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Maintaining shale stability using polyether amine while preventing polyether amine intercalation

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ABSTRACT

Polyether amine (PA) has recently been widely applied in water-based drilling fluid to improve shale stability. To study whether PA intercalation and the resulting increase of montmorillonite (Mt) d001-value have a negative effect on shale stability, a PA adsorption test on shale, a shale composites X-ray diffraction (XRD) test and a one dimensional swelling test of shale immersed in solution were conducted. PA can absorb on shale by exchanging Na⁺ in shale, resulting in a d001-value increase of sodium montmorillonite (Na-Mt) in shale and large vertical displacements, causing lots of micro cracks to develop in the shale with the shale matrix dispersed. For shale immersed in solution with KCl and PA mixed, PA intercalation was reduced and even prevented because K⁺ can exchange Na⁺ in the shale first. With the cation hydration reduced by K⁺ adsorption and the clay layer hydration decreased by PA adsorption on clay layer, vertical displacement was greatly reduced and stability was greatly enhanced for the shale immersed in solution with KCl and PA mixed. As a result, during drilling in shale containing Na-Mt, PA can cause shale instability. Using PA and KCl together can achieve better shale stability compared to using KCl only.

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1. Introduction

Approximately 90% of the wellbore stability problems were encountered while drilling through shale formations; examples such as hole collapses, tight holes, stuck pipes, poor hole cleaning, hole enlargement, plastic flow, fracturing, and loss of well control, as reported by Steiger and Leung (1992) and Zhang et al. (2013), cause a loss of about US\$ 1 billion per year worldwide. Water absorption in shale is often accompanied by a change in the basal spacing of clay minerals, which manifests itself as a swelling of the rock, leading to severe structural damage, which then threatens the stability of shale boreholes. Therefore, a critical factor in the design of drilling fluid is the ability to reduce hydration of clay minerals for the prevention of wellbore stability problems while drilling in shale formations (Morton et al., 2005; Bruton and McLaurine, 1993). Among the methods used to reduce shale hydration (Rosa et al., 2005; Caenn and Chillingar, 1996; Souza et al., 2010; Burchill et al., 1983), potassium chloride was the earliest and most widely used agent and low molar mass PA is a recent advance (Zhong et al., 2011; Qu et al., 2009; Wang et al., 2011; Cui and van Jeroen, 2010). It was accepted (Zhong et al., 2011; Qu et al., 2009; Wang et al., 2011; Cui and van Jeroen, 2010) that PA intercalation and the less water adsorption that resulted is beneficial to shale stability, neglecting PA intercalation can cause the increase of montmorillonite d001-value and then,

swelling of shale. It remains unclear whether exchange of Na⁺ by PA molecules was beneficial for shale stability or not. This may lead to severe wellbore stability problems if a suboptimal drilling fluid and stabilizer combination is used. In this paper, shale samples containing Na-Mt were studied. K⁺ and PA adsorption isotherms on shale were tested. XRD analyses were used to study K⁺ and PA intercalation in shale clay minerals. To evaluate shale stability, a one dimensional swelling test of shale immersed in solution was conducted. In addition, pictures of shale core immersed in different solution at different times were taken to characterize the effects of swelling on shale.

2. Experimental

2.1. Shale characterization

The mineralogical composition of the shale sample (H1) was determined by X-ray diffractometry using an X'Pert-Pro MPD diffractometer with a source of Cu-K α radiation equipped with solid-state detector and operating at 40 kV and 40 mA (PANalytical B.V.; Netherlands), following the procedure described in the SY/T 5163 (1995); SY/T 6210 (1996); SY/T 5983 (1995). Ions in shale were exchanged with Ba²⁺ (Jiang and Zhang, 2005) and the ion species and content was measured using Agilent ICP-720ES inductively coupled plasma atomic emission spectrometer (Agilent Technologies Corporation, US).

As shown in Table 1, quartz was dominant in the H1 shale sample and the total clay proportion was 36%. Illite and mixed-layer clay were

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Table 1
Mineralogical and exchanged cations composition of H1 shale sample.

Proportion of minerals in total sample/%							
Quartz	Potassium feldspar	Plagioclase	Calcite	Ankerite	Analcime	Hematite	Total clay
28	5	13	7	4	5	2	36
Proportion of clay minerals in total clay/%							
Illite	Kaolinite		Chlorite		Mixed layer (illite/montmorillonite)		
28	4		4		64		
Proportion of layers in mixed-layer clay/%							
Montmorillonite							Illite
20							80
Proportion of exchanged cations in clay minerals of shale/(mmol/100 g shale)							
Total exchanged cations contents	Ca ²⁺	K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺	Sr ²⁺	
20.204	1.030	0.140	0.168	0.002	18.860	0.004	

Contents of other cation species (Al, As, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Ni, P, Pb, Se, V, Zn) was 0.

the main type of clays in shale. The proportion of illite was 28%, and that of the mixed-layer clay was 64% with a little chlorite and kaolinite. The total I amount of exchangeable cations in the H1 shale sample was 20.204 mmol/100 g shale and Na⁺ was the main type of exchangeable cation. According to the SY/T 5163 (1995); SY/T 6210 (1996); SY/T 5983 (1995), the error of the method adopted to test shale mineralogy is up to 30%. Moreover, during shale mineralogy test, decantation method was adopted to separate silt and clay, resulting loss of certain clay minerals. Then, CEC in shale is higher than that predicted based on clay mineralogy. As can be inferred, the H1 shale contains more Na-Mt than the amount tested.

Shale samples were ground and sieved to generate the powder particles of size less than 50 μm. By using a low speed agitator at 800 rpm for 24 h, the shale powder was dispersed in water to generate 40 g/L aqueous dispersions that were subsequently washed with deionized water until the conductivity of the supernatant equaled that of deionized water. After washing, the shale sample was dispersed and stored as a stock suspension. The solid content was measured after drying at 100 °C for at least 48 h or until the weight remained constant.

2.2. Chemicals

PA used in this study was developed by the drilling fluid research team at the China University of Petroleum. The structure and properties of the PA molecule have been reported by Zhang et al. (2015). The PA molar mass was approximately 400 g/mol and had a typical chemical formula of CH₃—[OCH₂CH₂]_x—[OCH₂(CH₃)CH]_y—NH₂. Analytically pure KCl was purchased from Sinapharm Chemical Reagent Co. Ltd.

2.3. Adsorption isotherms of PA, K⁺ on the shale sample

The test procedure of adsorption isotherms for PA, K⁺ on the shale sample is the same as that of PA, K⁺ on Mt, as reported by Zhang et al. (2015). The carbon content in the dried shale-polyamine composite was analyzed using a Euro EA3000 elemental analyzer (Euro Vector S.P.A.; Italy). The K⁺ content in the supernatant was measured using an Agilent ICP-720ES inductively coupled plasma atomic emission spectrometer (Agilent Technologies Corporation, US).

2.4. Released ions measurement

The adsorption process can involve the release of ions species and released ions content in the supernatant was tested following the procedure reported by Zhang et al. (2015). The ion species and content in the supernatant were measured using an Agilent ICP-720ES inductively

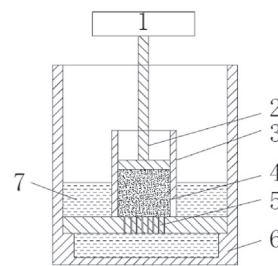
coupled plasma atomic emission spectrometer (Agilent Technologies Corporation, US).

2.5. XRD measurement

The shale and shale-PA (or K⁺) composite d001-value test was conducted by XRD measurement and the procedure adopted was the same as that reported by Zhang et al. (2015). The shale and shale composite suspensions were washed twice and centrifuged with 5000 g centrifugal force for 30 min. Following this, the pastes produced were applied liberally and evenly to glass slides that were subsequently placed in desiccators with a saturated K₂SO₄ solution at ~98% relative humidity (RH) for one month, and XRD analysis was conducted to measure the d001-value of both the shale and shale composite at ~98% RH using an X'Pert-Pro MPD diffractometer (PANalytical B.V.; Netherlands). Thereafter, the same samples were subsequently placed in desiccators with silica gel at ~0 RH for another month. XRD analysis was used to measure the d001-value of both the shale and shale composite at ~0% RH.

2.6. Shale one-dimensional swelling tests and shale immersion tests

One-dimensional swelling tests were carried out in fixed ring oedometers, as shown in Fig. 1. The procedure adopted for the swelling tests was similar to the procedure suggested in ASTM D 4546 as Method B, except that the ring diameter was 1 in. which is the same as one dimensional swelling test described in Modern Technology of Drilling Fluid Experiment (Zhang and Luo, 1999). In addition, 5 kN were loaded to the surface of shale specimens. The specimens were allowed to swell when immersed in water solution such as KCl solution or PA solution.



1) Digital Dial Gauge 6.0x0.001mm 2) Loadblock 3) Metal ring
4) Shale 5) Porous disc 6) Solution tank 7) Solution

Fig. 1. Sketh of shale one-dimensional swelling test apparatus.

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