Surface Chemistry and Rheological Properties of API bentonite drilling fluid: pH effect, yield stress, zeta potential and ageing behaviour

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Abstract

API bentonite, a key ingredient of drilling muds, displayed a negative zeta potential across the whole pH range of 2.5 to 12.3. It contained two very rheological active ingredients, sodium montmorillonite or Na+Mt (40.4%) and needle-shape sepiolite (16%). Due to the interplay of these two ingredients, the rheological behaviour displayed by the API bentonite suspensions is quite different to other bentonite suspensions. The gel displayed a very low or no yield stress at low acidic pH and a maximum yield stress at pH 8-12. Magnesium leaching from sepiolite at low pH and its hydrolysis plays a role in affecting the rheological properties at high pH. Yield stress and ageing behaviour was observed in suspensions with at least 3wt% solids. The Herschel-Bulkley (HB) model described the flow behavior of these gels. Both the HB yield stress and viscosity at a fixed shear rate of the 7 wt% gel peaked at pH 8.5 and were smallest at pH 5.2. The ageing or structural recovery behaviour is most pronounced at high pH for the most concentrated gels. Both the Leong and Nguyen-Boger ageing models described the structural recovery behaviour well. The recovery of the recently discovered very open honeycomb structure formed by Na+MT gel, after breakdown by shear was invoked to explain the ageing behaviour.

Key words: drilling muds; thixotropy; magnesium leaching; sepiolite; mixed clay interactions

1. Introduction

The composition of drilling fluids can be very simple or complex depending upon the drilling depth, formation composition and surface chemistry, temperature and pressure (O'Brien and Chenevert 1973, Clark et al. 1974). For shallow drilling, the composition of drilling fluid can just be a mixture of water and API (American Petroleum Institute) bentonite. API bentonite is the most important ingredient of drilling mud. It imparts the desired rheological and thixotropic behavior (Briscoe et al. 1992, Dolz et al. 2007, Yap et al. 2011, Yoon and El Mohtar 2013, Sehly et al. 2015). Bentonite suspension in a stable state is very impermeable. It is used as slurry wall in civil engineering construction site to isolate contaminated water from the ground water. It can also be used for drilling in water sensitive formation provided that the mud was correctly formulated dispensing with the need of many other ingredients such as potassium salt and fluid loss prevention additives. A typical drilling mud in addition to bentonite and water, will contain weighting agent such as API barite, dispersant, corrosion inhibitor, antioxidant, fluid loss prevention additives, pH modifier and salt (Bourgoyne et al. 1986, Bloys et al. 1994, Zheng and Ma 2010, Skalle 2011).

Bentonite (chemical composition is $(\text{Al}_2, \text{Mg}_3) \text{Si}_4\text{O}_{10} \text{OH}_2 \cdot n\text{H}_2\text{O}$) composed mainly of sodium montmorillonite ($\text{Na}+\text{Mt}$), displayed a number of unique properties such as swelling, caking, adsorption, catalytic, thixotropy, low permeability when wet and cation exchange. It has many commercial applications such as in casting, metallurgy, chemical and food industries (Hints et al. 2004, Belaroui et al. 2004, Isci and Turutoglu 2011, Au and Leong 2013, Anthony et al. 2014, Muzdybayeva et al. 2014). Bentonite slurries displayed pronounced thixotropic or ageing behavior which is exploited in many of these applications. This thixotropic behavior is related to its physical properties in particular swelling and delamination behavior in addition to heterogeneous charge behaviour and platelet particle shape (AbuJydal 2011, Paineau et al. 2011, Au and Leong 2013). Bentonite can expand by ten times its dry volume in water (Peng et al. 2013). Bentonite slurry

behaviour is very complex and not well-understood and this is reflected by the numerous rheological studies on this material (van Olphen 1955, 1957, M'Ewen and Mould 1957, Brandenburg and Lagaly 1988, Lagaly 1989, Luckham and Rossi 1999). Moreover, the usual Deryaguin, Landau, Verwey and Overbeek (DLVO) correlation between surface chemistry and rheology appeared not to apply to bentonite slurries (Goh et al. 2011, Au and Leong 2013, Chang and Leong 2014). The yield stress was found to be more sensitive to pH than the zeta potential. Bentonite as a naturally occurring mineral, has composition and impurities that vary from deposit to deposit. The non-constant composition is one such reason for the differences in behaviour being observed for the different bentonites. Many other factors also affect the rheological behaviour of bentonite slurries. Some of these factors included the effects of water mineralization, cation types, pH, dispersants, flocculants and other adsorbed additives (Fu et al. 2011, Yap et al. 2011, Xu et al. 2014).

Bentonite suspensions displayed high viscosity and yield stress at very dilute concentrations of only a few percent solids, ~5 wt % (Reid and Sen Gupta 1947, Kelessidies and Maglione 2008, Uriev 2011). There are a range of yield stress or plastic constitutive equations that can be used to fit the flow or shear stress-shear rate behaviour of these suspensions. These are the Bingham, Herschel-Bulkley and Casson models (Gungor 2000, Tunc 2012, Kk et al. 2000). At very low clay concentration these suspensions may display Newtonian and pseudoplastic (Power law) flow behaviour. Rheological property is a very critical parameter under some drilling conditions and environments. In some environments, a very high viscosity at very low shear rates may be required. An accurate rheological model will be needed to provide the necessary viscosity data especially when this value cannot be obtained experimentally. The flow behaviour of API bentonite suspensions will be characterised and fitted with these models.

The ageing or structural recovery behaviour of bentonite gel was recently investigated with a direct yield stress measurement technique (Yap et al. 2011, Lee et al. 2012, Chang and Leong 2014).

The ageing behaviour is characterised by an initial phase of rapid yield stress increase and then followed by a phase of gradual yield stress increase. At long time the increase in the yield stress eventually stop. This technique, also used here, allowed the collection of many more yield stress data in an experiment. This enables the increasing yield stress trend during ageing to be clearly mapped.

Na+Mt is a 2:1 clay with an alumina sheet sandwiched between two silica sheets and interlayer sodium ions for charge equalization. Bentonite particles are quite indistinguishable from kaolin clay under scanning electron microscope. It exfoliates in water into extremely thin plates that can be as little as about 1 nm in thickness, yielding increased particle concentration and leading to more particle-particle bonds being formed (Goh et al. 2011). Its face is negatively charge with a high proportion being permanent structural charges, and its edge has a pH-dependent charge and can be positively charge at pH below 9. This charge property determines the nature of interparticle force operating in the gel and the microstructures formed such as card-house and band-like structures. These space-filling structures will break down upon agitation, and reform and reconnect at rest (Baik et al. 2010, Goh et al. 2011, Ouellet-Plamondon et al. 2014). Lagaly proposed that bentonite clay particles form house of cards structures via face (-)/edge (+) attraction in an acidic medium and band-like structures are formed via cation-mediated face (-)/face (-) attraction in an alkaline medium (Lagaly 1989). The reformation of the space-filling structure for other bentonite suspensions have been adequately described by the Nguyen-Boger and Leong models (Yap et al., 2011, Lee et al. 2012, Chang and Leong 2014).

This time-dependent behaviour such as magnitude of the ageing yield stress was affected by a number of factors such as clay mineral composition, pH, dispersant such as pyrophosphate (Goh et al. 2011) and other additives including weighting agent (Yap et al. 2011). However the shape of the recovery curve is generally the same for all (Sehly et al. 2015). Most of the ingredients evaluated so far were not particularly rheological active. In many API bentonites, other rheological active clay

minerals are also present in large amount such as sepiolite and palygorskite. Sepiolite, a naturally occurring clay mineral, is present in significant concentration in the API bentonite to be evaluated. It is a hydrated magnesium silicate mineral with needle shape morphology. The needle particles have an average length of 1-2 μm and thickness of 0.01 μm . It is very porous and has a very high surface area of 300 m^2/g . The particles interact attractively via hydrogen bonding and the jamming of particles also occurred. It is used as a rheological additive to impart time-dependent properties to viscous suspensions according to sepiolite supplier, IMA-Europe. In this study, the effect of pH on this mixed clay mineral bentonite suspension was evaluated. The aim is to understand how the interplay of these highly rheological active clays affects the rheological properties at different pH or surface chemistry conditions.

A good understanding of the relationship between bentonite microstructure and interparticle forces at the equilibrium (breakdown) state and during structural recovery is also essential for understanding the rheological properties so that better control measures can be deployed. Physical and chemical factors that affect this relationship should produce a different spectrum of rheological properties-pH behaviour. The rheological properties-pH approach adopted should provide a much clearer picture and may reveal more clearly the mechanism involved.

Despite the strong effect on the rheological properties of bentonite gel, pH has little effect on the zeta potential (Goh et al. 2011, Au and Leong 2013). Bentonite particles in water do not display a point of net zero charge or isoelectric point (Goh et al. 2011) and possess a negative zeta potential across the whole pH range of 2-12 and is quite insensitive to pH (Callaghan and Ottiwell, 1974, Goh et al. 2011). The near constant zeta potential-pH behaviour should predict a yield stress and viscosity behaviour being insensitive to pH. This is however not the case. Therefore the use of the zeta potential as an indication of colloid stability (Yalcin et al. 2002) does not apply to bentonite suspension. In this study, the pH, zeta potential, yield stress, shear stress-shear rate and structural recovery of the API bentonite suspensions were investigated. The knowledge gained should provide

a better understanding of the rheological properties of this suspension and of the factors affecting these properties.

2. Experimental

2.1 Materials

The API bentonite used in the study was supplied by RHEOCEM LTD, Perth, Australia. The composition of the API bentonite determined by X-ray fluorescence are 62% SiO₂, 14.9% Al₂O₃, 0.975% TiO₂, 5.76% Fe₂O₃, 0.054% MnO, 1.78% CaO, 0.737% K₂O, 1.60% MgO, 2.18% Na₂O, 0.08% P₂O₅ and 0.02% SO₃ (Table 1). The molar ratio of Na/Ca is an important parameter affecting the rheological behaviour of the bentonite suspension (Madejova et al. 2002). With this bentonite, the molar ratio is 2.21. The mineral compositions of the API bentonite analysed by X-ray diffraction are 24.5% Quarts, 1.3% Cristobalite, 1.5% Calcite, 16.3% Kaolinite, 16.0% Sepiolite and 40.4% Smectite (amorphous). Sepiolite form thixotropic suspensions. However the rheological behaviour of these suspensions is quite insensitive to salt concentration. This makes it a good mud additive for drilling in high salt environment. Only 40% API bentonite is smectite which is low compared to other bentonites with 70-90% smectite.

The morphologies of the API bentonite are shown in the Figure 1. The API bentonite particles vary in size, are clearly nubby rather than spherical in shape. Most of the surface area of the powder was contributed by the platy clay particles. The thickness of the platelet particles is a few μm . Sheets of the Smectite and Kaolinite are clearly observed from [the SEM image](#).

Table 1 Result of XRF analysis of bentonites

Elements	Al ₂ O ₃ (%)	SiO ₂ (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	MnO (%)	CaO (%)	K ₂ O (%)	MgO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SO ₃ (%)
API bentonite	14.9	62.0	0.975	5.76	0.054	1.78	0.737	1.60	2.18	0.08	0.02
Sigma-Aldrich bentonite	21	60.5	0.153	3.88	0.009	1.02	0.318	2.76	2.11	0.04	0.74

Fig.1 SEM images of the API bentonite powder 100 kx magnification.

2.2 Methods

All suspensions were prepared by mixing the API bentonite powder with deionised water to the required weight percent solids. The initial or natural pH of these suspensions was 10.8. When pH adjustment was required, droplets of concentrated KOH were added. Concentrated KOH (9.32 mol/L) and HNO₃ (5 mol/L) solutions were used to change pH so as not to cause excessive dilution to the samples. The prepared sample was then sonicated with a Branson Sonifier (400 W and 20 kHz) for 3 times (at least 50 s at 70% amplitude for each time) and left to cool. The pH was measured with an Orion 4-STAR pH-conductivity meter. The zeta potential and conductivity were measured with a Colloidal Dynamic's ZetaProbe. The particle size distribution was characterised using a Malvern Mastersizer Microplus. The interlayer spacing of the API bentonite particles at different pH was measured by X-ray diffraction (XRD). The pH of a 7 wt% API bentonite suspension was adjusted to a range of fixed value and a small sample was removed at each pH for

XRD evaluation. Then these samples were centrifuged through PS-20 centrifuge at RPM of 3000. The sediment in each centrifuge tube was analyzed with X'pert PRO MPD diffractometer operating at 45 kV and 50 mA. Scanning was performed in a range of $2\theta = 3-15^\circ$ with a speed of $2^\circ/\text{min}$ and step size of 0.017° for the hydrophobic bentonite. The yield stress was measured using Brookfield LVDV-II+P and RVDV-II+P vane viscometers each with a different spring constant. Vanes of sizes were used that cover range of yield stress encountered in this investigation; a few Pa to hundreds of Pa (Nguyen and Boger 1983). The flow or shear stress-shear rate behaviour was characterised with a HAAKE VT 550 cone-and-plate rheometer.

The Mular-Robert salt-pH titration method (Mular and Roberts 1966) was used to determine the point of zero net charge or charge reversal or the isoelectric point of the API bentonite. Several suspensions containing 2 wt % solids with NaCl concentration of 0.001 M were first prepared at various pH levels. Then (reagent grade) solid NaCl was added to each suspension until a concentration of 0.1 M was attained. The steady state (final) pH of the suspension was measured. The difference between the equilibrium pH at 0.001 M NaCl and final pH at 0.1 M NaCl, ΔpH , was plotted as a function of the final pH. The pH where the change in sign of the ΔpH occurred is recognised as the point of zero charge. This M-R method may not be suitable for determining the pzc of complex clay minerals that possess permanent structural charges (Alvarez-Siva et al. 2010).

For ageing or structural recovery study, 7 wt % API bentonite slurries were prepared and left to rest for at least 24 hours. The prepared suspension was then stirred vigorously with a spatula for period of time to achieve the equilibrium (breakdown) structural state and the yield stress at this state was measured immediately. After that the suspension was allowed to rest undisturbed until the next measurement at a specified ageing time. At each specified ageing time, the yield stress was measured at a location in the suspension that was not disturbed by a previous measurement. A very small diameter vane was used so that more data points can be obtained from the undisturbed region. The insertion of the vane in the suspension will disturb the region in contact with the blades and

edges of the vane. However the disturbed area is small compared to the yielding surface area. This is reflected by the vane size having no effect on the yield stress value despite the larger vanes producing a relatively larger disturbed area.

3 Results and discussion

3.1 Relation between pH and Zeta potential

The zeta potential-pH behavior of the API bentonite suspension is shown in Fig.2. Across the pH range of 2.5 to 12.3, the zeta potential is negative. This meant that the bentonite particles are net negatively charged across that pH range. The zeta potential at pH 12.33 of -34.96 mV was reduced to -12.84 mV at pH 2.53. This zeta potential was more sensitive to pH than the other bentonite suspensions (Callaghan and Ottewill 1974, Goh et al. 2011). The concentration of pH-dependent positive charge must become more significant with decreasing pH. With bentonite, more than 90% of the total charges are permanent structural charge (Duc et al. 2005). The high concentration of other clay minerals such as sepiolite and kaolinite in this API Bentonite must be responsible for the greater sensitivity of the zeta potential to pH. Some kaolin clays displayed a point of zero charge at pH 3-5 while others may not displayed such a point (Au and Leong 2016). Sepiolite was reported to be negatively charged over the whole pH range (Kosmulski 2011). In another report, sepiolite showed strong buffering capacity in the acidic region (Celik 2004). A suspension sample adjusted to pH 3 took less than a minute to reach pH 8.5. Large amount of Mg ions in the crystal lattice were ion-exchange at low acidic pH. The point of zero charge (pzc) or isoelectric point was found to depend upon the concentration of the sepiolite suspensions. The pzc located at pH 3.2 for 0.2 wt% sepiolite increased to 6.5 at 5wt% sepiolite. The difference was attributed to larger content of Mg ions being released at the higher solid concentration. Another reason that needs to be considered is the formation and adsorption of magnesium hydrolysis product particularly at pH > 6 as this will affect the surface properties or pzc (Zhu et al. 2016).

Sodium montmorillonite, main ingredient of the normal bentonite, has a high content of permanent negative charge on the basal surface. This permanent negative charge is the result of a high degree of isomorphic substitution where the Al (III) element in the octahedral sheet is substituted by Mg (II) or Fe (II), in addition to some Si (IV) in the tetrahedral layer being substituted by Fe (III) or Al(III) (Avadiar et al. 2015). It accounts for 90-95 percent of the total charge (Duc et al. 2004). This explains the insensitivity of the zeta potential to pH as there are not enough positive charges even at very low pH to make a significant different to the total negative charges.

Fig.2 The zeta potential-pH behavior of 1.15 wt % API bentonite suspension over a pH range from 12.33 to 2.53. The average conductivity of this suspension is ~ 2 mS/cm.

The Mular-Robert salt-pH titration method was applied to this API bentonite. The plot of ΔpH

versus final pH is shown Fig.3. The change in sign of ΔpH was found to be located at pH 8.1. This point usually represents the point of zero charge for pure materials such as pristine inorganic oxides such as iron oxides, zinc oxides, alumina and titania (Alvarez-Silva et al. 2010). For clay minerals, this method of pzc determination produced a mixed result (Alvarez-Silva et al. 2010). This pH cannot be the point of net zero charge as the zeta potential-pH result did not show the presence of such a point. Strangely, this pH appeared to correlate strongly with the yield stress and particle size which will be shown later in a next section.

Fig. 3 Result of Mular-Robert method of determining “point of zero charge” of the API bentonite

3.2 pH effect on particle size and interlayer spacing

Particle size of clays has an important effect on their hydration performance, cation exchange capacity and the homogeneity of the charge density. Hydration process in bentonite can be divided into three stages. The first stage is surface energy driven hydration which deposits a four water

molecule thick layer on the surface of clay minerals leading particle swelling equivalent to a slight particle size enlargement. The second stage is cation hydration where a hydration shell is formed exchange cations bound to the permanent structural charge site further swelling the particles. In the last stage, osmotic hydration occurred where the hydrated cations on the charged sites moved to the surrounding liquid forming a diffuse electric double layer adjacent to the clay particle surface. Further swelling and delamination of the clay particle stacks occurred as the double electrode layers on the adjacent layers interacting repulsively. This is reflected by a large reduction in the particle size to less than 2 μm in suspension, forming the majority. Particle sizes of the 7 wt % API bentonite suspension over a pH range from 2.04 to 12.11 were shown in Fig. 4. With the pH of the 7 wt % API bentonite suspension (1 hour later after prepared) reduces from 12.11 to 8.1, the clay particle sizes ($D(v, 0.5)$ value) changed little and were all about 36 μm . When the pH was below 8.1 especially lower than 7, the particle sizes of bentonite decreased slightly to 33 μm . The delamination of particles via swelling appeared to be relatively minor in this API bentonite suspension.

However, the interlayer spacing of the API bentonite particles appeared to be larger in stronger alkaline environment than in the acidic environment (Fig. 5). As pH was between 8.5 and 12.2 the d-spacing is ~ 1.5 nm. This decreased to 1.2 nm at pH 5.23. At alkaline increased swelling or d-spacing did not lead to delimitation of the particles. The relation between particle size and pH of the API bentonite suspension in the initial hydration stage can be described by the Boltzmann function.

Fig. 4 Particle size of 7 wt % API bentonite suspension over a pH range from 2.04 to 12.11

Fig.5 X-ray diffraction curve and interlayer spacing of the API bentonite at different pH

3.3 Yield stress-pH behavior

The yield stress is a measure of the strength of the three-dimensional network structure formed by the particles in the bentonite suspension. At constant size distribution, yield stress is an indirect measure of the strength of the interparticle attractive force. The known attractive forces in the API bentonite suspension are van der Waals and heterogeneous charge attraction. Attractive interactions involving sepiolite will also be present. The yield stress-pH behaviour of the API bentonite suspensions with solid concentration ranging from 3 to 10 wt % solids is shown in Fig. 6 (a) and (b). For a given suspension, the yield stress is lowest in the low pH region of between 2 and 6, and then rises to a maximum at pH ~ 12 . The yield stress of the 3 wt % suspension is quite low ranging from ~ 0 to 4 Pa. The maximum yield stress of 4 Pa was located at pH ~ 11.8 . The torque reading associated with this yield stress value is 28.6% measured with a large vane indicating that the small yield stress is real. The spring constant of the viscometer given by the manufacturer is based on torque reading at 100% and is 0.0673 mN m. The 5 wt % solid suspension displayed a similar yield stress-pH behaviour. It displayed a maximum yield stress of 16 Pa at pH 12.1 and a minimum yield stress of 0.5 Pa at pH 4.0. The yield stress-pH curves of 7 wt % and 10% API bentonite suspensions were also quite similar in shapes. The yield stress increases with solid concentration at any given pH. The maximum yield stress for 7 wt % gel is 35.5 Pa located at pH $\sim 8-12$ and for the 10 wt % suspension is ~ 140 Pa located at pH $\sim 8 - 12$. For all suspensions, the yield stress decreased rapidly with decreasing pH from pH 8. Minimum yield stress values of all suspensions are observed at pH about 4. This yield stress-pH behaviour is opposite to that presented in an earlier study for bentonite slurries from another source, Sigma Aldrich B3378 (Velde 2004). Maximum yield stress of 7 wt % Sigma-Aldrich bentonite slurry was 230 Pa at pH 2 and a minimum yield stress of 60 Pa was measured at pH 8.

Sepiolite released Mg ions at low pH. At its natural pH of 8.5, the Mg ion concentration was

20 ppm which increased to 400 ppm at pH 3 (Celik 2004). Upon increasing the pH of sepiolite suspension from 3 to 8.5, most of the hydrated Mg ions will form hydrolysis product and adsorbed on the particles in the suspension (Zhu et al. 2016). At high pH the magnesium hydrolysis product will become magnesium hydroxide. When the particle surface is completely covered with magnesium hydroxide it should have a pzc of 12-13 (Kosmulski 2011). The high pH for the location of the maximum yield stress is attributed to the adsorption of magnesium hydrolysis products particularly at $\text{pH} > 6$ (Zhu et al. 2016). Some adsorbed metal ions hydrolysis products such as Cu(II) do impart an additional interparticle attractive force increasing the yield stress of the suspension (Leong 2005).

The Na+Mt in the bentonite controls the rheological behaviour of the suspension such as the yield stress-pH behaviour, even in the presence of large amount of kaolin clay and weighting agent barite being added by 3-8 times more in mass (Yap et al. 2011, Au and Leong 2013). Calcium montmorillonite or Ca+Mt displayed very different yield stress-pH behaviour to Na+Mt and required a much higher solid loading to develop a yield stress. The yield stress peaked at high pH – 9 similar to that displayed by this API bentonite. However, Ca+Mt suspensions do not display time-dependent behaviour at concentration less than 10 wt% solids unlike this API bentonite. So it was postulated that the high pH for the location of the maximum yield stress was due interaction between the two most rheologically active clay minerals; Na+Mt and sepiolite.

Although this API bentonite contained a relatively high CaO content of 1.78 wt %, a large component of Ca (II) must be locked in insoluble minerals such as gypsum and plagioclase. For a 7 wt % suspensions, if all the CaO dissolved it will produce a suspending medium with a Ca(II) or Ca^{2+} concentration of 68.66 meq/L. Soluble Ca(II) ions will push the location of the maximum yield stress to an alkaline pH due to the formation of Ca(II) hydrolysis product bridging the particles more strongly (Mpofu et al. 2003, Avadiar et al. 2014, Zhu et al. 2016) and exchanging with Na ions to form a non-swelling Ca+Mt (Au and Leong 2016).

Despite the lower negative zeta potential, the API bentonite slurries at pH 6 displayed a low yield stress and become unstable displaying phase separation. The images of phase separated bentonite slurries at low pH is shown in Fig. 7. Phase separation occurred within 60 min of resting. At low pH, the inter particle attractive force is very weak causing the composite Na+Mt-sepiolite gel to collapse. The medium particle size is slightly smaller at $\text{pH} < 7$ than at $\text{pH} > 8$ as can be seen in Figure 4. So the collapse of the Na+Mt-sepiolite gel must be due to a weaker interparticle attractive force since the number concentration of the particles is higher. Bentonite gel collapse was also observed at high ionic strength of 0.5 M Na^+ , K^+ and Cs^+ ions (Chang and Leong 2014).

Fig. 6 (a) The yield stress-pH behavior of the 3 wt % and 5 wt % API bentonite suspensions

Fig. 6 (b) The yield stress-pH behavior of the 7 wt % and 10 wt % API bentonite suspensions

Fig. 7 Images of layered API bentonite suspensions

3.4 Rheology - pH behavior

The effect of pH on the flow or shear stress-shear rate behavior of 7 wt % API bentonite suspensions is shown in Fig. 8. At any given shear rate, the shear stress is largest at pH 8.53. This means the viscosity at any given shear rate increased to a maximum as the pH increase from 5.2 to

8.5 and then decreased again with further increase in pH. This result mirrored the yield stress-pH result which is expected. The lowest viscosity flow curve is that at pH 5.2 and then followed by that at pH 12.2. The flow curves are generally convex in shape indicating a plastic or yield stress behavior. The flow curves of these suspensions were fitted with the three parameters Herschel Bulkley (HB) model. This HB model is a three-parameter model, given by (Khalil and Mohamed Jan 2012):

$$\tau = \tau_y + K\dot{\gamma}^n \quad (1)$$

where τ_y is the model yield stress, K is the consistency coefficient, n is the behaviour index.

Fig.8 Rheological curves of 7 wt % API bentonite suspensions at different pH

The fit of the Herschel-Bulkley model to the flow data is considered excellent as shown in Fig. 8. Values of R^2 of model fit shown in Table 2 were all greater than 0.986, certifying a very good fit. The values of the model parameters are presented in Table 2. Included in Table 2 are values for the vane τ_y for comparison with the HB model yield stress. The 95% confidence band for each plot was

also included [Longo et al. 2013a; 2013b] showing that these bands are very narrow. This is another indication of the excellent fit of the model.

Table 2 The parameters of Herschel Bulkley model in fitting the rheology curves of 7 wt % API bentonite suspensions and yield stress at different pH.

Rheological Parameters	pH=12.2	pH=10.4	pH=8.5	pH=7.3	pH=5.2
Vane τ_y (Pa)	14.7 $\pm$ 0.3	33.9 $\pm$ 0.6	30.8 $\pm$ 0.6	24.8 $\pm$ 0.5	2.7 $\pm$ 0.1
HB Model					
τ_y (Pa)	14.5	32.5	31.9	17.4	0
K(Pa·s ⁿ)	0.0218	0.862	0.112	0.330	0.0023
n(dimensionless quantity)	0.91	0.78	0.53	0.59	1.09
R ²	0.999	0.996	0.998	0.990	0.986

These rheological parameters showed contradicting correlation with surface chemistry. Low viscosity and HB yield stress (pH 5.2) occurred at a low negative zeta potential of ~ -17 mV. Highest viscosity and model yield stress (at pH 12.2) occurred at the state of largest negative zeta potential of -34 mV. Other bentonite suspensions also displayed similar contradicting correlation (Goh et al. 2011, Au and Leong 2013).

3.5 Structural recovery-pH behavior

The API bentonite suspensions with solid loading ranging from 3 to 8 wt % displayed structural recovery or ageing behaviour as shown in Fig. 9 and 10. This behaviour is characterised initially by a period of rapid yield stress increase followed by a period of more gradual increase. The recovered yield stress was larger for the suspension with higher loading of API bentonite. These more loaded suspensions also exhibited more pronounced structural recovery behaviour as reflected by a faster increase of the yield stress. The higher concentration of particles allowed a

higher density of particle-particle bond to be formed in given time resulting in faster recovery rate and stronger gel structure. The natural pH of these suspensions containing 3, 5, 7 and 8 wt % were similar 10.57, 10.54, 10.43 and 10.39 respectively, while their conductivity were also quite similar, 1.04, 1.34, 1.72 and 1.81 mS/cm representing an equivalent 1:1 electrolyte concentration of 0.01 to 0.02 M. An image of bentonite suspensions with different solid content is shown in the inset in Fig. 9.

The ageing or structural recovery behavior of 7 wt % API bentonite slurries at different pH levels is shown in Fig. 11 and 12. This behavior is more pronounced at higher pH levels where the magnitude of the yield stress at the equilibrium breakdown state is larger. The fully recovered yield stress is also higher. The conductivity of the 7 wt % suspensions at pH 12.22, 10.43 (natural pH), 8.53 and 7.25 were 4.81, 1.72, 2.53 and 3.47 mS/cm respectively. The equivalent 1:1 electrolyte concentrations at these conductivities ranged from 0.01 to 0.04 M. Since ionic strength difference is often measured in terms of a decade, this range of ionic strength is considered similar in the pH range of 7.2 to 12.2

Two structural recovery or ageing models, the Nguyen-Boger and Leong models were employed to fit temporal ageing yield stress data. The Nguyen-Boger (NB) model is based on 1st order structural recovery kinetics and is given by (Nguyen and Boger 1985):

$$\tau_y(t) = \tau_{y\infty} - (\tau_{y\infty} - \tau_{y0})e^{-kt} \quad (2)$$

where $\tau_y(t)$ is the time-dependent yield stress, τ_{y0} is the agitated state yield stress at equilibrium, $\tau_{y\infty}$ is the yield stress at complete structural recovery and $1/K$ is the model time constant. There is also a storage modulus version of this model. The Leong model based on second order aggregation kinetics is given by (Hattori and Izumi 1982):

$$\tau_y(t) = \tau_{y\infty} \left(1 - \frac{1 - \left(\frac{\tau_{y0}}{\tau_{y\infty}} \right)^{\frac{3}{2}}}{1 + k_r t} \right)^{\frac{2}{3}} \quad (3)$$

where $1/K_r$ is the time constant of this model. The full derivation of the Leong model can be found

in deKretser and Boger (2001). The methods for determining the model parameters for both models have been described elsewhere and will not be described here (deKretser and Boger 2001, Yap et al. 2011).

The results of NB model fit to the temporal yield stress data for API bentonite gels at different solids loading is shown in Fig.9 and the corresponding fit with the Leong model is shown in Fig.10. The quality of the fit of both models in describing the recovery behaviour is generally quite good especially at low solid loading. The fit was poorer for both models for the gels with 7 and 8 wt% solids. The values of the correlation coefficient R^2 for NB model fit were 0.9629, 0.9782, 0.8256 and 0.9366 for the 3, 5, 7 and 8 wt% gels respectively. The corresponding values for the Leong model fit were 0.9697, 0.9868, 0.7467 and 0.9018. Based on these R^2 values the Leong model fit is better for the 3 and 5 wt% gels and poorer for the 7 and 8 wt% gels. The R^2 values for the 7wt% gel was much smaller than 0.9 for both models. However, these R^2 values were greater than 0.9 for the 8 wt% gel. The 3 wt % bentonite gel displayed slight phase separation with a thin layer of clear liquid on top as shown as an insert in Fig 9.

The effect of pH ranging from 7.3 to 12.2 on the ageing behaviour of 7 wt % suspensions was evaluated. These ageing data at various fixed pH was fitted with both NB and Leong models and the results are shown in Fig. 11 and 12. The suspension with lowest ageing yield stress is at pH 7.2. This followed by the gels at pH 8.5, 10.4 and 12.2. The lower yield stress gels such as that at pH 7.2, 10.4 and 12.2 took a shortest time to reach the fully recovered state. The NB model fit shown in Fig. 12 is considered quite good especially for the gels at pH 8.53 and 7.25 as reflected by the high correlation coefficients listed in Table 3. The Leong model fit to these temporal yield stress data is shown in Fig. 12. The Leong model performed better for the suspensions at pH 10.4 and 12.2 (see the correlation coefficients listed Table 3). The fully recovered state yield stress is smallest at pH 7.3 of 40 Pa and the largest of 80 Pa at pH 12.2.

Fig. 9 Structural recovery behaviors of suspensions with different API bentonite content and their Nguyen-Boger model fittings (solid dark square: 3 wt% solids, solid red circle: 5 wt%, solid blue triangle: 7 wt%, solid inverted pink triangle: 8 wt%). Inset is the cryo-SEM image of Na-Swy2 gel taken from Mouzon et al. (2016) and gel samples used in this ageing experiment.

Fig. 10 Structural recovery behaviors of suspensions with different API bentonite content and their Leong model fittings (solid dark square: 3 wt% solids, solid red circle: 5 wt%, solid blue triangle: 7 wt%, solid inverted pink triangle: 8 wt%). Inset is the cryo-SEM image of Na-Swy2 gel taken from Mouzon et al. (2016) and gel samples used in this ageing experiment.

wt%, solid inverted pink triangle: 8 wt%). Inset is the cryo-SEM image of Na-Swy2 gel taken from Mouzon et al. (2016).

Fig. 11 Structural recovery-pH behaviors of 7% API bentonite suspensions at different pH and their Nguyen-Boger model fits represented by the solid lines.

Fig.12 Structural recovery-pH behaviors of 7% API bentonite suspensions at different pH and their Leong model fits represented by the solid lines.

Table 3 Correlation coefficients of two models for structural recovery behavior of 7 wt % API bentonite suspension at different pH

pH	pH=12.22	pH=10.43	pH=8.53	pH=7.25
Nguyen-Boger model	0.7660	0.8257	0.9098	0.9946
Leong model	0.8785	0.8714	0.7486	0.9358

A recent study on the microstructure of Na+Mt or SWy-2 gel sourced from the Clay Mineral Society using Cryo-XHR-SEM imaging technique showed a very open honeycomb structure being formed by the Na+Mt particles (Mouzon et al. 2016). The image is shown in the inset of Figure 10.

The sample for imaging was prepared by plunge-freezing in liquid nitrogen and the sublimation of several microns of ice. Most of the smectite sheet forming the honeycomb structure took an upright position. The authors claimed that this structure maybe formed by the volume expansion during ice formation. We argued that the density increase during the phase change from water to ice assuming that the sublimation process is very slow, is only a few percent and this would only have a small effect on the open honeycomb structure. The small fully dispersed fraction dispersed within this entangled gel structure could be the quartz and K-feldspar impurities present in SWy-2.

We argued that the very open honeycomb structure is the fully recovered state equilibrium structure. The strength of this structure must therefore be strongest or at the lowest energy state. Upon stirring this structure breakdown and will take time at rest to recovered back to this origin structure. The temporal increase in the ageing yield stress is thus a reflection of this structural rebuilding process. The presence of needle-like sepiolite may affect the structure and the pH at which ageing become more prominent but the general explanation remained valid. There is an equilibrium structure at the fully recovered state which is at the lowest energy state. All disturbed state will recover to this minimum energy state.

Conclusions

The API bentonite contained two very rheological active ingredients; sodium montmorillonite and needle-like sepiolite. The interplay between these two ingredients was responsible for the API bentonite displaying unusual rheological behaviour; maximum yield stress and viscosity at high pH and low yield stress and viscosity at low pH. Magnesium ions leaching from sepiolite at low pH and its subsequent hydrolysis will affect the rheological and surface chemistry of the API bentonite suspensions at high pH. Yield stress was highest in the pH range of 8 to 12 especially for the high

solid loading gel of 7 and 8 wt % bentonite. Minimum yield stress and viscosity were observed at pH of about 4. The concentration at which the suspension displayed yield stress behaviour is still low ~ 3 wt% solids. The yield stress suspensions also displayed time-dependent or ageing rheological behaviour. These suspensions appeared not to conform to the DLVO theory. Mular-Roberts salt-pH titration method produced a “point of zero charge” at pH 8.1 where the maximum yield stress was located. No point of zero charge was however observed in the zeta potential-pH data.

Na+Mt formed a very open honeycomb structure reported in the literature recently. This structure arguable at the minimum energy state explained the structural recovery or ageing behaviour of the bentonite suspensions. Quantitatively the structural recovery behaviour can be described quite adequately by the Leong and Nguyen-Boger models. The time scale of structural recovery for API bentonite suspensions was in hours. The Nguyen-Boger model described the structural recovery behavior more accurately for more loaded suspensions at low pH levels, while the Leong model perform better the gels at low solid content and at a higher pH level.

The Herschel-Bulkley model described the flow behavior of the 7 wt % API bentonite suspensions at various pH levels very well.

Nomenclature

API	American Petroleum Institute
SEM	Scanning electron microscope
XRD	X-ray diffraction analysis
XRF	X-ray fluorescence
Na+Mt	sodium montmorillonite
Ca+Mt	calcium montmorillonite

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References

Abu-Jdayil, B., 2011. Rheology of sodium and calcium bentonite-water dispersions: Effect of electrolytes and aging time. *Int. J. Miner. Process.* 98, 208-213.

Alvarez-Silva, M., Uribe-Salas, A., Mirnezami, M., Finch, J.A., 2010. The point of zero charge of phyllosilicate minerals using the Mular–Roberts titration technique. *Miner. Eng.* 23, 383-389.

Anthony, D.M., Benoit, N.A., Nicolas, T.D., Pagnoux, A.A., Claire, C.P., 2014. Influence of the ice front velocity and of the composition of suspensions on thermal properties of bentonite materials prepared using freeze-casting process. *J. Eur. Ceramic Soc.* 34, 4433-4441.

Au, P.I., Leong, Y.K., 2013. Rheological and zeta potential behaviour of kaolin and bentonite composite slurries. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 436, 530-541.

Au, P.I., Leong, Y.K., 2016. Surface chemistry and rheology of slurries of kaolinite and montmorillonite from different sources. *KONA powder particle J.* 33, 17-32.

Avadiar, L., Leong, Y.K., Fourie, A., Nugraha, T., Clode, P.L., 2014. Source of Unimin kaolin rheological variation- Ca^{2+} concentration. *Colloids Surfaces A: Physicochem. Eng. Aspects* 459, 90-99.

Avadiar, L., Leong, Y.K., Fourie, A., 2015. Physicochemical behaviors of kaolin slurries with and without cations-Contributions of alumina and silica sheets. *Colloids Surfaces A: Physicochem. Eng. Aspects* 468, 103-113.

Baik, M.H., Lee, S.Y., 2010. Colloidal stability of bentonite clay considering surface charge properties as a function of pH and ionic strength. *J. Indust. Eng. Chem.* 16, 837-841.

- Belaroui, L.S., Millet, J.M.M., Bengueddach, A., 2004. Characterization of lalithe, a new bentonite-type Algerian clay, for intercalation and catalysts preparation. *Catalysis Today* 89, 279-286.
- Bloys, B., Davis, N., Smolen, B., Bailey, L., Fraser, L., Hodder, M., 1994. Designing and managing drilling fluid. *Oilfield Rev.* 6, 33-43.
- Bourgoyne, A., Millheim, K., Chenevert, M., Young, F., 1986. *Applied Drilling Engineering*, Society of Petroleum Engineers (SPE).
- Brandenburg, U., Lagaly, G., 1988. Rheological properties of sodium montmorillonite dispersions. *Appl. Clay Sci.* 3, 263-279.
- Briscoe, B.J., Luckham, P.F., Ren, S.R., 1992. The rheological properties of barite-loaded drilling fluids. *Chem. Eng. Res. Design* 70, 55-62.
- Callaghan I. C., Ottewill R. H., 1974. Interparticle Forces in Montmorillonite Gels. *Faraday Discuss. Chem. Soc.* 57, 110-118.
- Celik, M.S., 2004. Electrokinetic behaviour of clay surfaces. In: F Wypych and K.G. Satyanarayana (Eds) *Clay Surfaces: Fundamentals and Applications*. Elsevier Academic Press, pp57-89.
- Chang, W.Z., Leong, Y.K., 2014. Ageing and collapse of bentonite gels—effects of Li, Na, K and Cs ions. *Rheol. Acta* 53, 109-122.
- Clark, R.K., Scheuerman, R.F., Rath, H., Van Laar, H.C., 1976. Polyacrylamide/potassium-chloride mud for drilling water-sensitive shales. *J. Pet. Tech.* 28, 719-727.
- De Kretser R.G., Boger D.V., 2001. A structural model for the time-dependent recovery of mineral suspensions. *Rheol. Acta* 40, 582-590.
- Dolz, M., Jiménez, J., Hernández, M.J., Delegido, J., Casanovas, A., 2007. Flow and thixotropy of non-contaminating oil drilling fluids formulated with bent and sodium carboxymethyl cellulose. *J. Petrol. Sci. Eng.* 57, 294-302.

- Duc, M., Gaboriaud, F., Thomas, F., 2005. Sensitivity of the acid-base properties of clays to the methods of preparation and measurement: 1. Literature review. *J. Colloid Interface Sci.* 289, 139-147.
- Fu, J., Chen, Y.J., Ju, J.Y., Li, Q.S., An, S.Q., Zhu, H.L., 2011. Treating Dye Wastewater of Reactive Brilliant Red K-2BP by Cetyltrimethylammonium Chloride-Modified Bentonite with Polyacrylamide Flocculant. *Polish J. Environ. Studies* 20, 61-66.
- Goh, R., Leong, Y.K., Lehan, B., 2011. Bentonite slurries-zeta potential, yield stress, adsorbed additive and time-dependent behaviour. *Rheol. Acta* 50, 29-38.
- Güngör, N., 2000. Effect of the adsorption of surfactants on the rheology of Na-bentonite slurries. *J. Appl. Polym. Sci.* 75, 107-110.
- Hattori, K., Izumi, K., 1982. A rheological expression of coagulation rate theory. 1 time dependent viscosity of unagitated dispersions. *J. Disp. Sci. Tech.* 3, 129-145.
- Hints, R., Kirsmae, K., Kallaste, T., Kiipli, T., 2004. Early diagenetic control on Lower Paleozoic K-bentonite composition in Baltic Basin. *Geochim. Et Cosmochim. Acta* 68, A351-A351.
- Isci, E., Turutoglu, S.I., 2011. Stabilization of the mixture of bentonite and sepiolite as a water based drilling fluid. *J Petrol. Sci. Eng.* 76, 1-5.
- Kelessidis, V.C., Maglione, R., 2008. Yield stress of water-bentonite dispersions. *Colloids Surfaces A: Physicochem. Eng. Aspects* 318, 217-226.
- Khalil, M., Mohamed Jan, B., 2012. Herschel-Bulkley rheological parameters of a novel environmentally friendly lightweight biopolymer drilling fluid from xanthan gum and starch. *J. Appl. Polym. Sci.* 124, 595-606.
- Kök M.V., Batmaz T., Gücüyener I.H., 2000. Rheological behavior of bentonite suspensions. *Petrol. Sci. Tech.* 18, 519-536.
- Kosmulski, M., 2011. The pH-dependent surface charging and points of zero charge V. Update. *J.*

Colloid Interface Sci. 353, 1–15.

Legaly, G., 1989. Principles of flow of kaolin and bentonite dispersions. *Appl. Clay Sci.* 4, 105-123.

Lee, C.E., Chandra, S., Leong, Y.K., 2012. Structural recovery behaviour of kaolin, bentonite and K-montmorillonite slurries. *Powder Tech.* 223, 105-109.

Leong, Y.K., 2005. Yield Stress and Zeta Potential of Nanoparticulate Silica Dispersions Under the Influence of Adsorbed Hydrolysis Products of Metal Ions - Cu(II), Al(III) and Th(IV). *J. Colloid Interface Sci.* 292, 557-566.

Longo, S., Di Federico, V., Chiapponi, L., Archetti, R., 2013. Experimental verification of power-law non-Newtonian axisymmetric porous gravity currents, *J. Fluid Mech.* 731, R2-12.

Longo, S., Di Federico, V., Archetti, R., Chiapponi, L., Ciriello, V., Ungarish, M., 2013. On the axisymmetric spreading of non-Newtonian power-law gravity currents of time-dependent volume: An experimental and theoretical investigation focused on the inference of rheological parameters, *J. Non-Newtonian Fluid Mech.* 201, 69–79.

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite dispersions. *Adv. Colloid Interface Sci.* 82, 43-92.

M'Ewen, M.B., Mould, D. L., 1957. The gelation of montmorillonite, Part 2-The nature of the interparticle forces in sols of Wyoming bentonite. *Trans. Faraday Soc.* 53, 548-564.

Madejová, J., Janek, M., Komadel, P., Herbert, H.J., Moog, H.C., 2002. FTIR analyses of water in MX-80 bentonite compacted from high salinary salt solution systems. *Appl. Clay Sci.* 20, 255-271.

Mouzon, J., Bhuiyan, I.U., Hedlund, J., 2016. The structure of montmorillonite gels revealed by sequential cryo-XHR-SEM imaging. *J. Colloid Interface Sci.* 465, 58-66.

Mpofu, P., Addai-Mensah, J., Ralston, J., 2003. Influence of hydrolyzable metal ions on the interfacial chemistry, particle interactions, and dewatering behavior of kaolinite dispersions. *J. Colloid Interface Sci.* 261, 349-359.

Mular, A.L., Roberts, R.B., 1966. A simplified method to determine isoelectric points of oxides. *Trans. Can. Inst. Min. Metal.* 69, 438-439.

Muzdybayeva, S.H., Musabekov, K., Muzdybayev, N., Gaskarova, G., Nurbaeva, N., Taybaeva, P., 2014. Effectiveness of use of Nanostructure Minerals - Bentonite of Taganskiy Deposit for Waste Water Clearing in Metallurgy Industry. *Eur. J Sustainable Dev.* 3,195-200.

Nguyen, Q.D., Boger, D.V., 1985. Thixotropic behaviour of concentrated bauxite residue dispersions. *Rheol. Acta*, 24, 427-437.

Nguyen, Q.D., Boger, D.V., 1983. Yield stress measurement for concentrated suspensions. *J. Rheol.* 27, 321-349.

O'Brien, D.E., Chenevert, M.E., 1973. Stabilizing sensitive shales with inhibited potassium-based drilling fluids. *J. Petrol. Tech.* 25, 1089-1100.

Ouellet-Plamondon, C.M., Stasiak, J., Al-Tabbaa, A., 2014. The effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite. *Colloids Surfaces A: Physicochem. Eng. Aspects* 444, 330-337.

Paineau, E., Michot, L.J., Bihannic, I., Baravian, C., 2011. Aqueous suspensions of natural swelling clay minerals. 2. rheological characterization. *Langmuir* 27, 7806-7819.

Peng, B., Luo, P.Y., Guo, W.Y., Yuan, Q.Y., 2013. Structure-property relationship of polyetheramines as clay-swelling inhibitors in water-based drilling fluids. *J. Appl. Polymer Sci.* 129, 1074-1079.

Reid, A., Sen Gupta, N.C., 1947. Effect of sodium hexametaphosphate on the yield value and viscosity of a hydrogen bentonite suspension. *Nature* 159, 336-337.

Skalle, P., 2011. Drilling fluid engineering. Paal Skalle and Ventus Publishing ApS.

Sehly, K., Chiew, H.L., Li, H., Song, A., Leong, Y.K., Huang, W., 2015. Stability and ageing

behaviour and the formulation of potassium-based drilling muds. *Appl. Clay Sci.* 104, 309-317.

Tunç, S., Duman, O., Kanc, B., 2012. Rheological measurements of Na-bentonite and sepiolite particles in the presence of tetradecyltrimethylammonium bromide, sodium tetradecyl sulfonate and Brij 30 surfactants. *Colloids Surfaces A: Physicochem. Eng. Aspects* 398, 37-47.

Xu, T.Y., Liu, Y. Ge, F., Ouyang, Y.T., 2014. Simulated solar light photooxidation of azocarmine B over hydroxyl iron–aluminum pillared bentonite using hydrogen peroxide. *Appl. Clay Sci.* 100, 35-42.

Uriev, N.B., 2011. Rheological and thixotropic properties of aqueous bentonite clay suspension preliminarily subjected to electrohydrodynamic treatment. *Colloid J.* 73, 104-109.

Van Olphen, H., 1955. Forces between suspended bentonite particles. *Clays Clay Miner.* 4, 204-224.

Van Olphen, H., 1957. Forces between suspended bentonite particles Part II-calcium bentonite. *Clays Clay Miner.* 6, 196-206.

Velde, B., 2004. Composition variation of illite-vermiculite smectite mixed-layer minerals in a bentonite bed from Charente. *Clay Miner.* 39, 317-332.

Yap, J., Leong, Y.K., Liu J.S., 2011. Structural recovery behavior of barite-loaded bentonite drilling muds. *J. Petrol.Sci. Eng.* 78, 552-558.

Yoon, J., El Mohtar, C., 2013. Dynamic rheological properties of sodium pyrophosphate-modified bentonite suspensions for liquefaction mitigation. *Clays Clay Miner.* 61, 319-327.

Yalçın, T., Alemdar, A., Ece, O.I., Gungor, N., 2002. The viscosity and zeta potential of bentonite dispersions in presence of anionic surfactants. *Materials Lett.* 57, 420-424.

Zheng, X., Ma, X., 2010. *Drilling fluids*. China University of Geosciences, Beijing.

Zhu, S., Avadiar, L., Leong, Y.K., 2016. Yield stress- and zeta potential-pH behavior of washed α -Al₂O₃ suspensions with relatively high Ca(II) and Mg(II) concentrations: hydrolysis product and

bridging. Int. J. Miner. Process. 148, 1-8.