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FULL LENGTH ARTICLE

Study the effect of synthesized graft copolymer on the inhibitive water based drilling fluid system

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Abstract This research paper consists of the synthesis of carboxymethyl-graft-polyacrylamide copolymer by free radical polymerization technique and its characterization using Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM) and thermogravimetric analysis. This graft copolymer was used as a drilling fluid additive and its effect on the Indian reactive shale sample was analyzed. The characterization of the shale sample used in this study was done by X-ray diffraction technique (XRD), FTIR, FESEM, and energy-dispersive X-ray spectroscopy (EDX) to determine the presence of various clay minerals. Experimental investigations revealed that the synthesized graft copolymer has a significant effect on the rheological and filtration properties of the inhibitive drilling fluid system and has high shale recovery performance. Hence, inhibitive drilling fluid system using synthesized graft copolymer may be used for the drilling of water sensitive shale formations.

1. Introduction

The drilling fluid which slows or stops the hydration, swelling and disintegration of shales is called inhibitive drilling fluid. In the inhibitive water based drilling fluid system the salt concentration is kept above 10,000 ppm. It consists of salt, synthetic and natural compounds to serve the purpose of drilling the oil/gas wells safely and efficiently. This type of aqueous drilling fluid system is used to inhibit the swelling tendency of the water sensitive geological formations like shale, mudstones, claystones etc thus, providing minimal reactivity of the drilling fluid with the borehole. Apart from inhibitive function of this mud system, it has to perform other functions such as the circulation of cuttings, bore hole cleaning, pressure maintenance inside the wellbore, cool and lubricate the drill bit and to smoothen the functioning of drilling strings [1–5].

Several types of organic polymers are used to control the rheological and filtration properties of drilling fluid systems [6–8]. Among these, natural polymers are biodegradable, fairly shear stable, and cause drag reduction at relatively higher concentration. The synthetic polymers are much more effective than the natural polymers due to their versatile flexibility. But, these polymers are not shear resistant and hence, natural

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polymers like xanthan gum are generally preferred to control rheological properties of water based drilling fluid system. To control the filtration characteristics of drilling fluid, semi-synthetic and biopolymers like carboxy methyl cellulose (CMC), polyanionic cellulose (PAC), starch etc are widely used [9–11].

Many industries use polyacrylamide to mitigate wellbore instability problems arising due to swelling & dispersion of shale and the cuttings inside the wellbore because of its unique property of shale encapsulation. The probable mechanism is based on the adsorption of the polymer on the reactive clay sites present in the shale. The adsorption of the polymer is increased in the presence of potassium chloride (KCl) salt, which also aids in the inhibition of swelling tendency of shale [12–15].

Sodium carboxymethyl cellulose (CMC) is a linear, long chain, water-soluble, anionic polysaccharide produced by reacting alkali cellulose with sodium monochloroacetate which is used generally in the development of different drilling fluid systems. The various properties of the CMC depend on the distribution of carboxyl substituents along the polymer chain, molecular weight of the polymer, and average number of carboxyl content per anhydroglucose unit [16,17]. The rheological and filtration properties of the CMC solutions depend on many factors like concentration of polymer, temperature, pH, salt content, total degree of substitution of the polymer, molar mass, and presence of the surfactant [18,19].

To overcome the difficulties faced during the application of synthetic polymers, the grafting of synthetic polymers on the natural polymers is suggested by many researchers [20–22]. The graft copolymers have relatively high shear stability as grafting improves the shear stability during the turbulent flow [23]. Grafting of natural polysaccharides and synthetic polymers such as polyacrylamide has been reported earlier for different applications [24,25].

In the present study, CMC-g-PAA graft copolymer is synthesized in an aqueous medium using potassium persulfate (KPS), an inorganic compound with the formula $K_2S_2O_8$ as initiator. The free radical polymerization process took place in nitrogen gas (N_2) atmosphere. Then, the synthesized graft copolymer is used to develop an inhibitive water based drilling fluid system and calcium carbonate was used as a bridging agent to minimize the API fluid loss volume in this drilling fluid system. In addition, mineralogical studies are carried out on the shale sample to determine the presence of reactive clay minerals in the shale. Then, the shale recovery tests are done to analyze the performance of the graft copolymer on the shale recovery.

2. Experimental

2.1. Materials

Acrylamide and potassium chloride salts were procured from the Merck Pvt. Ltd., Mumbai, India. Low viscosity grade CMC and calcium carbonate were obtained from the CDH, chemicals Ltd., New Delhi, India. Low viscosity grade polyanionic cellulose and xanthan gum were procured from the ONGC, India. Potassium persulfate was purchased from Qualigens, Mumbai, India. The shale sample was collected from Damodar valley basin, India.

2.2. Synthesis of the graft copolymer (CMC-g-PAA)

The graft copolymer of CMC and PAA has been synthesized in an inert atmosphere of nitrogen using potassium persulfate (KPS) as initiator. The procedure for the synthesis of the graft copolymer is as follows: 2 g of CMC was slowly dissolved in 200 ml of double distilled water in 500 ml 3-neck round bottom flask. The flask was kept in an oil (silicon) bath maintained at a temperature of 68 ± 1 °C fitted with an electrically operated magnetic stirrer (Tarsons, Model-Spinot Digital), for constant stirring. At this stage, 20 ml acrylamide solution of the desired concentration (14.28 M) was poured into the flask, acrylamide was allowed to mix with CMC solution and continued to heat at the same temperature for 3 h at 550 rpm. After proper mixing of the acrylamide with CMC, 5 ml of potassium persulfate solution (9.25×10^{-3} M) was added slowly and the reaction was continued for another 1.5 h at same stirring speed and temperature. The nitrogen gas was purged continuously during the reaction. The CMC is water soluble and it has imparted viscosity to the solution. Hence, sufficient time for mixing of acrylamide with CMC solution was given so that the resulted aqueous solution would be a homogenous solution. The reaction mixture was cooled at room temperature (25 °C), it was separated by precipitation using acetone. The solid product was filtered and washed with ethanol and then extracted using acetone as solvent in a Soxhlet apparatus for the removal of impurities [26,27]. Afterward, the graft copolymer was dried in a hot air oven at 50 °C for 24 h, pulverized by mortar–pestle. Then, the synthesized graft copolymer was used to develop inhibitive water based drilling fluid system.

2.3. Characterization of graft copolymer

2.3.1. FTIR analysis

FTIR spectra of various samples were recorded in PerkinElmer model Spectrum Two (USA) and range of the above measurements was 450–4000 cm^{-1}. 1 mg of the sample was mixed with a very small amount of KBr and KBr pellet was prepared using a hydraulic press by applying a pressure of 100 psi for 60 s. The IR spectrum of the KBr pellet is recorded and 100 scans were collected.

2.3.2. FESEM analysis

The morphology of the various samples used in this study was analyzed by FE-SEM Supra 55 model, Carl Zeiss (Germany) with Air Lock chamber to examine the morphology of different samples. Samples were charged with platinum coating to get clearer images.

2.3.3. Thermal analysis

Thermal stability of the graft copolymer, and CMC was examined using thermogravimetric analysis (TGA) in Netzsch-STA 449 Jupiter (Germany). TGA analysis was performed up to 370 °C in a nitrogen gas atmosphere with a heating rate of 10 °C/min.

2.4. Characterization of the shale sample

2.4.1. XRD analysis

The shale sample was characterized by X-ray diffraction (XRD) analysis to determine the qualitative mineral content

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