Applied Clay Science 127–128 (2016) 70–77

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Polyethyleneimine as shale inhibitor in drilling fluid

Jiang Guancheng, Qi Yourong, An Yuxiu *, Huang Xianbin, Ren Yanjun

[a] State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, (Beijing), Changping District, Beijing 102249, China
[b] MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, (Beijing), Changping District, Beijing 102249, China

ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 11 April 2016
Accepted 12 April 2016
Available online 19 April 2016

Keywords:
Polyethyleneimine
Shale inhibition
Hydration swelling
Adsorption
Clay particle

ABSTRACT

In this paper, the inhibition property of polyethyleneimine (PEI) in drilling fluid was studied. The inhibition property was evaluated by linear swell test and roll recovery. The addition of PEI_{70000} resulted in the lowest swelling height, compared with the others inhibitor. Especially PEI was environmental and friendly. The inhibition mechanism was investigated by Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Scanning electron microscopy, Zeta potential and Surface area analyzer. The negative charge in the surface of montmorillonite (Mt) was neutralized by the positive charge of PEI. PEI was adsorbed in the surface of Mt and intercalated into the interlayer of Mt, which reduced the hydration repulsion of diffuse electric double layer and leaded to inhibit the hydration of clay. Hydrogen bonding between amino groups in PEI and hydroxyl in the surface of Mt can be formed in the process. The coordination of electrostatic interaction and hydrogen bonding presented water molecules from the interlayer space of Mt, which resulted from the adsorption and intercalation of PEI in the surface and interlayer space of Mt. There was an amount of nitrogen in the backbone and side of PEI, leading to more positive ion than chitosan quaternary ammonium salt (HTCC). The more positive ion resulted in the stronger force between inhibitor and clay due to the protonation of nitrogen in water. The molecular weight of PEI has great influence on inhibition property. The larger molecular weight of PEI performed the better inhibition property except for PEI_{1800}. Indicating the molecular weight of PEI was not the sole factor to control the inhibition property. What was more, the larger molecular weight of PEI leaded to the worse water-solubility.

1. Introduction

Wellbore instability problems of shale are frustrated drilling engineers as these rocks make up over 75% of drilled formation (Rajnauth, 2012). >90% of wellbore instability problems are caused by problematic shale (Al-Bazali, 2011). It is one of the most significant technical problems in petroleum exploration and a major source of lost time and revenue. Shale reservoirs have distinctive features compared with traditional reservoirs (Josh et al., 2012). Shale is organic rich and comprised of consolidated clay mineral, natural fractures and nanopores predominantly. Shale instability manifests itself in a number of different ways, leading to a variety of different problems (Bybee, 2009; Rahman et al., 2000; Yu et al., 2003; Chen et al., 2003; Mohiuddin et al., 2007). For example, the wellbore may collapse, enlarge holes. Cuttings from drilling shale may disperse and disintegrate when encounter drilling fluid, or agglomerate around the drill bit. These problems result in wellbore instability.

Clay mineral composition is considered as a major causal factor in shale instability (Van Oort, 2003). The nature of the clay mineral remains as the most cited primary causes of wellbore instability, even though the existence of overpressure may be major factors in causing wellbore instability (Riley et al., 2012; Díaz-Pérez et al., 2007; Paikaray et al., 2008). The charged nature of clay minerals and the hydrophilic enables them to swell and take part in cation exchange reactions. Clay mineral such as Mt results in an increase in swelling and osmotic pressure of shale through hydration of the clay and cation exchange (Balaban et al., 2015). Inhibiting the hydration of clay is an effective way to control wellbore instability (Bunger et al., 2014). Oil based fluid is the preferred system in these shale formations (Shivhare and Kuru, 2014). The clay is unhydrated in oil based fluid, but it exists in the fatal environment issues (Patel et al., 2007). Oil based fluid is not biodegradable and harm for health and environment. Due to potential detrimental effect of non-environment friendly oil based fluid, Environment Protection Agency and other regulatory bodies are imposing increasingly stringent regulations on the use and disposal of non-environment friendly oil based drilling fluid. It has been desirable to drill with water based fluid, but water based fluid exists in issues as well (Chenevert and Pernot, 1998; Ji et al., 2012; Patel and Gomez, 2013). When water-sensitive shale formation is exposed to conventional drilling fluid, shale has an immediate tendency to take up water from the drilling fluid and swell and disperse rapidly, leading to wellbore instability issues such as bit-balling, disintegration of cuttings, borehole wash-out, high torque and drag, and stuck pipe. The drilling fluid industry was searching for inhibitive water based drilling fluid all

---

* Corresponding author at: State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, (Beijing), Changping District, Beijing 102249, China.

http://dx.doi.org/10.1016/j.clay.2016.04.013
0169-1317/© 2016 Elsevier B.V. All rights reserved.

the time. Many approaches have been taken over the years, including inorganic salts (Huadi et al., 2010), such as KCl, $CaCl_2$, NH_4Cl, modified gilsonites and asphalts (Davis and Tooman, 1989), functionally cationic poly quaternary amines polymers (Patel, 2009), amphoteric polyamino acids (Gholizadeh-Doonechaly et al., 2009; Xiong et al., 2012; Zhong et al., 2011) and nonionic polymer (Brady et al., 1998; Guo et al., 2006; Zhang et al., 2013), cationic polymers (Rosa et al., 2005). However, these approaches have some disadvantages, for example, short effectiveness, worse inhibiting capability, toxicity, low heat and salinity tolerance, worse compatibility. Even if some issues have been solved, but the hydration of water-sensitive shale is not completely controlled (Ramirez et al., 2007). High performance water based mud (HPWBM) newly developed water based fluid comprised a unique polymeric amine which is polyether ended with amine group; nevertheless it is poor heat tolerance duo to the hydrolysis reaction of the polyether. It is urgent need of researching the effective and environment friendly shale inhibitor. Clay particle is electronegative (Bonini et al., 2009), and it is obviously that the effective shale inhibitor is electro positivity based on fundamental laws of electricity which the opposite charges attract each other. Positive groups enter into interlayer space and prevent clay particle from swelling and dispersing. Electro positivity is an essential characteristic as excellent shale inhibitor. Atom with lone pair electrons is liable to form hydrogen bonds between hydrogen atom and these typical atoms of oxygen atom, nitrogen atom and sulphur atom. Hydrogen bond is the main driving force of preventing clay particle from swelling and dispersing (Tang et al., 2014), and these clay particle have a number of hydrogen atoms and oxygen atoms with lone pair electrons, and atoms with lone pair electron are another essential characteristic as shale inhibitor.

Polyethyleneimine (PEI) is water soluble polymer with an amount of cation groups (Poghosyan et al., 2015; Foundas et al., 2015; Neville et al., 2013). Their solutions are alkaline (Rajagopalan et al., 2015). Meanwhile, there are a number of nitrogen atoms which form hydrogen bond. What is more important, PEI was environmental and friendly (Wang et al., 2015a and b). In fact, polyethyleneimine has been widely applied in bioengineering (Liu et al., 2015; Zhu et al., 2015), waste water treatment industry (Adewunmi et al., 2015), oil treatment industry (Wang et al., 2015a and b), sensor (Li et al., 2015), coating industry (Sunintaboon et al., 2009), catalyst (Park and Kim, 2015; Zakharova et al., 2009), membrane (Fang et al., 2015). Polyethyleneimine is synthesized by ring opening polymerization of ethyleneimine. There are a series of products which are classified by molecular weight and structure. In this work, the evaluation of the inhibiting property classified by different molecular weight was studied and the inhibition mechanism was explored vis a variety of characterization methods. The application of polyethleneimine is provided in drilling fluid.

The study of inhibition properties of PEI as shale inhibitor was invested. PEI exhibited high performance as an outstanding shale inhibitor according to shale linear swelling and rolling recovery. The mechanism of PEI vis Mt was observed (Fig. 1).

2. Materials and methods

2.1. Materials

Polyethleneimine was purchased from Aladdin Inc. Chitosan quaternary ammonium salt (HTCC) (Mn 54,000 Da, Quaternary salt graft degree 60–80%, Purity ≥95%) was purchased from Jiaxing Kerui Biological Technology Co., Ltd. Polyether amine was obtained from oil field. Montmorillonite (Mt) which was sodium bentonite was purchased from Weifang Huawei Company. Shale was obtained from oil field. The other experimental chemicals were purchased from domestic reagent company. All the chemical materials were used without further purification.

2.2. Methods

2.2.1. Linear swell tests

The expansion heights of inhibitors solutions with time were determined by CPZ-2dual channel linear swell meter (Tongchun, Qingdao). A filter paper was put on the bottom of pressure tank, then 5 g Mt was poured into pressure tank. The pressure tank bears 10 MPa pressure for 5 min by hydraulic press. A series of concentration of polyethyleneimine solutions were prepared. Then the solutions were poured into pressure tank and the value is recorded zero.

2.2.2. Rolling recovery tests

The debris of shale between 6 mesh and 10 mesh were prepared. The concentration of inhibitor solution is fixed on 2 wt%. 300 ml solution and 20 g shale debris were poured into digestion tank. Then the digestion tanks were put into the BGRL-5 roller furnace (Tongchun, Qingdao) and rolled at 120°C for 16 h. After cooled into room temperature took away upper suspension, then 200 ml deionized water was added. This procedure was repeated for three times. Precipitate was dried at 100 °C for 48 h. The dried precipitate was sieved thought 40 mesh and weighted. The Calculated rolling recovery as the following formula: Recovery $= W_2 / W_1$. Shale debris denoted by W_1 and after hot rolled denoted by W_2.

2.2.3. Preparation of Mt/PEI hybrids and purification of PEI

300 ml 2 wt% of PEI solution was prepared. Then 9 g Mt was added into PEI solution to make Mt/PEI dispersion, following fierce stirred for 30 min at 8000 rpm. Then the dispersion endured at 120 °C for 16 h to balance the adsorption and hydration between Mt and PEI. The dispersion was carried out centrifugal treatment at 10,000 rpm for 15 min. The precipitate was washed several times by deionized water until the upper liquid was clearly. Finally the precipitate was dried at 100°C for 24 h. Then be grinded into powder for XRD, XPS and FT-IR.

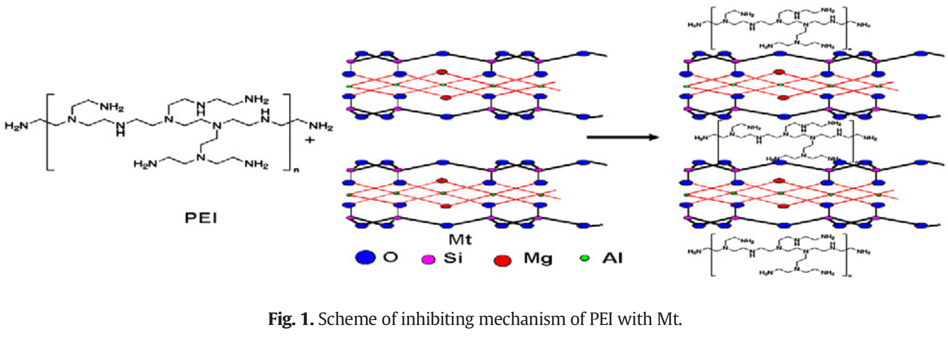

Fig. 1. Scheme of inhibiting mechanism of PEI with Mt.