The Role of Temperature on the Egyptian Drilling Mud Performance in the Presence of Cationic Polyethylene Imine and Anionic Polyacrylamide

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ABSTRACT: The flow properties of Egyptian bentonite suspensions were determined in the presence of cationic polyethylene imine followed by anionic polyacrylamide at different clay/water ratios. This sequence of addition was examined at four different temperatures (20, 40, 60, and 80°C). The aging time was kept constant after 24 h. The data showed that there is an inverse relation between temperature and plastic viscosity of the bentonite suspension. Contrary to that, apparent viscosity, yield point, gel strength, and consistency index are increased as temperature increases. The zeta potential of bentonite suspension in the presence of 50 mg/L cationic polyethylene imine followed by 10 mg/L anionic polyacrylamide were investigated at different temperature. The results showed that there is a direct relation between temperature and ζ potential. Potential energy profiles were constructed to investigate the relation between rheological and electrical properties. Potential energy profile at different bentonite suspensions gave a high-repulsion potential energy between clay surfaces by increasing temperature, which means that the suspension stability improved. From the above results, it might be possible to say that the Egyptian clay suspension can give desired drilling mud properties using 6% clay suspension concentration treated with 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide at 80°C up to 24-h aging time. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2958–2963, 2010

Key words: anionic polyacrylamide; cationic polyethylene imine; bentonite; rheological properties; drilling mud; zeta potential; potential energy; temperature

INTRODUCTION

The use of polymers to control the stability of clay dispersions and their flocculation is of great technological importance. The adsorption of polymers onto the surfaces of clay particles influences the rheology and stability of the system. Bentonites are used in a wide range of industrial processes such as paints, coatings, ceramics, pesticides, pharmaceuticals, cosmetics, cement, and drilling fluids. On the other hand, clays are much less expensive compared with common adsorbants like activated carbon. Clay can also remove unbiodegradable polymers from waste waters.[1–5]

The polymers in the bentonite suspensions interact with clay particles according to their ionic or nonionic character. The ionic polymers induce electrostatic interactions, but the nonionic polymers are adsorbed on the surface of clay minerals by the steric interactions. Polymer concentration, its molecular weight and hydrolysis groups of polymer, size and shape of clay particle, its surface charge, clay concentration in suspension, pH, and temperature may all affect the clay/polymer interactions. The effects of salts, polymers and surfactant materials on the bentonite–water systems are extensively studied.[6–10]

The electrical properties of bentonite suspensions in the presence of polymers can give information on the thickness of the adsorbed layer and the configuration of polymers on the clay surfaces.[11–17]

In the present work, the rheological and electrical properties of Egyptian bentonite were investigated in the presence of anionic polyacrylamide and cationic polyethylene imine concentrations at different temperatures.

EXPERIMENTAL WORK

Egyptian bentonite clay was used in this study. Cation exchange capacity and specific surface area were 77.3 mequiv/100 g and 346.7 m^2/g, respectively. Also, chemical analysis of bentonite clay sample was listed in Table I. X-ray diffraction analysis for this bentonite was showed in Figure 1.

Figure 2 showed the Fourier transform infrared (FTIR) spectrum for bentonite using IR Prestige-21 FTIR-8400S Shimadzu spectrophotometer (Shimadzu, Japan). The scan in the 4000–400 cm^{-1} spectral range

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TABLE I
Chemical Analysis of Bentonite Clay

Test	Value (wt %)
Ignition loss	8.44
SiO_2	52.52
Al_2O_3 (Before ignition)	21.76
Al_2O_3 (After ignition)	23.66
Fe_2O_3	10.72
TiO_2	1.54
CaO	0.42
MgO	3.23
Na_2O	0.82
K_2O	0.40
P_2O_5	0.10

Figure 2 FTIR spectrum of bentonite clay.

was recorded with resolution of 4 cm^{-1}. The FTIR spectrum of the sample Bentonite (washed twice with deionized water and the solid was dried under vacuum at 60°C for 24 h) indicates that dominant mineral phase in this clay.

The polymers used were polyacrylamide sodium salt of a molecular weight 1,000,000 g/mol and polyethylene imine of a molecular weight 700,000 g/mol.

The rheological properties of different bentonite clay suspensions (4–8% w/w) in the presence of 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide were carried out using Fann viscometer (model 35). This sequence of addition was performed at different temperature (20, 40, 60, and 80°C). The aging time was kept constant at 24 h.

The electrophoretic mobility of the bentonite clay particles in the presence of 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide at different temperature were determined using micro electrophoresis apparatus (Zeta meter, NY).

RESULTS AND DISCUSSION

Effect of temperature on bentonite suspensions in the absence of polymer

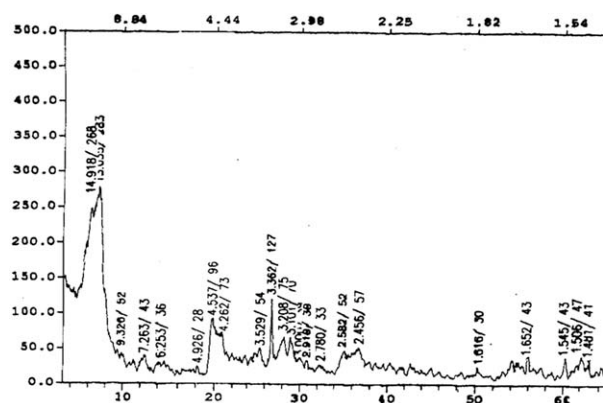Figure 1 showed the X-ray diffraction for bentonite clay. X-ray diffraction illustrated that a macroscopic particle of bentonite is composed of many thousan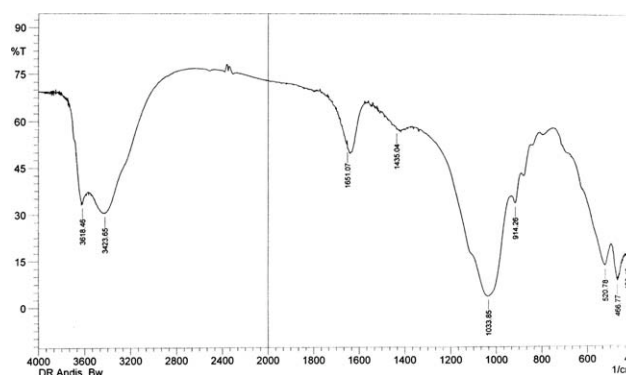ds of stacked and/or overlapped submicroscopic flakes. These are ~ 1-nanometer thick by several hundred nanometers across and are separated by a highly oriented layer of water. The flake faces carry a negative charge, whereas edges have a slightly positive charge. The overall negative charge is balanced by exchangeable sodium ions. When the clay and water are mixed, water penetrates the area between the flakes, forcing them farther apart. The exchange ions then begin to diffuse away from the flake faces. Further penetration of water between the flakes then proceeds in an osmotic manner until they are completely separated. For most bentonites, the speed with which flake separation occurs is directly related to the amount of energy introduced during hydration. Mechanical and thermal energy accelerate delamination. The bentonites produce thixotropic, pseudoplastic dispersions with yield value. These clays are available in a range of viscosities, although their primary function is to impart yield value and thereby stabilize emulsions, suspensions, and foams. They are often used in combination with anionic and nonionic polymers to finely tailor rheology and for advantageous synergism in viscosity and/or yield value.[18]

The FTIR spectrum for bentonite sample (Fig. 2 and Table II) showed absorption band at 3618 cm^{-1} is due

Figure 1 X-ray diffraction analysis of bentonite.

TABLE II
Important IR Bands of Bentonite Along with Their Possible Assignments

Band (cm^{-1})	Transmittance (%)	Assignments
3657	37	Al···O—H (interoctahedral)
3423	34	H—O—H str.
1633	46	H—O—H str.
1427	57	H··O··H weak
1033	7	Si—O—Si, Si—O str.
914	56	Al···O—H str.
520	22	Si—O str., Si—O—Al str.
462	17	Si—O str., Si—O—Fe str.
420	26	Si—O

Figure 3 Plastic viscosity of bentonite suspensions at different temperatures after 24 h.

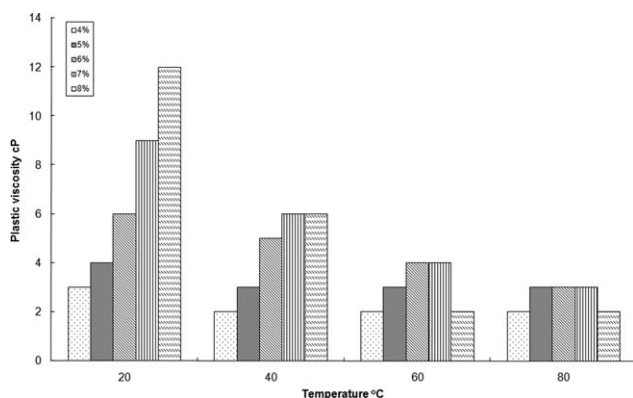**Figure 5** Yield point of bentonite suspensions at different temperatures after 24 h.

to the stretching vibrations of structural OH groups coordinated to Al–Al pair, the complex broad band around 1033 cm^{-1} corresponds to Si—O stretching, and the 520, 466, and 420 cm^{-1} triplet is related to the Al—O—Si, Si—O—Si, and Si—O deformations. Adsobed water gives a broad band at 3423 cm^{-1} corresponding to the H$_2$O-stretching vibrations.[19,20]

The effect of temperature on rheological properties of bentonite suspensions was examined. The rheological properties of bentonite suspensions at different temperatures (20, 40, 60, 80°C) after 24 h were shown in Figures 3–5. The plastic viscosity was decreased as temperature increased. By increasing the temperature, bentonite platelets flow becomes more non-Newtonian and shear-thinning. The exposure to high temperatures for long times makes the bentonite more dispersed, which increases the number of individual platelets in the suspension and consequently, plastic viscosity decreases see Figure 3. Annis et al.[21] report that increasing temperature up to 80°C, displays higher yield stresses, and lower plastic viscosities.

Also, Figures 4 and 5 showed that the apparent viscosity, and yield point were increased as temperature increased. These properties are related to the
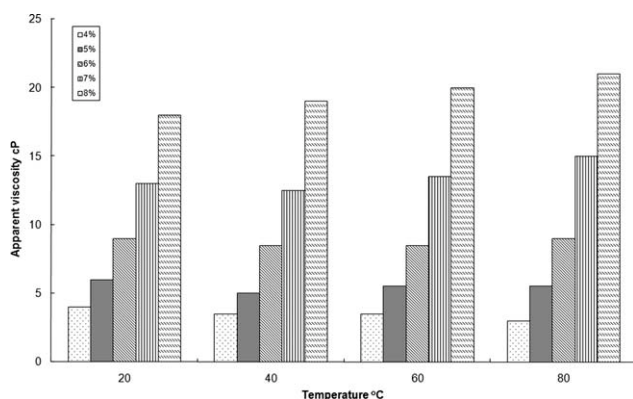
clay suspension percentage. At higher temperatures, the internal energy of the system increased which provides the clay water interactions. The more of such interaction, the more would be the swelling. Consequently, these properties will be increased.[22]

Effect of temperature on the rheological properties of bentonite suspension in the presence of polyethylene imine followed by polyacrylamide

The rheological properties of bentonite suspensions in addition sequence of 50 mg/L polyethylene imine followed by 10 mg/L anionic polyacrylamide after 24 h at 20°C was examined.[23] As temperature increases, the plastic viscosity of bentonite suspensions decreases Figure 6. Because of increasing the temperature a weakening of the hydrophobic associations is produced, and thereby the strength of the network decreases. Consequently, the plastic viscosity decreased.[24]

Also, Figures 7 and 8 showed the apparent viscosity and yield point of bentonite suspensions are in addition sequence of 50 mg/L polyethylene imine followed by 10 mg/L anionic polyacrylamide as a function of temperature after twenty four hours

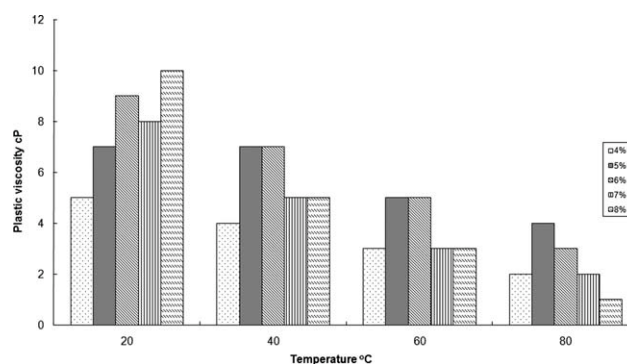**Figure 4** Apparent viscosity of bentonite suspensions at different temperatures after 24 h.

Figure 6 Plastic viscosity of bentonite suspensions in the presence of 50 mg/L PEI followed by 10 mg/L PAM at different temperature after 24 h.
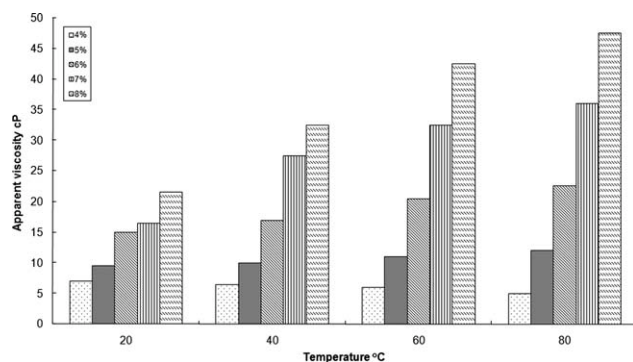
Figure 7 Apparent viscosity of bentonite suspensions in the presence of 50 mg/L PEI followed by 10 mg/L PAM at different temperature after 24 h.

aging time. By increasing the temperature, the bentonite becomes more dispersed and the number of individual platelets in the suspension increase.[25] As temperature enhances, the cationic end group of the polyethylene imine span the distance between two particles, and consequently, they lose their contact. The positive charge of the polymer is attracted by negative surface site of anionic polyacrylamide (forming a loop) at a neighboring particle, that is, a bridging is produced. More and more loops are formed during shearing, so that the network is fragmented. Both effects increase the apparent viscosity and yield point with rising temperature.[26]

Effect of temperature on the electrical properties of bentonite suspension in the presence of polyethylene imine followed by polyacrylamide

The stability of bentonite suspension in the presence of polyethylene imine followed by polyacrylamide at different temperatures was examined. The zeta potential of 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide at 20°C was −82 mV.[23] As temperature increased zeta potential increased as observed in Table III. Also, it was observed that from Table III the zeta potential of bentonite suspensions in
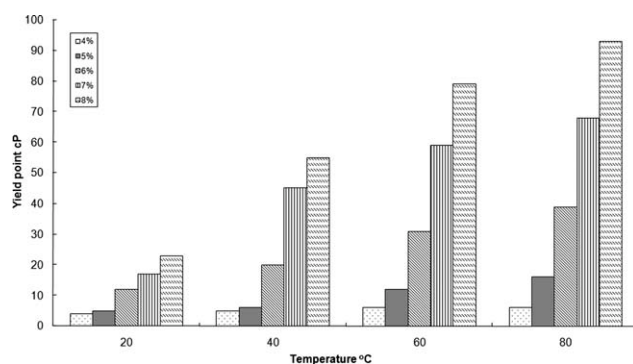

Figure 8 Yield point of bentonite suspensions in the presence of 50 mg/L PEI followed by 10 mg/L PAM at different temperature after 24 h.

TABLE III
Electrokinetic Properties of Bentonite Suspension in Absence and Presence of 50 mg/L Polyethylene Imine and 10 mg/L Polyacrylamide at Different Temperatures

Temperature (°C)	Without additives		50 mg/L PEI + 10 mg/L PAM	
	Mobility (μm/s per V/cm)	Zeta potential (mV)	Mobility (μm/s per V/cm)	Zeta potential (mV)
20	2.4	−32	6.2	−82
40	2.8	−38	6.4	−86
60	3.2	−42	6.8	−90
80	3.5	−47	7.2	−95

the absence of polymer were increased as temperature increased, but zeta potential value of bentonite suspension at 80°C in the absence of polymer (−47 mV) was lower than that of bentonite suspension in the presence of polymer at 20°C (−82 mV). Therefore, the electrical stability of bentonite suspension in the presence of polymer at 20°C is much greater than that of bentonite suspension in the absence of polymer even if it measures at 80°C. The electrical stability of bentonite suspension at different temperatures was illustrated clearly by drawing the potential energy profiles. Figures 9–12 showed the potential energy profiles for bentonite suspensions in the absence of polymers at different temperatures. From this energy profile, it can be seen that the clay particles possess potential energy barrier of about 0.05×10^4 KT at intermediate distance of 400 Å at 20°C, whereas potential energy barrier was increased as temperature increased at intermediate distance of 200 Å. So, the repulsion between clay particles will be increased and the clay particles separated from each others at high temperatures which mean the system is more stable at high temperature ($80 > 60 > 40 > 20°C$).

On the other hand, Figures 13–16 showed the potential energy profiles for bentonite suspensions in the presence of 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide at different temperatures. From this energy profile, it can be seen that the clay particles possess very high-potential energy barrier of about 13.52×10^4 KT at
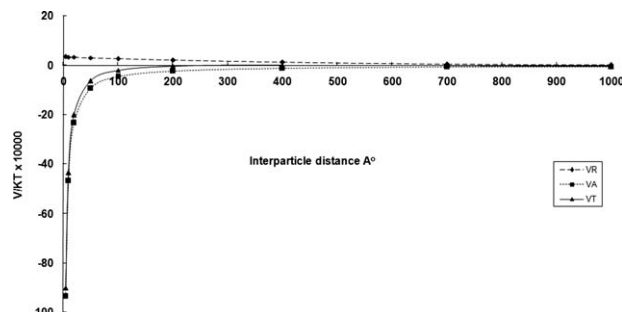

Figure 9 Potential energy profile for bentonite suspension at 20°C.
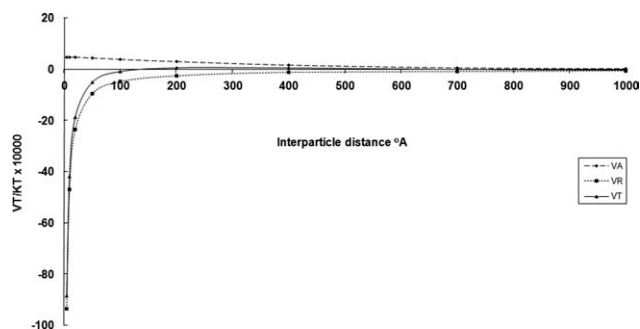
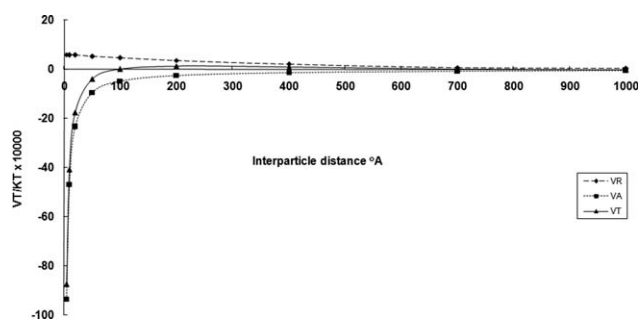**Figure 10** Potential energy profile for bentonite suspension at 40°C.

Figure 11 Potential energy profile for bentonite suspension at 60°C.
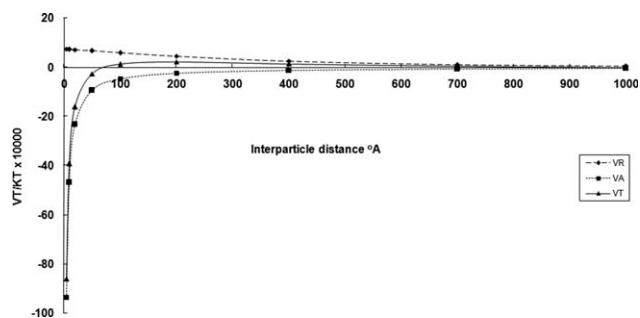

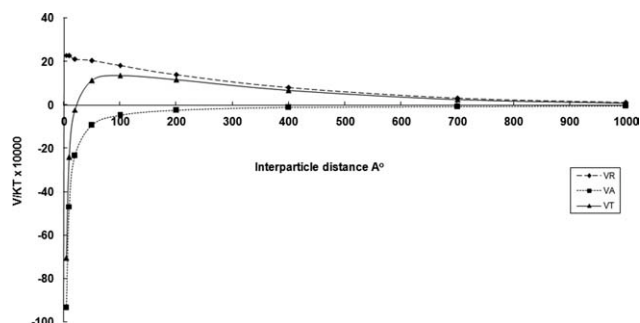**Figure 12** Potential energy profile for bentonite suspension at 80°C.

Figure 13 Potential energy profile for bentonite suspension in the presence of 50 ppm polyethylene imine and 10 ppm polyacrylamide at 20°C.
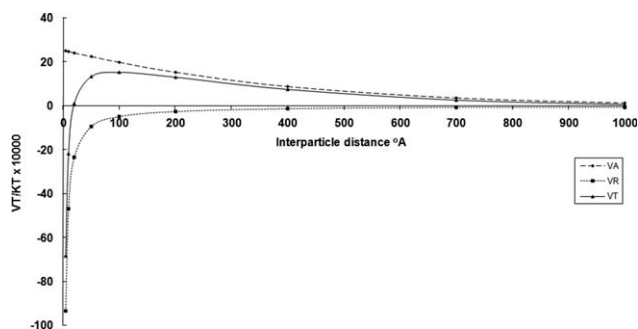
Figure 14 Potential energy profile for bentonite suspension in the presence of 50 ppm polyethylene imine and 10 ppm polyacrylamide at 40°C.

intermediate distance of 100 Å at 20°C. This energy barrier value depends upon the value of zeta potential. As the zeta potential of bentonite suspension is high (about −95 mV at 80°C), the repulsion between clay particles will be high (potential energy barrier of about 19.74×10^4 KT at intermediate distance of 100 Å at 80°C) and the clay particles separated from each other, which means the system is more stable at high temperature (80 > 60 > 40 > 20°C) in the presence of polymers compared with bentonite suspensions without any additives.[27]

CONCLUSIONS

1. The rheological properties of Egyptian bentonite suspensions were increased as temperature increased.
2. The rheological properties of Egyptian bentonite suspensions in the presence of 50 mg/L cationic polyethylene imine followed by 10 mg/L anionic polyacrylamide after 24-h aging time were increased as temperature increased and gave a more desired rheological properties at higher temperature compared with bentonite suspension without any additives.
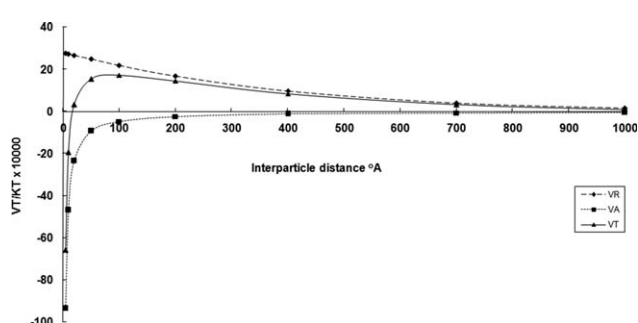3. Addition of 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide to bentonite

Figure 15 Potential energy profile for bentonite suspension in the presence of 50 ppm polyethylene imine and 10 ppm polyacrylamide at 60°C.
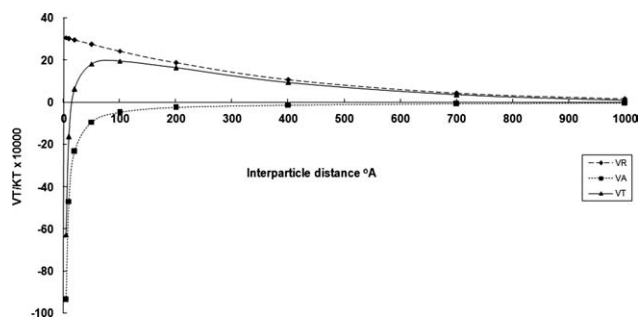
Figure 16 Potential energy profile for bentonite suspension in the presence of 50 ppm polyethylene imine and 10 ppm polyacrylamide at 80°C.

suspensions produced highly stable bentonite suspension at high temperature compared with the bentonite suspensions without addition of polymers.

4. The Egyptian clay suspension can give desired drilling mud properties using 6% clay suspension concentration treated with 50 mg/L polyethylene imine followed by 10 mg/L polyacrylamide at 80°C up to 24-h aging time.

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