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Research paper

Ageing and collapse of Bentonite gels — Effects of Mg(II), Ca(II) and Ba(II) ions

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ABSTRACT

The ageing and stability behaviour of Bentonite slurries were evaluated under the influence of Mg^{2+}, Ca^{2+} and Ba^{2+} ions at concentration ranging from 0.005 to 1 M. Stable gels were formed at low metal ion concentration of <0.05 M. These gels displayed pronounced ageing or structural recovery behaviour. A well-defined initial state of ageing was employed. This was the surface-chemical equilibrium (SCE) state. The dissolved metal ion salt hastened the attainment of this SCE state of freshly prepared gel to less than 100 min. As the structure recovered during ageing, the yield stress increased. The temporal ageing yield stress displayed an initial period of rapid increase, followed by a period of gradual increase and then a period of no increase. The Leong model described this ageing behaviour well. At metal ion concentration of 0.05 M or greater, the gels became unstable and collapsed. In contrast, gel instability occurred at a much higher concentration of 0.5 M for Na^+, K^+ and Cs^+ ions. Also the settling layer of divalent metal ion weakened gels did not consolidate as effectively. The stability time of these weakened gels was found to decrease with increasing hydration bond length of the divalent metal ions, i.e. Ba(II) < Ca(II) < Mg(II).

1. Introduction

1.1. Background

Bent (Bentonite), comprising 70–85% sodium montmorillonite (Na^+Mt), is used in many applications. It is an important ingredient in drilling muds, paper coating, pharmaceutical and cement products (Luckham and Rossi, 1999). Due to its swelling property and the lack of impermeability in water, it is also used as slurry walls to isolate contaminated ground water in civil engineering constructions and as storage barriers for nuclear waste against water and chemical infiltrations in the container (Pusch, 1992; Choi et al., 2001). Low density mineral tailings usually contain a high content of this clay mineral. These tailings are impractical to dewater effectively. Such tailings are found in coal washery (McKee and O'Brien, 1989) and mineral sand mining in Australia requiring a large land area for storage creating a large environmental footprint. New technology to reduce the size of this footprint is essential. A method that can densify these tailings significantly before disposal is one such technology. Controlling particle swelling and packing, and the nature and strength of the particle interaction via surface chemistry tools is one such approach to discover an effective method. A range of surface chemistry tools such as pH, ionic strength, exchangeable cations and adsorbed additives, are available. These surface chemistry tools have a pronounced effect on the rheological behaviour of Bent slurries. The surface chemistry tools evaluated were pH (Lagaly, 1989; Tombácz and Szekeres, 2004), salt type and concentration (Brandenburg and Lagaly, 1988; Luckham and Rossi, 1999; Yildiz et al., 1999; Abend and Lagaly, 2000; Abu-Jdayil, 2011), and a range of adsorbed additives such as polyphosphates (Lagaly, 1989; Goh et al., 2011), polymers (Dolz et al., 2007; Tunc and Duman, 2008), and surfactants (Permien and Lagaly, 1994; Luckham and Rossi, 1999; Tunc et al., 2012). Many investigations on salt effects focused mainly on one salt, NaCl (Abend and Lagaly, 2000; Ramos-Tejada et al., 2001; Tombácz and Szekeres, 2004). Studies on the effect of divalent salts were deficient (van Olphen, 1957; Abu-Jdayil, 2011).

Unstable low density Bentonitic tailings that settled and consolidated rapidly are a highly desirable behaviour with the mineral processing operators responsible for tailing thickening, disposal and management. However, such unstable Bent slurries will lose its performance as an impermeable slurry wall and storage barrier material for the containment of nuclear waste as a result of phase separation into a clear solution and sediment. Compacted Bent of density ~2000 $kg \cdot m^{-3}$ is currently being evaluated for storing high level radioactive wastes. Bent gel was found to become highly unstable when exposed to high concentration of weakly hydrated K^+ and Cs^+ ions (Chang and Leong, 2014). With the compacted Bent barrier, infiltration of large amount of these metal ion solutions is required for destabilisation.

Stable Bent gels display complex rheological and ageing behaviour at a very low solid concentration, <10 mass% solids (van Olphen, 1955; Brandenburg and Lagaly, 1988; Lagaly, 1989; Luckham and Rossi, 1999; Kelessidis et al., 2007; Liang et al., 2010; Abu-Jdayil, 2011). The

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ageing behaviour of the stable gel is characterised by a yield stress increasing with time until no further increase was possible (Lee et al., 2012; Chang and Leong, 2014). This increase in gel strength accompanied by a decrease in swelling potential during the ageing process was attributed to particle rearrangement and bond formation with time (Ye et al., 2013). Similar ageing behaviour was also observed in Bent-based drilling muds that have several other ingredients present such as barite, pyro- and tri-phosphates, and carboxymethylcellulose (CMC) fluid loss agent (Yap et al., 2011; Sehly et al., 2015). Despite the very high barite content in these muds, the same type of ageing behaviour was displayed. This showed the dominance of Bent in controlling the slurries rheology and this dominance was even observed in slurries containing a mixture with another clay mineral such as kaolinite (Au and Leong, 2013).

Various techniques and approaches were employed to characterise the time-dependent properties of Bent gels (van Olphen, 1955; Abend and Lagaly, 2000; Galindo-Rosales and Rubio-Hernández, 2006; Kelessidis and Maglione, 2008; Abu-Jdayil, 2011). Quantitative comparisons of these time-dependent results were often not possible due to a number of factors such as different parameters (viscosity, compliance and hysteresis loop area) being used to quantify thixotropy, and the initial state of the gel not being defined. In this study, a different approach was applied where a well-defined initial state was adopted for the ageing or structural recovery study. Prior to the commencement of the ageing experiment, the gels must be at this well-defined state, which is also the surface chemical equilibrium (SCE) state (Goh et al., 2011). At this state, all the surface processes of charging, hydration, and ion transport to the surface have reached equilibrium. This approach was employed in all previous ageing studies on thixotropic clay mineral gels (Yap et al., 2011; Lee et al., 2012; Chang and Leong, 2014; Au and Leong, 2015; Sehly et al., 2015).

The nature of the monovalent cation; Li^+ (ionic radius 90 pm), Na^+ (116 pm), K^+ (152 pm) and Cs^+ (181 pm), was found to have a significant effect on the ageing and stability of Bent gels (Chang and Leong, 2014). Gels containing the strongest hydrated cation Li^+, displayed the most pronounced ageing behaviour at low to moderate Li^+ concentrations. The increase in the ageing yield stress was largest for these gels. Surprisingly, the ageing yield stress was found to decrease significantly at high salt concentration for all four metal ions despite strong interparticle attraction being predicted by the DLVO theory. The gels with Na^+, K^+ and Cs^+ at concentration of 0.5 M and greater, became unstable and collapsed. The time to instability was quickest for the most weakly hydrated Cs^+ ions. The Bent slurries with 1 M Cs^+ formed a settled layer almost immediately. The weakly hydrated Cs^+ ion can shed its hydration shell easily forming a high charge density cation (Eberl, 1978). When these ions are located in the interlayer space in large quantity, it can bind the layers strongly together via electrostatic attraction with negatively charged face of the sheets. This strong interlayer binding is responsible for the phase separation of the Bent gel.

One of the earliest studies on the effect of a divalent metal ion on the ageing behaviour of Bent gels was conducted by van Olphen (1957). He observed that the Ca-Bent slurries did not display time-dependent behaviour and found that the particles were thicker. This suggested that the swelling and delamination of Ca-Bent particles were not significant. Abu-Jdayil (2011) found that $BaCl_2$ reduced the yield stress and viscosity of Bent gels significantly. In this study, the effect of Mg^{2+} (66 pm), Ca^{2+} (114 pm) and Ba^{2+} (149 pm) on the ageing and stability of Bent gel will be investigated in details.

1.2. Models for ageing or structural recovery

There are currently three ageing models based on yield stress for thixotropic gels. These are the two-parameter model of Rich et al. (2011) and the two three-parameter models of Leong and Nguyen–Boger (NB). For Bent-based gels the performance of the Leong model was found to be superior (de Kretser and Boger, 2001; Yoon and El Mohtar, 2013; Chang and Leong, 2014). The derivation of the Leong model can be found in de Kretser and Boger (2001). Other ageing models based on storage modulus, compliance and viscosity are also available (Barnes, 1997; Pujala and Bohidar, 2013; Yoon and El Mohtar, 2013).

The NB model, based on 1st order structural recovery kinetics (Nguyen and Boger, 1985), is given by:

$$\tau_y(t) = \tau_{y\infty} - (\tau_{y\infty} - \tau_{y0}) e^{-Kt}. \tag{1}$$

The Leong model, based on second-order particle aggregation kinetics (Hattori and Izumi, 1982), is described by de Kretser and Boger (2001):

$$\tau_y(t) = \tau_{y_\infty} \left(1 - \frac{1 - \left(\frac{\tau_{y_0}}{\tau_{y_\infty}} \right)^{3/2}}{1 + K_r t} \right)^{2/3} \tag{2}$$

where $\tau_y(t)$ is the time-dependent yield stress in Pa, τ_{yo} is the equilibrium structural breakdown (agitated) state yield stress, $\tau_{y\infty}$ is the yield stress at complete structural recovery, $1/K$ is the Nguyen–Boger-model time constant in min or h and $1/K_r$ is the Leong model time constant. The methods employed to determine the parameters of both models have been reported elsewhere (de Kretser and Boger, 2001; Yap et al., 2011; Lee et al., 2012) and will not be described here.

The two-parameter model describes the logarithmic growth of the yield stress with ageing time and is given by Rich et al. (2011):

$$\tau_y(t) = \beta \ln \frac{t}{t_m} \tag{3}$$

where β is a constant in Pa and t_m is the microstructural development time constant in min. This model described the ageing behaviour of Laponite gels well at relatively short ageing time (Rich et al., 2011; Pujala and Bohidar, 2013; Au and Leong, 2015). It however predicts an infinite yield stress at $t = 0$ and zero yield stress at $t = t_m$. This model is therefore not suitable for ageing Bent gels at $t \le t_m$ where the yield stress remained finite (Yap et al., 2011; Lee et al., 2012).

2. Materials and methods

The commercial Bent used in this study was sourced from Sigma Aldrich (product code B3378). Its composition determined by X-ray fluorescence (XRF) spectroscopy comprised of 60.5% SiO_2, 21.0% Al_2O_3, 0.153% TiO_2, 3.88% Fe_2O_3, 0.009% MnO, 1.02% CaO, 0.318% K_2O, 2.76% MgO, 2.11% Na_2O, 0.04% P_2O_5 and 0.74% SO_3. Like all clay minerals the major components are silica and alumina. The TiO_2 content was quite low while the Fe_2O_3 content was relatively high. Nevertheless the zeta potential of this Bent slurries remained negative throughout the pH range of 2 to 12 (Goh et al., 2011) reflecting the small effect of Fe_2O_3 (point of zero charge of 6.5–8.5) on its surface properties. The X-ray diffraction (XRD) result showed the strong presence of Mt and quartz (see supporting material). This B3378 Bent has a similar composition to MX-80 Wyoming Bent; 75–85 mass% Na^+Mt and several minerals each <5% are K-feldspar ($KAlSi_3O_8$), quartz, cristobalite (SiO_2), plagioclase ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$) and calcite ($CaCO_3$) (Carlson, 2004). A trace amount of gysum ($CaSO_4 \cdot 2H_2O$) was also detected. Except for quartz, the noise in the XRD data masked the presence of these other minerals. This batch of Bent has a Brunauer, Emmett and Teller (BET) surface area of 39.3 m^2/g and a cation exchange capacity (CEC) of 0.88 meq/g (Galindo-Rosales and Rubio-Hernández, 2006).

Electrolytes used in this study were $MgCl_2$, $CaCl_2$ and $BaCl_2$. The $MgCl_2 \cdot 6H_2O$ salt crystals were sourced from Optigen scientific. The anhydrous $CaCl_2$ was supplied by Ajax Finechem. The $BaCl_2 \cdot 2H_2O$ was purchased from Fluka AG.