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High-performance shale plugging agent based on chemically modified graphene

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ABSTRACT

Ethylenediamine-modified graphene (EDA-G) performed high performance to plug nanopores of shale formation. A simple method was designed to evaluate the plugging capability of EDA-G solution. Compared with inorganic nano-materials, the addition of EDA-G in drilling fluid resulted in the lowest filtration volume in some specific condition. EDA-G was adsorbed in the surface of shale and formed the tight film, which prevented the invasion of water from shale formation. Artificial cores with low permeability were used to measure membrane efficiency by membrane efficiency tester. The time of downstream reaching to equilibrium in 0.4 wt% EDA-G solution was about 120 times than in 4 wt% NaCl solution. Native shale cores with ultralow permeability were used to test membrane efficiency in 0.4 wt% EDA-G solution and 4 wt% NaCl solution. Downstream pressure began to increase after 300 min in 4 wt% NaCl solution and was stable quickly. But downstream pressure did not increase until 3660 min in 0.4 wt % EDA-G solution. EDA-G solution was suitable to plug nanopores of ultralow permeability shale. More importantly, EDA-G solution inhibited the hydration of clay as well. EDA-G solution exhibited high performance as inhibitor at concentration of 0.2 wt% by carbon content. In a study of linear swelling test using bentonite samples, the addition of water, KCl, polyether amino, Chitosan quaternary ammonium salt (HTCC) and EDA-G caused the expansion height of 4.67 mm, 2.47 mm, 2.02 mm, 1.79 mm and 1.79 mm respectively, which corresponded to the reduction rate of 47%, 57%, 62% and 62%. EDA-G solution exhibited both excellently plugging nanopores property and inhibiting hydration of clay capability. And the two performances were most key factors to stabilize shale formation during drilling operation for water drilling fluid.

1. Introduction

With development of economic and increasing demand for energy, the depletion of conventional oil and gas reserves has increased the importance of exploration and development of unconventional oil and gas reserves effectively (Rajnauth, 2012). Shale gas has changed the energy equation around the world as a kind of unconventional reserve after exploited industrially in United States (Riley et al., 2012). It has been estimated that the drilled formations be made up by more than 75% shale formations and shale (Josh et al., 2012). Wellbore instability is a major factor technical problem in drilling shale formation (Bol et al., 1994; Bybee, 2009; Díaz-Pérez et al., 2007; Al-Bazali, 2011; Hu et al., 2016). Shale is responsible for 90% of wellbore stability problems. Shale reservoirs have distinctive features compared with traditional reservoirs. It is organic rich and comprised of consolidated clay particles, native fractures and nanopores predominantly, which results in the low-permeability of shale formation (Paikaray et al., 2008; Dokhani et al., 2015; van Oort, 2003). The invasion of water raises the loss pressure of shale and the swelling of clay, resulting in some problems of wellbore stability including the holes collapse, wellbore weakening and stuck pipe (Rahman et al., 2000; Lyu et al., 2015; Yu et al., 2003). This is due to the interaction between the clay minerals inside shale and water in drilling fluid (Chen et al., 2003). A filter cake is formed by fluid loss agent in the surface of the wellbore and prevents water from invading into shale in drilling process for conventional oil and gas reserves, but the filter cake can't be formed in drilling shale formation on the account of the low-permeability of shale and a large scale of fluid loss agent can't enter into nanopores of shale formation (Tang et al., 2014). How to reduce the invasion of water into shale formation through nanopores is an important work to solve wellbore stability problems. Oil

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based mud (OBM) is the best choose in drilling shale formation. OBM with well lubricity property is preferred to plug nanopores of shale because of the clay mineral is no hydration in OBM (Bunger et al., 2014). However, OBM is expensive and not environmental friendly (Simpson et al., 1995; Young and Friedheim, 2013; Shivhare and Kuru, 2014). Increasingly stricter environmental regulations will require more environmental friendly water based drilling fluid (WBM). Several issues need to be resolved before the use of WBM. The invasion of water thought nanopores of shale is a critical factor to raise the problem of wellbore stability. The diffusion of water into shale matrix results in swelling, delaminating, fracturing of clay mineral of shale (van Oort, 1994). Otherwise, horizontal drilling increases the difficulty of WBM in drilling shale formation operations, which requires better wellbore stability due to the long time interaction of WBM with shale formation (Mohiuddin et al., 2007). There is not a suitable WBM system to drill shale formation without wellbore instability problem. To resolve the problem of wellbore instability, some researchers have carried out some works (Akhtarmanesh et al., 2013; Karatela et al., 2016; de Fontoura et al., 2002; Ma et al., 2015; Shen et al., 2015). Chenevert and sensoy group reported that nanosilica plug the nanopores of shale formation and prevent the invasion of water, but the dosage is large even the addition is up to 29% (Cai et al., 2012). More researchers focus on the use of nanosilica and other inorganic materials as plugging agent to plug nanopores of shale formation (Metin et al., 2011). These nanomaterials are easily aggregated and precipitated in water solution (Mukharjee and Barai, 2014; Pourhossaini and Razzaghi-Kashani, 2014). On the account of the weak acting force between nano material and shale formation, it needs the large dosage to up to the required effect. Some other researchers use micro emulsion as plugging agent to prevent water from shale, but micro emulsion is instability and sensitive with the change of environment (Tabibiazar et al., 2015). Most of works are in laboratory stage and there is no industrial production reported. Synthesis of plugging agent is a novel work for WBM in drilling shale operations.

Graphene materials have been widely explored in many fields on the account of their atom-thick two dimensional conjugated structures, large specific surface area and high conductivity (Wu et al., 2010; Xu et al., 2008; Novoselov et al., 2005; Stankovich et al., 2006; Geim, 2009; Stoller et al., 2008). Up to now, graphene materials were prepared by epitaxial growth (Pearce et al., 2011), chemical vapor deposition (Reina et al., 2009), mechanical exfoliation (Robinson et al., 2008), and thermally or chemically (Park and Ruoff, 2009). Graphene oxide (GO) has been used for this purpose. Furthermore, the oxygenated groups provide GO sheet with process ability and the possibility of chemical modifications (Dreyer et al., 2010). Tour and co-workers reported the fluid loss agent based on graphene materials (Kosynkin et al., 2012). The results showed that graphene material performed well as fluid loss agent, comparing with polymer-based fluid loss agent. Some patents reported the use of graphene and modified graphene materials to stabilize shale formation during drilling operation, but the patents did not provide the interaction mechanism and were lack of experimental date to represent plugging capability. Graphene and modified graphene material with laminated structure is flexible nanosheet, and it is adsorbed in the surface of shale to plug nanopores of shale formation and prevents water from invading. The swollen clay of shale is another important factor caused wellbore instability. KCl is widely applied in oil field as inhibitor, but it is short effectiveness. Polyether amino is widely applied in oil field as excellent performance inhibitor. Chitosan quaternary ammonium salt (HTCC) is researched as inhibitor in our previous work (An et al., 2015). But these inhibitors exist in some disadvantages. If modified graphene exhibits inhibiting capability, it will be the better plugging agent to resolve the problem of wellbore instability. Here, we report the kind of plugging agent with inhibition capability based on chemically modified graphene material, which is ethylenediamine-modified graphene (EDA-G). Compare with inorganic nano-materials, the addition of EDA-G in drilling fluid results in the lowest filtration volume in some specific conditions. More importantly, EDA-G solution inhibits the hydration of clay as well.

2. Experimental section

2.1. Materials

Nanosilica (20 nm, 99 wt%), amino nanosilica (20 nm, 99 wt%), nano-zinc oxide (20 nm, 99 wt%) and nano graphite (30 nm) powder were purchased from China nano network. Chitosan quaternary ammonium salt (HTCC) was purchased from JiaXing Kerui Company. Polyether amino was acquired from M-I Company. Ethylendiamine was brought from An Naiji Reagent Company. Polytetrafluoroethylene film (220 nm) was acquired from secco experimental equipment company. Montmorillonite (MMT) was purchased from HuaWei Company. Graphite power (325 meshes) was purchased from Alfa Reagent Company. KCl, NaCl, xanthan gum (XC) and other reagents were purchased from domestic reagent company. All the reagents were used without further purification.

2.2. Methods

2.2.1. Synthesis of GO

GO was synthesized using a modified Hummers' method from graphite powder and the detail were reported in the literature (Hummers and Offeman, 1958; Xu et al., 2009).

2.2.2. Synthesis of EDA-G

EDA-G was prepared according to the procedures reported in the literature (Che et al., 2010; Yuan et al., 2013). 150 mg of GO were dispersed in 200 ml of water via mild sonication, then the addition of 40 ml of ethylendiamine. The mixture was refluxed in a flask at 80 °C for 8 h. The black dispersion was obtained. The ethylendiamine acted as both a reducing agent and a modification component during this process.

2.2.3. Linear swelling tests

The expansion heights of bentonite in solution of GO and EDA-G with time are determined in the laboratory by CPZ-2 dual channel linear swellmeter (Qingdao, China). 5 g montmorillonite (MMT) is poured into pressure tank, then beard 10 MPa pressure by hydraulic press for 5 min. A certainly concentration of GO and EDA-G be soluble in water. Then be poured into the pressure tank meanwhile the value is zero. The expansion height of MMT with time is determined.

2.2.4. Rolling recovery tests

Shale be crushed and sieved between 6 mesh and 10 mesh. 20 g shale debris was poured into digestion tank with 300 ml xanthan gum(XC), GO/XC and EDA-G/XC solutions. The concentration of XC was 0.3 wt%, and the concentration of GO and EDA-G was 0.2 wt%. Put the digestion tanks into the BGRL-5 roller furnace (Qing dao, China), Hot rolling in 120 °C for 16 h. Dried the shale debris in 105 °C for 48 h. Sieved thought 40 mesh and weighted. The weight of the shale before hot rolling denoted by W_1 and after hot rolling denoted by W_2. The Calculated rolling recovery by the following formula: A recovery = W_2/W_1.

2.2.5. Filtration volume tests

Fluid property tests were measured according to American