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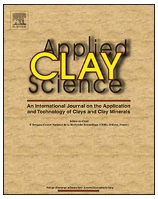

Research paper

Effects of sodium carbonate addition, heat and agitation on swelling and rheological behavior of Ca-bentonite colloidal dispersions

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ABSTRACT

The effects of the addition of sodium carbonate (Na_2CO_3) and the subsequent simultaneous heating and stirring on the rheological behavior of Ca-bentonite colloidal dispersions have been investigated in this study. Ca-bentonite dispersions were treated with Na_2CO_3 at various ratios (2, 4, 12 g/100 g bentonite), and then subjected to heating and stirring for variable periods. It was found that the swelling and the viscosity of the treated bentonite samples increased with increasing Na_2CO_3 content and the optimal Na_2CO_3 level (relative to the bentonite content) was found to be 4 g/100 g of Ca-bentonite (4%). The results also showed that simultaneous heating and stirring enhanced the bentonite swelling and ion exchange processes for sodium activation. The rheological properties of the Ca-bentonite suspensions depend on the strength of the bentonite gel structure and the interparticle interactions. Although the treated and untreated bentonite samples showed gel and solid-like behavior in the linear viscoelastic region (LVR), the region where the storage (G′) and loss (G″) moduli are independent of applied strain and/or stress, the G′ values of the Na_2CO_3 treated bentonite samples were higher than those of untreated samples. All bentonite samples (whether Na_2CO_3 treated or untreated) showed more elastic than viscous response (i.e., $G' > G''$) within the LVR. The results showed that bentonite dispersions treated with 4% Na_2CO_3 displayed the highest elastic behavior. The relationship between zeta potential and pH for the untreated and Na_2CO_3 treated Ca-bentonite dispersions were investigated. Bentonite colloids were stable in the examined range of pH ($3 - 12$); such wide pH range stability is essential for many industrial applications. Finally, the effect of heat treatment on the swelling behavior of 4% Na_2CO_3 treated bentonite dispersions was extracted from particle size measurements using a laser scattering particle size analyser. The results showed that the particle size increased with the combined heating and stirring treatment for the first 3 h then remained constant. This increase in particle size is likely due to improved swelling and the existence of some of weak particle-particle interactions bentonite (aggregates).

1. Introduction

The commercial value of bentonites as raw materials is high due to their applications in many industries such as cosmetics and medical products, paints, water treatment (de Figueirêdo et al., 2014; Vipulanandan and Mohammed, 2014; Zhuang et al., 2015), pharmaceuticals (Cara et al., 2000a,b; Viseras et al., 2010), dyes (Bergaya and Lagaly, 2013; Al-Hussaini and Eldars, 2014; Chang et al., 2014; Wang et al., 2014) and papermaking (Li et al., 2011; Wu et al., 2013; Yoon et al., 2013). Bentonites are also used in drilling fluids because of their exceptional rheological properties. In drilling applications, good quality bentonite provides the required viscosity and acceptable filtration loss (Lebedenko and Plée, 1988; Yildiz et al., 1999; Falode et al., 2008). Bentonite consists mainly of montmorillonite [$(Al,Mg)_2(OH)_2(Si,Al)_4O_{10}(Ca)_x \times nH_2O$] and different amounts of other minerals such as quartz (SiO_2), calcium and sodium feldspar [($CaAl_2Si_2O_8$), ($NaAl_3Si_2O_8$)] (Abu-Jdayil, 2011; Mierczynska-Vasilev and Smith, 2016). There are two types of bentonites: sodium bentonite (Na-bentonite), which has a high swelling capacity, and calcium bentonite (Ca-bentonite), which is a non-swelling clay and spontaneously forms colloidal dispersions in water (Hassan and Abdel-Khalek, 1998; Dill, 2016; Yan et al., 2016). Bentonite is mainly composed of layers including silica and alumina sheets linked together and arranged on top of each other. Bentonite lamellar platelets are packed together by

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electrochemical forces and form aggregates that contain interposition water. The platelets are composed of a central octahedral alumina (Al_2O_3) layer and two tetrahedral silica (SiO_2) layers.

Bentonite surface carries negative charges on its face; these anions are balanced by alkaline earth cations intercalated between the structural platelets/sheets such as Ca^{2+}, Mg^{2+} or Na^{+}. The cation intercalation between the negatively charged sheets occurs through bridging cations (typically Na^{+}) which holds the structural platelets/sheets together by electrostatic forces. When Na^{+} cation is dominant on the montmorillonite surface, the clay is classified as Na^{+}-bentonite (Luckham and Rossi, 1999). Typical chemical formula for Na-bentonite is $Na_{0.33}$ $[(Al_{1.67}Mg_{0.33})(O(OH))_2(SiO_2)_4]$ (Luckham and Rossi, 1999).

When water is added to the bentonite surface, bentonite adsorbs water in the interlayer region and this adsorption process initiates swelling (Rand et al., 1980; Lagaly, 1989; Tombácz and Szekeres, 2004; Nasser and James, 2006a,b,c,d; Nasser et al., 2016). The degree of swelling of the platelets depends on the type of cations in the interlayer region. If the interlayer cations are monovalent and strongly hydrated such as Na^{+} or Li^{+}, the inter-platelet repulsion will be strong and the swelling capacity will be high (van Olphen, 1959; Luckham and Rossi, 1999; Murray, 2000). Na^{+} content was found to be the most influential factor for enhancing the rheological properties of bentonites (Kumar et al., 2014; Agha et al., 2016; Komadel, 2016; Mokni et al., 2016; Xu et al., 2016). In addition to the ability of Na^{+} contained in bentonite to adsorb water, it also increases viscosity and forms thixotropic suspensions with a good gel strength. Unlike Na-bentonites, Ca-bentonites have low swelling capacity and form unstable suspensions with high settling rates (Kirsner et al., 2008; Kurečič et al., 2013).

DLVO (Derjaguin-Landua-Verwey-Overbeek) theory is a good starting point to describe the stability of colloidal particles (Tadros, 1986; Tadros, 1990; Nasser and James, 2006a,b,c,d; Nasser and James, 2007a,b). Simply, DLVO theory considers the contributions of the attractive van der Waals potential and the repulsive electrostatic potential. Therefore, according to DLVO theory, the dispersed particles are under the effect of two independent forces: attractive van der Waals forces and the repulsive electrostatic forces arising from the presence of electric double-layer at particles' surfaces. The electric double layer may be compressed by increasing the concentration of counter ions in the solution that reduces this repulsive energy, hence destabilizing the suspension (Durán et al., 2000). The possibilities of having stable or unstable colloidal dispersion can be accurately revealed through zeta potential measurements using Zeta sizer equipment (Nasser and James, 2008a,b; Onaizi et al., 2014); these measurements provide estimation for zeta potential.

Researchers have attempted to upgrade Ca-bentonites by treating them with inorganic additives such as sodium carbonate (Na_2CO_3) (Lebedenko and Plée, 1988; Yildiz et al., 1999; Karagüzel et al., 2010). They observed that the Na^{+} content in the treated samples was the most influential factor for enhancing the swelling behavior of Ca-bentonites. In addition to the chemical treatment by Na_2CO_3, some researchers used H_2SO_4 and/or MgO to upgrade the Ca-bentonite suspension properties in order to improve the swelling capacity (Eades and Grim, 1960; Önal, 2007; Karagüzel et al., 2010). They found that such treatments have resulted in improved gel strength. Furthermore, several other studies have been performed to assess the rheological properties of bentonite dispersions under different conditions of pH, salt content and the presence of polymeric additives (Abu-Jdayil et al., 2016; Barast et al., 2016; Kelessidis et al., 2007; Abu-Jdayil, 2011; Santagata et al., 2014; Choo and Bai, 2015; Ben Azouz et al., 2016; Benslimane et al., 2016; Lin et al., 2016; Nasser et al., 2016). The rheological properties of bentonite dispersions can provide useful information on the possible structures of the montmorillonite suspensions, which is a key factor in several bentonite-based applications. The surface of the bentonite suspensions depends on the mode of particle-particle association, which might take the form of: face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE) (van Olphen, 1959; Nasser and James, 2006a,b,c,d; Nasser and James, 2007a,b). Association of the FF types results in thicker aggregates of high density whereas EF and EE associations lead to low density aggregates with larger volumes (van Olphen, 1959; Nasser and James, 2006a,b,c,d; Nasser and James, 2008a,b). Khandal and Tadros (1988)) and Sohm and Tadros (1989)) used viscoelastic properties such as elastic modulus (G′) and viscous modulus (G″) obtained from dynamic oscillatory measurements for assessing the gelation kinetics of bentonite suspensions. The information gathered from such rheological measurements might shed light on the gel strength and gelation mechanism of bentonite colloidal dispersions.

In addition to the chemical treatment of Ca- bentonite with sodium carbonate (Yildiz et al., 1999; Önal, 2007; Karagüzel et al., 2010; Yan et al., 2016), heat treatment might improve its rheological properties. Heating is an important parameter controlling the Brownian motion and the overall attractive/repulsive forces between colloidal particles which is often correlated with the zeta potential of colloidal particles (Lin et al., 2016). Heating is expected to cause expansion of the bentonite particles and allows water to invade the bentonite layers and enhance the gel formation ability. In addition to heat treatment, agitation (i.e., stirring) of the bentonite suspensions during the heat treatment could accelerate the release sodium ions from the sodium carbonate, leading to the acceleration of exchanging sodium ions with the exchangeable cations within the Ca-bentonite platelets. Such heat and agitation effects on the rheological properties of Ca-bentonite is still lacking in the published literature to the best of the authors' knowledge.

Therefore, we aim in this work to study the combined effects of chemical (i.e., sodium carbonate addition), thermal (i.e., heating) and mechanical (i.e., agitation) treatments on the rheological properties of aqueous Ca-bentonite colloidal dispersions. Both static and dynamic rheological behaviors of aqueous Ca-bentonite dispersions will be investigated to assess the influence of these three different treatments (alone or in combinations) on the rheological behaviors of colloidal Ca-bentonite dispersions.

2. Material and methods

2.1. Materials

The Ca-bentonite used in this study was sourced from Saudi Arabia. The analysis showed that the Ca-bentonite contains about 90% smectite with kaolinite and/or quartz varied from 5 to 10 wt.%. The average particle size and specific gravity of the Ca-bentonite are 2.4 μm and 2.65, respectively. For the determination of clay minerals compositions, silicate, cement and limestone were used as standard reference materials. The chemical composition of the Ca-bentonite sample was obtained following standard procedures and methods of analysis (Yilmaz and Civelekoglu, 2009). Table 1 summarizes the detailed chemical compositions of the provided Ca- bentonite. The texture and shape of the particles were observed in Scanning Electron Microscopy (SEM) as shown in Fig. 1. It can be seen that the bentonite particles are plate-like structure, with small bumps and variable degree of roughness.

Table 1
Chemical composition of the obtained Ca-bentonite.

Composition	Wt.%
SiO_2	63.1
Al_2O_3	20.2
Fe_2O_3	6.9
CaO	2.9
Na_2O	2.43
MgO	2.03
K_2O	0.255