was conducted in a three-neck flask under continuous stirring at constant temperature using nitrogen purging to degas oxygen. Total monomer concentration of 16.7-34.6wt/v%, pH of 7.0-10.0, temperature of 28-40°C, initiator dosage of 0.2-1.0wt%, reaction time of 1.0-3.5 hr and monomer feed ratios of 75-50% AM, 24-44% AMPS, and 1-5% NBP were varied to achieve optimal reaction parameters. First, AMPS monomer was dissolved in 0.5M NaCl aqueous solution and the pH adjusted using 2M KOH. Acrylamide was added to a separate portion of 0.5M NaCl aqueous solution and N-buthyl propenoate dissolved in ethanol before mixing the portions together while ensuring that the required pH environment. Prior to dosing the mixed reactants system with the initiators to start polymerisation, the content in the flask was purged with  $N_2$  for at least 20 minutes. The reaction was considered complete when a visible thick mass was formed. The KAMPSAMP polymer was then isolated and purified in excess acetone and dried in an oven at 50°C to constant weight. The results are presented in Table 2. The relative viscosity was determined as the ratio of polymer solution viscosity to that of the solvent (0.5M NaCl).



#### Scheme 1.

#### 2.2. KAMPSAMP polymer characterization

FTIR spectra, <sup>1</sup>H-NMR spectra and intrinsic viscosity of the KAMPSAMP polymer were determined according to previous reports <sup>[26-27]</sup>.

Effects of shear (6-240 rpm), temperature (25- 90 °C) and pH (4- 11) on the polymer solution viscosity were determined independently by dissolving a known quantity of the KAMPSAMP polymer sample in 100 ml of aqueous 0.1% NaCl/0.01% CaCl<sub>2</sub> brine. The solution viscosities were recorded using the Brookfield rheometer.

#### 2.3. Formulation of muds

Mud formulations comprising the ingredients in Table 1 were carefully prepared according to American Petroleum Institute (API) procedure <sup>[28]</sup>. Mud characteristics particularly, AV, PV, YP, and gel strength were determined initially and after heated for 16 hrs in a rolling oven using ZNN-D6 six-speed rotary viscometer (Qingdao Haitonghai Specialized Instrument Factory). API fluid loss at ~700 kPa and high temperature-high pressure fluid loss at100-150°C and ~3500 kPa were also determined based on API <sup>[28]</sup> procedure.

Mud components	Salt-free blank mud	Salt-free mud with KAMPSAMP	Salted blank mud	Salted mud with KAMPSAMP
Water (cm <sup>3</sup> )	500	500	500	500
Bentonite clay (g)	25	25	25	25
Sodium hydroxide (NaOH) (g)	1.25	1.25	1.25	1.25
Sodium chloride (NaCl) (g)	-	-	25	25
Sulfonated lignite resin(SPNH)(g)	-	-	7.5	7.5
Sulfomethylated tannin(SMT) (g)	-	-	7.5	7.5
Barite ( $BaSO_4$ ) (g)	-	-	100	100
KAMPSAMP polymer	-	4.0	-	3.0

Table 1. Formulation of salt-free and salted muds.

#### 3. Results and discussion

## **3.1. Optimum synthesis of KAMPSAMP polymer**

The optimum parameters for synthesis were obtained using monomer mole ratios of AMPS:AM:NBP of 40:55:5, at total monomer quantity of 2.4M (30.5wt/v%) and initiator dose of 0.3 wt% (in respect of total monomer weight) at 30°C with process time of 3 hours and pH of 9.5. At the optimum conditions, the reactants were considered to have reacted almost completely and formed a polymer with comparatively bulkier molecular weight and intrinsic

viscosity (Table 2). An average yield of about 90% of the purified dried polymer based on total monomer weight of reactants fed into the flask was obtained under the optimum conditions. The intrinsic viscosity [ $\eta$ ] and viscosity-average molecular weight of the KAMPSAMP polymer were determined as 14.94 dL/g and 9.41 x10<sup>6</sup> g/mol, respectively.

AMPS:AM:NBP (Mole % ratio)	Total moles (mol/100cm <sup>3</sup> )	Temperature (°C)	pН	Initiator dosage (wt%)	Relative viscosity (ŋ <sub>rel</sub> )
24:75:1	0.16	40	7.5	1.0	28.1
28:70:2	0.18	35	8	0.8	28.7
32:65:3	0.20	35	8.5	0.6	34.4
36:60:4	0.22	30	9	0.4	33.4
40:55:5	0.24	30	9.5	0.3	37.5
44:50:6	0.26	28	10.0	0.2	36.7

Table 2. Parameters for synthesis of KAMPSAMP polymer.

#### 3.1.1. Structural composition and properties of KAMPSAMP polymer

KAMPSAMP polymer as presented in Scheme 1 intrinsically has a C-C backbone which primarily is hydrophobic and can offer thermal stability. The sulphonate ( $-SO_3$ -) and amide groups in the polymer functionally imparts ionic and hydrophilic character in a broad pH spectrum which tremendously facilitate polymer solubility and viscosity enhancing properties. Their affinity for water and provide enhanced water absorption ability of the polymer in drilling muds. The dimethyl ( $-C(CH_3)_2$ -) and the sulfomethyl ( $-CH_2$ -SO<sub>3</sub>-) groups on the bulky AMPS pendant contribute steric hindrance and provide thermal stabilities in the polymer structure <sup>[29]</sup>. Furthermore, the N- butyl propenoate incorporates a hydrophobic content for salt tolerance in aqueous medium and carboxylate group for temperature resistance.

## 3.1.2. FTIR spectra and <sup>1</sup>H-NMR spectra and SEM/EDX analysis of KAMPSAMP polymer

The FTIR and <sup>1</sup>H-NMR spectra (Table 3., Figs. 1-2) exhibited characteristics of components coherent with the structural composition of the KAMPSAMP copolymer.

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) analysis shown in Fig. 14b and Table 6 in the appendix revealed the main elements contained in the KAMPSAMP polymer as carbon, oxygen, nitrogen, sulphur and potassium excluding hydrogen which technically could not be detected by the method.

Table 3. FTII	R spectrum	and <sup>1</sup> H-NMR	spectra.
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Peaks	Interpretations	
FTIR spectra		
3340.84cm <sup>-1</sup>	-NH stretching vibration	
1662.08 cm <sup>-1</sup> (Strong)	Stretching of carbonyl group from AMPS and AM	
1188.38 cm <sup>-1</sup> (strong), 1043.27 cm <sup>-1</sup> (strong)	Sufonate group of AMPS stretched asymmetrically and symmetrically	•
1300.19 cm <sup>-1</sup> , 1452.86 cm <sup>-1</sup>	Amide characteristic peaks of -CN- assigned to AM and AMPS	
1390.06 cm <sup>-1</sup>	Carboxylate asymmetric stretching of NBP	
1542.34 cm <sup>-1</sup>	Carboxylate asymmetric stretching of NBP and hydrolysed AM	
<sup>1</sup> H-NMR spectrum		
1.55 ppm	corresponds to the hydrogens of $-C(CH_3)_2$ of AMPS and NBP and $-CI$ on the polymer backbone and side chain of the NBP .	<b>-1</b> 2
2.15 ppm	Hydrogen atoms of -CH in the backbone	
3.40 ppm	Detection of protons of -CH <sub>2</sub> group attached to SO <sub>3</sub> Na and in CH <sub>2</sub> -C C=O	)-
4.25-4.7 ppm	Correspond to the hydrogens of the D <sub>2</sub> O solvent, -NH, and -NH <sub>2</sub> group	s.





## 3.1.3. Solution behaviour of KAMPSAMP bopolymer

The initial step in considering a polymer as a viscosifier in muds is essentially its solubility in aqueous media. When tested in aqueous media within pH scale (1- 14), the KAMPSAMP polymer completely dissolved in the full pH spectrum. Being ionic and hydrophilic, the polymer initially absorbs molecules of water into its matrix to first form a gel, then progressively disintegrates with the molecules dispersing and stretching out in the solution, thus, generating an enormous hydrodynamic volume and an increase in viscosity. Solution viscosities as shown in Fig.3. were recorded in a pH range of 4.0 to 11.0 for the safety of the viscometer.

Fig. 4. shows a slight shear-dependent viscosity behaviour in aqueous medium. The slight shear thinning behaviour suggests that the copolymer solution can be used as solid-free polymer mud. Shear thinning at higher shear rates reflects a reduction in associative interactions of polymer molecular chains in the fluid which causes a reduction of viscosity.



Fig. 3. pH variation on KAMPSAMP polymer solution viscosity.



Fig. 5. Response of KAMPSAMP polymer solution viscosity to shear.



Fig. 4. Response of KAMPSAMP polymer solution viscosity to shear.

The polymer solution viscosity declined steadily from 45.5 to 21.0cP with rising temperature in the range of  $25^{\circ}$ C-90°C as displayed in Fig. 5. This represents a reduction of about 54%, compared to brine only viscosity which decreased from1.00 to 0.32cP (68%) over the same temperature range. Meaning that the KAMPSAMP copolymer mitigated the solution viscosity loss by more than 10%. The significant viscosity retention is ascribable to the (-C-C-) backbone of the polymer, particularly, the pendent-sulphonate which strengthens its thermal resilience.

## 3.2. Mud rheological properties

## 3.2.1. Heat treatment effects on unsalted mud properties

Wellbore operations on high temperature formation zones with aqueous-based mud is generally problematic because of substantial changes in mud properties because of the deleterious effect of temperature on mud ingredients <sup>[17,30]</sup>. In Fig. 6, the AV, PV and YP enriched tremendously with increasing dosage of KAMPSAMP polymer, revealing the efficacy of the polymer to greatly modify the rheological properties of mud as expected. As the polymer dissolved in the aqueous medium, molecules of water moved into its matrix to first form a gel, then progressively broke up and dispersed with the polymer molecules stretching out in the solution and thereby expanding the hydrodynamic volume with improvement in viscosity.

Fig. 7 presents the impact of heat treatment on the properties of salt-free mud with and without KAMPSAMP copolymer. The KAMPSAMP polymer generically modified the apparent viscosity, plastic viscosity and yield point of the salt-free mud in comparison with the polymer-free mud (blank). The copolymer-mud retained 54% of its initial (unaged sample at 25°C) viscosity after hot-roll aging at 160°C. The PV changed from 22Pa at 25°C to 17 Pa after hot-aging at 160°C. While the YP of the blank disappeared following heat-treatment at 120°C, the

copolymer-incorporated mud, however, retained about 21.4% of its yield point at 160°C. Indicating that KAMPSAMP copolymer improved the thermal resistance of the low-solid bentonite-based mud and can extend its potential use for drilling operation to a temperature of 160°C. That implied that in the absence of KAMPSAMP copolymer, the mud would break down and become unsuitable for drilling purposes above 120°C





Fig. 6. Effect of KAMPSAMP polymer concentration on mud properties.

Fig. 7. Heat-treatment effects on properties of unsalted blank and KAMPSAMP polymer muds.

#### 3.2.2. Combined effects of salt and heat treatment on mud properties

The salted mud contained 5 wt% NaCl (based on mass of water) and other ingredients as listed in the Table 1. The test examined the efficacy of the KAMPSAMP copolymer in salt contaminated mud subjected to high heat treatment. As presented in Fig.8, contrasted with the blank, the inclusion of KAMPSAMP in the mud effected and sustained twice as much of viscosity of the mud at 25°C and after hot-rolled at 100-150°C under similar conditions. The comparatively high viscosity build-up efficiency of the copolymer indicates that the drill mud will effect appropriate resistance to reduce cuttings slip velocity and favourably suspend or transport cuttings during drilling operations. The loss in apparent viscosity of copolymer incorporated mud after heat treatment at 150°C was 33.3% compared to its initial value at 50°C while blank mud reduced by 52.0%. PV of the muds also dropped slightly after heating at 150°C compared to the values of the unaged samples.



Fig. 8. Heat-treatment effects on properties of blank and KAMPSAMP polymer salted muds.

The blank experienced high reduction in plastic viscosity of 57.1% while copolymermud retained its initial PV. Although the blank has a lower plastic viscosity and would promote faster penetration of formation, the abnormal seepage of fluid coupled with poor viscosity renders it low grade for cuttings transport with respect to polymer- dosed mud. YP measures the stress level that initiates the deformation of fluids and also the mud capacity to pipe-hole annular cuttings conveyance. KAMPSAMP polymer incorporated-mud generally with a higher YP comparatively reflects better efficacy for cuttings conveyance in the annulus with reference to the blank.

# 3.2.3. Filtration losses of unsalted and salted muds under standard API and high-temperature-high-pressure conditions

To prevent influx of formation fluids into the wellbore, the hydrostatic pressure of the mud column must be greater than the pore pressure of the formation. Muds, in most cases the base fluids, have the propensity to seep into permeable formations during drilling operations. It is imperative to allow as little filtrate loss as possible for a thin cake to form around the walls of permeable zones to minimal filtrate invasion, formation damage and ensure wellbore stability.

Standard API fluid loss reflects a seepage of mud into the formation at ambient temperature and 0.7MPa pressure drop. It assumes surface environment and may not simulate downhole conditions. The API filtration loss at 25°C for unaged copolymer- incorporated unsalted mud was 11.0 cm<sup>3</sup>. This increased by 22.7% after aging at 140°C and 36.4% at 160°C, compared to the blank which suffered excessive increase in filtration loss of about 350% after similar heat treatment at 140°C (Fig. 9). For the salted Mud as shown in Fig.9, the API filtration loss of the blank increased by 37.9% after heat treatment in the temperature range of 25– 150°C whereas the fluid loss for the copolymer fortified salted mud increased marginally by 5.3% under the same treatment conditions.

The high-temperature- high-pressure filter press of mud measures the filtration and filtercake building of the mud at elevated temperature and pressure. The HTHP fluid loss test provides information on mud filtration into the formation under a static condition over a period of time. Although higher pressures and temperatures can be applied, the conventional practice employs 500 psi differential pressure and 149°C (~150°C) for filtrate volume collected over a 30-minute period. For HTHP filtrations at 100 °C - 150°C and 3.5MPa (Fig. 10), the fluid loss for KAMPSAMP copolymer incorporated salted mud increased by 15.0% (12.5-13.8 cm<sup>3</sup>) compared to the blank of 88.3 % (60-113 cm<sup>3</sup>). Thus, the blank suffered more than seven-fold fluid loss compared to the KAMPSAMP copolymer-incorporated salted mud at 150°C.





Fig. 10. Joint effect of high temperature -high pressure and salt treatment of mud fluid loss.

In both unsalted and salted muds, the KAMPSAMP enhanced the viscosity of muds through mechanisms such as polymer-polymer interaction and polymer-water associations. This creates a relatively stable colloidal suspension between the base fluid and the solids in the mud which reduces water mobility into the permeable media thereby decreasing filtration rate and forming a thin cake which mitigates fluid permeation across the cake. Per its composition, the copolymer is anionic and therefore can mitigate mud fluid mitigation through adsorption on the of the hydrated charged clay particles in the aqueous medium via interactions of electrostatic forces can build thin polymer-clay filter system that tends to reduce water penetration across the cake.

The excessive fluid loss experienced by the polymer-free muds underpin thermal deterioration of the mud ingredients. However, in the case of KAMPSAMP polymer incorporated muds, the polymer offered thermal stability through protection by encapsulation or insulation. This was attributed to the presence of -C-C and  $-CO_2$ - structures that tend to impart thermal resistance besides the positive influence of the bulky AMPS-pendant which offered both conformational distortions and thermal resistance.

#### 3.3. Rheology of muds

The rheological behaviours of the unsalted and salted blank muds and the KAMPSAMPpolymer muds at varied temperatures were examined by considering the relationship between the shear rate and shear stress of the muds as shown in Figs. 11-14. The data were fit (using non-linear least squares function in SciPy) into existing rheological models *viz* Bingham plastic model (eqn.1), Power law model (eqn.2), and Herschel-Bulkley model (eqn.3) to determine the model that best reflected the muds behaviours. The parameters of each model along with the estimated determinant coefficients are presented in Tables 4-5 for both unsalted and salted blank and the KAMPSAMP polymer-incorporated muds. It was observed that the Herschel-Bulkley model consistently and strongly correlated to the muds behaviour compared to the other models.

Bingham plastic model	$ au =  au_y + \mu_p \gamma$	(1)
Power law model	$\tau = k\gamma^n$	(2)
Herschel-Bulkley model	$\tau = \tau_0 + k \gamma^n$	(3)

where:  $\tau$ -shear stress;  $\mu_p$ -plastic viscosity;  $\tau_y$ -yield point;  $\tau_0$ -yield stress; k-consistency factor;  $\gamma$ -shear rate; n-flow behaviour index.



Fig.11. Herschel Bulkley model fit for salt-free drilling mud.



Fig.12. Herschel Bulkley model fit for salt-free drilling mud salt-free mud with KAMPSAMP

A comparison of the parameters obtained for rheological models for unsalted mud with and without the KAMPSAMP-polymer given in Table 4.

		Н	Herschel-Bulkley model				Bingham-Plastic model			Power-law model		
Samples	Temperatures	τ <sub>o</sub> (Pa)	k (Pa.s <sup>n</sup> )	n	R <sup>2</sup>	τ <sub>o</sub> (Pa)	μ <sub>p</sub> (Pa.s)	R <sup>2</sup>	k	n	R <sup>2</sup>	
BF	25 140	6.32 0	0.089 0.007	0.580 0.950	0.99 0.98	6.950 0.003	0.004 0.004	0.94 0.99	5.230 0.006	0.99 0.94	0.88 0.99	
BF+KAM PSAMP	25 140 150 160	7.17 0.67 0.16 0.08	0.25 0.16 0.13 0.09	0.69 0.80 0.80 0.78	0.99 0.99 0.99 0.99	9.55 1.821 1.66 1.11	0.028 0.013 0.031 0.019	0.970 0.960 0.990 0.948	2.71 0.20 0.14 0.09	0.36 0.49 0.76 0.77	0.95 0.99 0.99 0.99	

Table 4. Unsalted mud rheology parameters.

Results obtained from analysis showed that the flow behaviour index obtained for both samples showed shear thinning properties. For both samples an increase in temperature resulted in reduced shear thinning behaviour as evidenced by the increasing value of flow index behaviour for both samples. For the salt-free drilling mud without the KAMPSAMP-polymer a drastic reduction in shear thinning behaviour was observed (n= 0.58 to n=0.95). However, the introduction of the KAMPSAMP-polymer resulted in consistent shear thinning behaviour with varied temperatures as observed in the fairly constant flow behaviour index values ( $n \approx 0.8$ ) presented in Table 4. From the same, increasing temperatures resulted in decreasing flow consistency factors for both samples, however, the KAMPSAMP incorporated drilling mud showed improved behaviour under the conditions of increasing temperature. A reduction in flow consistency is indicative of reduced annular viscosity and therefore reduced hole cleaning capacity.

From Table 5, the results for rheological parameters obtained for salt-contaminated mud demonstrated patterns consistent with data obtained from salt-free mud. The salt contaminated drilling mud showed stable shear thinning behaviour and hole cleaning capacity with increasing temperature.

		Н	Herschel-Bulkley model				Bingham-Plastic model			Power-law model		
Samples	Temperatures	τ <sub>o</sub> (Pa)	k (Pa.s <sup>n</sup> )	n	R <sup>2</sup>	τ <sub>o</sub> (Pa)	μ <sub>p</sub> (Pa.s)	R <sup>2</sup>	k	n	R <sup>2</sup>	
BF	50 150	6.35 0.14	0.02 0.11	0.86 0.58	0.97 0.99	6.54 0.89	0.06 0.006	0.97 0.94	4.62 0.13	0.12 0.55	0.77 0.99	
BF+KAM PSAMP	50 120 150	4.15 3.11 1.51	0.10 0.12 0.11	0.75 0.72 0.70	0.99 0.99 0.99	5.29 4.37 2.59	0.018 0.017 0.013	0.98 0.98 0.96	1.23 0.87 0.38	0.41 0.45 0.53	0.93 0.97 0.98	

Table 5. Salted mud rheology parameters.



Fig. 13. Herschel-Bulkley model fit for salt-contaminated drilling mud.



Fig.14. Herschel-Bulkley Model fit for Salt-Contaminated Drilling Mud with KAMPSAMP.

## 4. Conclusions

For the experimental conditions of consideration, optimum reaction conditions for synthesizing the KAMPSAMP copolymer were obtained using monomer mole percent ratios of AMPS:AM:NBP of 40:55:5, at total monomer concentration of 2.4M (30.5wt/v%) using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> redox initiation of 0.3 wt% (in respect of total monomer weight) at 30°C in process time of 3 hours and pH of 9.5.

The KAMPSAMP copolymer provided thermal stability and enhanced the rheological properties of the unsalted and salted aqueous bentonite-based mud at elevated temperatures.

Based on HTHP filtration at elevated temperatures within 100°C-150°C and pressure at 3.5MPa, the fluid loss for salted KAMPSAMP-copolymer incorporated mud increased by 15.0% compared to the blank of 88.3 %. Indicating that KAMPSAMP copolymer improved fluid loss control and thermal stability to the low fraction bentonite mud at elevated temperatures.

The improved rheological properties, thermal and salt stability of the mud at elevated temperatures is accredited to the influence of KAMPSAMP polymer which contains -C-C and  $-CO_2$  that tend to impart thermal resistance in addition to the sulphonate side chain of AMPS which offers steric hindrance and thermal resistance.

The muds behaviour consistently and strongly correlated with Herschel-Bulkley model compared to the Power law model and Bingham plastic model.

# Appendix



Figure14a. SEM-EDX analysis of KAMPSAMP polymer.





Table 0. SLIT-LDA Analysis of KAMPSAMP polymen.										
Element	At. No.	Netto	Mass (%)	Mass norm. (%)	Atom (%)	Abs. error [%] (1sigma)	Abs. error [%] (1sigma)			
Carbon	6	12134	29.32	34.03	46.51	4.02	13.72			
Nitrogen	7	1992	13.40	15.55	18.23	2.57	19.15			
Oxygen	8	6423	18.29	21.22	21.77	2.77	15.13			
Sodium	11	2273	0.65	0.76	0.54	0.07	11.17			
Aluminum	13	638	0.18	0.21	0.13	0.04	21.20			
Silicon	14	542	0.11	0.12	0.07	0.03	30.44			
Sulfur	16	43668	8.92	10.35	5.30	0.35	3.91			

15.31

Table 6 SEM-EDX Analysis of KAMPSAMP polymer

63678

Potassium

19

0.49

3.22

17.77

7.46

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