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Rheology of sodium and calcium bentonite–water dispersions: Effect of electrolytes and aging time

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ABSTRACT

Bentonitic clays are largely composed of the mineral montmorillonite. Today, bentonites are used in different branches of industry, such as in drilling fluids, dyes, Pharmaceuticals, paper, cement, nanocomposites, polymer composites and ceramics. Bentonite dispersions are widely used in industrial processes because of their exceptional rheological behavior. In this work, the rheological behavior of three types of bentonites with different Na^+/Ca^{+2} ratios was investigated. The bentonite dispersions showed Newtonian, Bingham plastic and shear thinning behaviors depending on the solid concentration and bentonite type. Although, all bentonite dispersion exhibited a thixotropic behavior, the Na-bentonite showed a greater degree of thixotropy which was two order of magnitudes greater than that of Ca-bentonite. The rheological behavior of bentonite suspensions developed significantly in the first 24 h of preparation. The addition of electrolytes in a concentration range of 0.02–0.2 M reduced the apparent viscosity of the bentonite suspensions and changed its rheological behavior from shear thinning to Newtonian and shear thickening. The divalent cation salts experienced more reduction in the apparent viscosity and yield stress of suspension than the monovalent cation salts.

1. Introduction

Bentonite is a type of clay consisting mainly of a hydrous silicate of aluminum; its color varies from gray to brown. Bentonites have formed by weathering of volcanic tuff and ash and consist mainly of montmorillonite [$(Al,Mg)_2(OH)_2(Si,Al)_4O_{10}(Ca)_x$ on H_2O] and contain varying amounts of other minerals like quartz (SiO_2) and calcium and sodium feldspar [$(CaAl_2Si_2O_8)$,$(NaAl_3Si_2O_8)$]. In general, the bentonite is classified into two types: Na-bentonite, which has a high swelling capacity, and Ca-bentonite, which is a non-swelling clay and forms colloidal very quickly in water (Hassan and Abdel-Khalek, 1998).

Today, bentonites are used in different branches of industry, such as in drilling fluids (Bekkour et al., 2001; Mostafa et al., 2010), dyes, Pharmaceuticals (Cara et al., 2000a, b; Viseras et al., 2010), paper, cement, nanocomposites (Lee and Lee, 2004; Araújo et al., 2004), polymer composites (Abu-Jdayil et al., 2002; Al-Malah and Abu-Jdayil, 2007; Abu-Jdayil and Al-Malah, 2008) and ceramics. Although bentonites are abundant in many sites, in a good quality and large quantities in different Middle East countries (Hassan and Abdel-Khalek, 1998), these materials have not been utilized efficiently.

Bentonite suspensions are widely used in industrial processes because of their exceptional rheological properties. The rheological behavior of bentonite dispersions depends on different factors, including the type and concentration of bentonite, the size and shape of bentonite particles, the electrostatic properties of the bentonite particles, the exchangeable ions, and the concentration of the electrolytes in dispersions (Yildiz et al., 1999). Generally, the flow of bentonite dispersions is very sensitive to the Na^+/Ca^{+2} ratio.

The rheological measurements of bentonite dispersions, an important route to revealing the flow and deformation behaviors of materials, cannot only improve the formulation process of commercial products but can also be very important in design and process evaluation, quality control, and storage stability. Finally all of these factors can significantly affect the final properties of the product and economic aspects of the process (Tunc and Duman, 2008).

Different additives have been used in bentonite dispersions to control the rheological behavior of the dispersions that meet the specification of the desired applications, such as electrolytes (Yildiz et al., 1999; Luckham and Rossi, 1999; Kelessidis et al., 2007; Duman and Tunç, 2009; Liang et al., 2010), polymers (Isci et al., 2004; Mahto and Sharm, 2004; Alemdar et al., 2005; Tunc and Duman, 2008; Menezes et al., 2010) and surfactants (Güngör and Ece, 1999; Yalcin et al., 2002; Günister et al., 2006; İşçi et al., 2008). The NaCl electrolyte has been widely used in bentonite dispersions. Several investigations were performed to evaluate the effect of NaCl on the rheological behavior of dilute and concentrated bentonite concentrations (Adachi et al., 1998; Abend and Lagaly, 2000; Ramos-Tejada et al., 2001; M'bodj et al., 2004; Tombacz and Szekeres, 2004). Other types of electrolytes did not receive much attention in the literature.

In this study, the rheological properties of three different types of bentonite dispersions with different Na^+/Ca^{+2} ratios at a high range

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of solid concentration (0.5–10 wt.%) and different aging times were investigated. In addition, the effects of different types of electrolytes on the rheological behavior of bentonite suspensions were studied.

2. Materials and methods

2.1. Materials

Three different types of bentonite clays were used in this study. Bentonite 1 (B1) is a lab grade sample supplied by Sigma-Aldrich Company Ltd.,Germany. Bentonite 2 (B2) and bentonite 3 (B3) are commercial samples which are used by the oil companies in UAE. Bentonite 2 (B2) is OCMA specifications and produced by Abu-Dhabi Drilling Chemicals and Products, UAE. Bentonite 3 (B3) is produced by MilPark Drilling Fluids, USA, with the commercial name of MIL-BEN API BENTONITE. The chemical analysis of these bentonites is shown in Table 1. B1 and B2 can be classified as Na-bentonite with Na^{+}/Ca^{+2} ratios of 3.73 and 1.12, respectively. On the other hand, the ratio of Na^{+}/Ca^{+2} in B3 is 0.81 and can be classified as Ca-bentonite.

Electrolytes $BaCl_2 \cdot 2H_2O$, $CaCl_2$, NaCl, KCl and Na_2SO_4, were used in this study and obtained from BDH Chemicals, UK.

2.2. Rheological measurements

Rheological properties of prepared suspensions were measured with a RheolabQC viscometer from Anton Paar, Germany. The concentric cylinder measuring system used is according to ISO 3219 and DIN 53019 standards. The shear stress (τ) of the samples was measured as a function of shear rate ($\dot{\gamma}$) at a constant temperature. All rheological tests were performed at 25 °C ± 0.1. The measurements were carried out with increasing (forward measurements) and decreasing (backward measurements) shear rates. The calculated area between the upward and downward curves was used as a measure of thixotropy using the data analysis option of RHEOPLUS/32 V3.31 software.

Bentonite suspensions were prepared in different concentrations ranged from 0.5 wt.% to 10 wt.%. After mixing, each bentonite dispersion was poured in a covered container and left for a specific time at room temperature. The flow curves of samples were measured at different aging times, namely; immediately after the preparation, 1 h after preparation and 24 h after preparation. In addition, the flow curves of 6 wt.% samples were also measured at 2, 3, and 48 h after preparation. Prior to rheological measurement, the sample was stirred in the viscometer for 1 min at a shear rate of 5 s^{-1}, followed by a rest time for 2 min.

3. Result and discussion

3.1. Bentonite suspension

Fig. 1 shows the typical effect of solid concentration on the apparent viscosity of the bentonite suspensions stored for 24 h. An increase in the solid concentration, as would be expected, increased the apparent viscosity. The bentonite samples tested here exhibited a significant increase in apparent viscosity at a solid concentration of 6.0 wt.%. Naturally, the bentonite concentration will bring about an increase of all rheological properties. If the concentration of bentonite is high enough, flocculation will cause the formation of a continuous gel structure instead of individual flocs. The gel structure builds up slowly with time, as the particles orient themselves towards positions of minimum free energy under the influence of Brownian motion (Luckham and Rossi, 1999). The concentration of bentonite in the system is an important factor which can affect the length of time required for a gel to attain maximum strength. For Na-bentonite, this concentration was found to be above 3 wt.% (Luckham and Rossi, 1999).

Table 1
Chemical analysis of bentonite samples in wt.%. *Bentonite 1 and 2* are Na-bentonite, and *Bentonite 3 is* Ca-bentonite.

Bentonite type	Na_2O	K_2O	Fe_2O_3	MgO	Al_2O_3	SiO_2	CaO	FeO
Bentonite 1	2.425	0.245	3.25	2.67	21.08	63.02	0.65	0.35
Bentonite 2	2.857	0.081	17.22	2.953	17.03	36.98	2.558	15.31
Bentonite 3	3.215	0.432	1.889	2.233	12.74	67.82	3.986	1.681

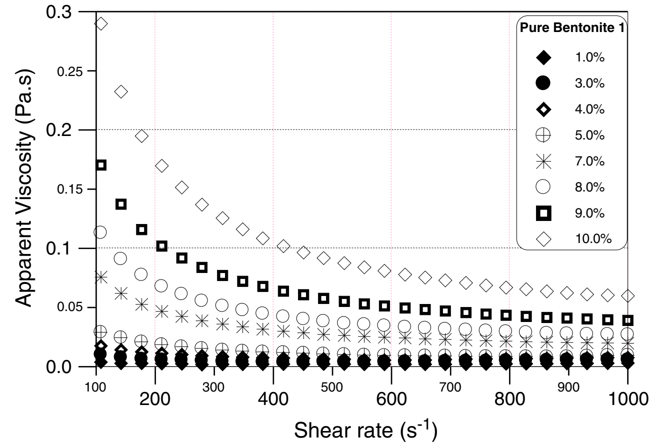

Fig. 1. Apparent viscosity of bentonite 1 at different solid concentrations (aging time = 24 h).

The Herschel–Bulkley (H–B) model was used to describe the rheological behavior of bentonite suspensions:

$$\tau = \tau_0 + m\dot{\gamma}^n \tag{1}$$

where τ is the shear stress, τ_0 is the yield stress, $\dot{\gamma}$ is the shear rate, m is the consistency coefficient and n is the flow behavior index. Typically the H–B model is used for many suspensions as the Newtonian, shear thinning, shear-thickening and Bingham plastic may be considered as special case. The H–B model has been used in several studies to describe the rheological behavior of bentonite dispersions (Maglione et al., 2000; Kelessidis et al., 2007, 2009).

The effects of solid concentration on the flow curves of bentonite dispersions were quantified using the H–B model, which fitted well the τ versus $\dot{\gamma}$ data for bentonite suspensions giving correlation coefficients between 0.980 and 0.999, and as indicated in Fig. 2. All bentonite suspensions tested here exhibited both Newtonian and non-Newtonian behaviors at low and high solid concentration, respectively, as can be

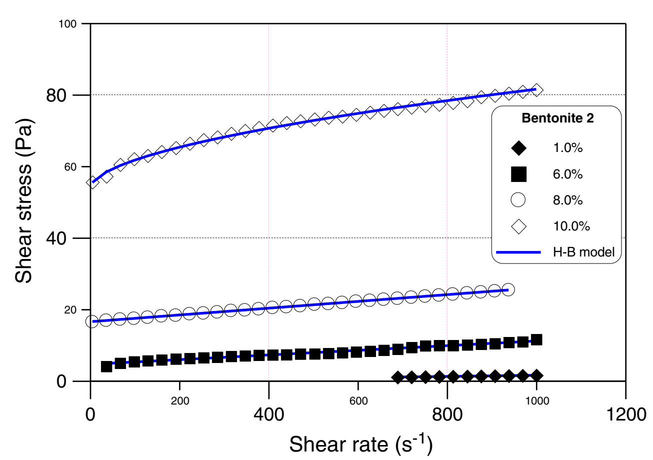

Fig. 2. The flow curves of bentonite 2 at different solid concentrations fitted with the Herschel–Bulkley model.