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Research paper

Structures and rheological properties of organo-sepiolite in oil-based drilling fluids

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ABSTRACT

This work reports the characterization of organo-sepiolite (OSep) and the evaluation of the rheological properties of OSep in oil-based drilling fluids. Sepiolite was modified with benzyl dimethyl octadecyl ammonium chloride and OSep samples were prepared. X-ray diffraction, scanning electron microscope, specific surface area and thermal analysis were applied to characterize the structure of OSep. Viscosity, yield point, dynamic rheological behavior and thixotropy were used to appraise the rheological properties of OSep/oil fluids aged at different temperatures. Surfactants coat on the surface of Sep and insert into the channels and tunnels, resulting in lipophilicity and decline of surface area of OSep. Individual fibers, crystal bundles and small particles of OSep form big particles with smooth surface after organic modification. Rheological properties of OSep/oil fluids can be promoted by the increase of surfactants while extremely high surfactant's loading level results in decrease of rheological properties. OSep modified with 35% of surfactant shows the best rheological properties. Temperature rising promotes the rheological properties of OSep/oil fluids by changing the organizations of OSep. However, extremely high temperatures result in deterioration of rheological properties. OSep is a potential rheological additive in oil-based drilling fluids with excellent rheological properties.

1. Introduction

Sepiolite is a hydrous magnesium silicate with the ideal formula of $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4(H_2O)_8$ (Alvarez, 1984; Álvarez et al., 2011; Suárez and García-Romero, 2011). Like all ideal phyllosilicates containing 2:1 layers (TOT) where there is an octahedral sheet (O) between two opposing tetrahedral sheets (T), sepiolite has continuous planes tetrahedral basal oxygen atoms approximately 6.6 Å apart. However, unlike the ideal 2:1 phyllosilicates, the apical oxygen atoms point away from the basal oxygen plane in opposing direction to form ribbons of joined pyroxene-like chains (Galan, 1996; Guggenheim and Krekeler, 2011). Because of the discontinuous octahedral sheets, many channels and tunnels occur in the sepiolite structure, with the size of 3.7 Å × 10.6 Å (Galan, 1996; Álvarez et al., 2011). In addition, oxygen atoms in the octahedra at the edge of the ribbons are coordinated to cations on the ribbon side only, and coordination and charge balance are completed along the channel by protons, coordinated water and a small number of exchangeable cations (Alvarez, 1984; Santaren, 1990; Galan, 1996; Guggenheim and Krekeler, 2011).

Sepiolite is one of the natural nanofibrous materials. Fiber sizes vary widely but generally range from 0.2 μm to 2 μm in length, 100 nm to 300 nm in width and 50 nm to 100 nm in thickness (Alvarez, 1984; Álvarez et al., 2011). Due to its unique structure and morphology, sepiolite shows high specific surface area of 300 m^2/g (Sun et al., 1995; Rytwo et al., 2002; Álvarez et al., 2011) and cation exchange capacity of 4–40 mmol/100 g (Galan, 1996), rheological properties in polar solvents, adsorptive properties and microporous, etc. (Alvarez, 1984; Álvarez et al., 2011). Therefore, sepiolite is usually used as catalyst carriers (Güngör et al., 2006; Núñez et al., 2014), adsorbents (Rytwo et al., 2002; Sabah et al., 2002; Özdemir et al., 2007; Duman et al., 2015), etc. In addition, because of the fibrous morphology, sepiolite fibers can disperse well in high-polarity solvents (e.g. water-based drilling fluids) and build network structure, resulting in excellent rheological properties.

Clays and organoclays are widely used in drilling fluids as rheological additives to support several fundamental functions, such as (i) to remove the cuttings generated by the drill bit from the borehole, (ii) to control the downhole formation pressures, (iii) to overcome the fluid pressure of the formation, (iv) to avoid damage to the producing formation and (v) to cool and lubricate the drill bit, etc. (Chilingarian and

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Vorabutr, 1983; Caenn and Chillingar, 1996; Meng et al., 2012). Generally, drilling fluids can be divided into two types based on the continuous phase, i.e., water-based drilling fluids and oil-based drilling fluids. Water-based drilling fluids are limited by their abilities of dissolving salts and interfering with the flow of oil and gas through porous rocks. Oil-based drilling fluids, owing to their excellent lubricity, high rate of penetration, shale inhibition, wellbore stability, high lubricity, high thermal stability (Caenn and Chillingar, 1996; Khodja et al., 2010), are advised to be used to drill difficult wells.

The successful completion of an oil well and its cost depend to a considerable extent on the rheological properties of the drilling fluids. Rheological properties of clay minerals such as sepiolite, Na-bentonite and kaolinite show serious differences depending on the adsorption of cationic surfactants and polymers onto clay minerals (Tunç et al., 2008, 2011, 2012; Duman et al., 2012). Clay minerals such as montmorillonite (Kok, 2004; Mahto and Sharma, 2008; Abdo and Haneef, 2013; Li et al., 2015; Temraz and Hassanien, 2016), palygorskite (Dahab and Jarjarah, 1989; Dahab, 1991; Galan, 1996; Baltar et al., 2009; Álvarez et al., 2011; Abdo et al., 2016) and sepiolite (Guven, 1981; Galan, 1996; Altun and Serpen, 2005; Osgouei, 2010; Abdo et al., 2016) are used in water-based drilling fluids as rheological additives. Accordingly, organoclays are also used in oil-based drilling fluids as rheological additives. Generally, organo-montmorillonite (OMt, commercially called organobentonite) is used to control the rheological properties of oil-based drilling fluids (Caenn et al., 2011; Dino and Thompson, 2013; Zhuang et al., 2016, 2017a). Previously, we studied the structure and rheological properties of organo-palygorskite in oil based-drilling fluids (Zhuang et al., 2017b, 2017c). Organo-palygorskite was proved to be an excellent rheological additive in oil-based drilling fluids, with high thermal stability. Sepiolite shows the similar structure and properties with palygorskite. However, the structures and rheological properties of organo-sepiolite (OSep) in oil-based drilling fluids has never been reported in detail. Literature had reported that sepiolite showed excellent rheological properties in water-based drilling fluids and exhibited great thermal stability and excellent salt resistance (Galan, 1996). Thus, OSep may be a potential rheological additive in oil-based drilling fluids and the rheological properties of OSep in oil-based drilling fluids are worthy of studying.

Recently, OSep attracts more attention because its special use in polymer/clay nanocomposites (Tartaglione et al., 2008; Álvarez et al., 2011; Garcia-Lopez et al., 2013; Fernandez-Barranco et al., 2016) and removal of organic contaminants in water (Li et al., 2003; Rytwo et al., 2011). Inspired by the excellent rheological properties of sepiolite in water-based drilling fluids and organo-palygorskite in oil-based drilling fluids, OSep potentially owns excellent rheological properties in oil-based drilling fluids. Aiming to evaluate the possibility of OSep as a rheological additive in oil-based drilling fluids, the structure and rheological properties of OSep in oil-based drilling fluids were studied in this paper.

2. Materials and methods

2.1. Materials

Raw sepiolite (Sep), which was milled and sieved with a 200-mesh sieve, was obtained from Spain, with the cation exchange capacity of 35 mmol/100 g. The constitutes of Sep derived from XRF test are listed in Table 1. Benzyl dimethyl octadecyl ammonium chloride (C18-B, 97%) was bought from Shantou Xilong Chemical Co., Ltd., China. The white oil (No. 5) was bought from China National Petroleum Corporation.

Table 1
Constitutes of Sep derived from the XRF test.

Constitute	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	Na_2O	Others
Mass (%)	64.68	9.08	19.51	3.35	1.27	0.89	1.22

2.2. Preparation of OSep

OSep was prepared as the following steps: a certain amount of cationic surfactant was firstly dissolved into 200 mL distilled water (keep at 60 °C in the whole process), 50 g of Sep was added into the previous solution, stirred for 1 h and thickened slurry was obtained; at last, after drying at 60 °C for 24 h, milling and sieving with a 200-mesh sieve, OSep was prepared. The amount of C18-B was 15%, 25%, 35% and 45% of the mass of raw Sep.

2.3. Preparation of OSep/oil fluids

OSep (12 g) was added into 400 mL white oil (concentration of 30 kg/m^3) and blended at 10000 rpm for 20 min. A drilling fluid should be aged at different temperatures to model the real drilling operation. According to the standards of API SPEC 13A and API RP 13B-2, the resulting fluid was placed in a rotary oven heated to 66 °C, 150 °C, 180 °C and 200 °C where it was aged for 16 h.

2.4. Characterization

The X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance X-ray powder diffractometer operating at Cu Kα radiation, 40 kV, 40 mA and a scan speed of 0.05 s per step (step size: 0.02°). The XRD patterns were collected from 3° to 70°. Thermogravimetry (TG) analysis was tested on a NETZSCH STA 449 F3 type DTA-TG instrument from 50 °C to 900 °C in air, with the heating rate of 10 °C/min. Derivative thermogravimetric (DTG) curves are used to analyze different mass loss stages precisely. Scanning electron microscope (SEM) images were obtained with a HITACHI SU8000 type SEM and the operating voltage was 10 kV. Before the SEM test, conductive coating is required for OPal samples. The conductive coating was completed on a Quorum SC7620 sputter coater, with electric current of 20 mA and coating for 120 s. The electrically-conducting metal, i.e., platinum (Pt), was coated on the samples' surface. The thickness of Pt coating was 10 nm. BET surface area was performed on a Quantachrome Autosorb-iQ instrument (N_2 adsorption at 77 K). The samples were degassed at 120 °C for 2 h under vacuum on the apparatus prior to the measurement. The molecular cross section of nitrogen used in the data analysis was 0.1620 nm^2. The typical range of thickness chosen for t-plot measurements was 3.5–5 Å. Gel volume results were obtained by adding 100 mL aged fluid into a graduated cylinder with a stopper and standing for 24 h. The rheological properties (such as apparent viscosity (AV), plastic viscosity (PV) and yield point (YP)) of aged oil-based drilling fluids were determined at 20 °C, using a FANN 35A viscometer and repeated for three times. AV = $1/2\theta_{600}$ (θ_{600} is the dial reading at 600 rpm, corresponding to shear rate of 1021.8 s^{-1}). PV = θ_{600}–θ_{300} and YP = $1/2(\theta_{300}$-PV). The dynamic rheological behavior of oil-based fluids was tested by a Thermo Scientific HAAKE Roto Visco 1 rotational viscometer. The tested program was: the shear rate linearly increased from 0 s^{-1} to 100 s^{-1} in 5 min (up step), and then linearly decreased from 100 s^{-1} to 0 s^{-1} in 5 min (down step).

3. Results and discussion

3.1. XRD

The XRD patterns of materials and OSep samples are presented in Fig. 1. All the reflections of Sep samples are in accord with the JCPDS card of sepiolite (No. 13-0595) and no other reflections are observed. This fact indicates that Sep is of high purity. The organic surfactant, i.e., C18-B exhibits obvious reflections, demonstrating that some organic surfactants exist in the form of crystal. It should be pointed out that the