Activation of (Na, Ca)-bentonites with soda and MgO and their utilization as drilling mud

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A B S T R A C T

This study explores, as an alternative to sodium bentonite, the possibility of (Na, Ca)-bentonites to meet the required drilling mud properties. Activation of the bentonites was performed using the most popular (\(\text{Na}_2\text{CO}_3\)) and also the most controversial additive (MgO) and their blends. Upgrading the (Na, Ca)-bentonites was elaborated on the basis of viscosity, swelling index, filtration loss and electrokinetic measurements. The combination of soda and MgO produced a significant synergy.

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1. Introduction

Bentonite often contains >80% montmorillonite. Bentonite is used in a wide range of applications including drilling mud, bleaching earth, water and solvent based rheological additives, cat litter, desiccant clay, and animal feed additive (Lagaly, 2006).

Due to high viscosity and swelling and low filtration loss, (Na–Ca)-bentonites are in high demand in commercial applications (İpeköglu et al., 1997; Murray, 2000). It is commonly known that even good quality sodium bentonites may not meet the required standards for drilling muds as drilling-fluid additives in their natural forms. Their main functions are to viscosify the mud and reduce fluid loss to the formation (Bol, 1986). By alkali activation or by introducing some polymer additives, it is possible to upgrade some (Na, Ca)-bentonites and even calcium bentonites to meet the API or TS EN ISO 13500 (30 cP minimum viscosity at 600 rpm; 15 cm² filtration loses and 22 ml swelling index) standards. Because raw (Na–Ca)-bentonites exhibit high filtration losses and do not develop sufficient viscosity, they cannot meet the above standards and thus require appropriate activation formulations. These activations typically employ various additives such as soda, MgO, and a polymer, usually CMC (carboxyl methyl cellulose). While soda and MgO improve the swelling or viscosity, CMC and soda hinder filtration losses. Modification of bentonite with polymers (soluble in water) and similar compounds has been studied by different investigators and outstanding rheological behaviors such as viscosity, thixotropy etc. have been measured (Scott and Okla, 1962; Lumus and Okla, 1969; Swanson and Okla, 1970; Glass, 1985; Bol, 1986; Burdick, 2002). The mechanisms governing activation can be usually advanced as ion exchange, ion adsorption and also particle–particle interactions (heterocoagulation). Organic compounds, in particular polymers, are generally far more effective additives than inorganic salts. High friction and temperature (>120 °C) causes structural and bacterial damage during the storage of organic material (Çinku, 2008; Kocakuşak et al., 1997; Koroğlu et al., 1998).

The effect of inorganic additives on bentonite dispersions has been investigated in a number of studies. The activation with 2–4% soda is traditionally used to process lower quality bentonites in the industry. Lebedenko and Plee (1988) observed that the Na⁺ content was the most significant parameter enhancing the rheological properties. They explained that Mg²⁺ ions were necessary to create better gel strength. Rollins (1969) found that sufficient sodium is required to prepare a well dispersing bentonite. Bentonite with a mass ratio of Na/Ca/Mg of 60/20/20 was proposed. Formation of different types of networks was proposed to vary with pH, Ca/Na and Ca/Mg ratio (Allther, 1986). Considering that gelling properties improve at all pH range except neutral pH, edge–face (EF) interaction becomes dominant at acidic pH while long range repulsive interaction is dominant at alkaline pH; MOH⁺ (MgOH⁺, MnOH⁺ and PbOH⁺) type cations make the surface charge of edges positive by specific adsorption of MOH⁺ (Obut and Girgin, 2005). Gelling
properties of bentonite can be improved by employing such cations to induce the formation of the EF and EE (edge–edge) networks, which also depends on pH and Ca/Na ratio (Lagaly, 1989). Lagaly (1989) reported that kaolin and bentonite dispersions are governed by EF contacts (card-house structure) in acidic medium and FF (face–face) contacts (band-like structure) in alkaline medium. Also Ca$^{2+}$ ions promoted FF contacts and stabilized band-like structure.

The objective of this study is to upgrade (Na, Ca)-bentonites with the addition of chemicals such that they meet the accepted standards and also to explain the physicochemical phenomena underlying interactions between bentonites and additives.

2. Materials and methods

Two (Na, Ca)-bentonites hereafter referred as CGB (gray in color) and CYG (yellow in color) mined from Çanbısnan Bentonite Company of Çankırı/Turkey were investigated. Some properties and chemical analyses made by XRF (X-ray fluorescence) are shown in Tables 1 and 2. The viscosity and swelling characteristics (Table 1) and the mass ratio of (Na$_2$O + K$_2$O)/(CaO + MgO) = 0.57 (Table 2) fall within the classification of mixed bentonites (Günyay et al., 2001).

The sodium content of 2.3 and 2.5% indicates a relatively better quality bentonite. The relatively high MgO content is also one of the favorable points considered in terms of swelling and viscosity features. LOI value of 14.8 generally indicates medium level of impurities.

Mineralogical compositions of representative bentonite samples (Fig. 1) were determined by XRD using air-dried and ethylene glycol wetted samples. The Rigaku diffractometer with Cu($\text{Kα}$) radiation was used. In addition, mineral contents of the samples were estimated by the quantitative XRD modal analysis recommended by Chung (1974, 1975) and Davis and Walavender (1982). The reflections of highest intensity were used and the intensity ratios (calcite standard/ mineral) of 50/50 were calculated. Reference intensity constants for the minerals used in this procedure were given elsewhere (Bulut et al., 2009).

Amorphous material contents were estimated from the broad band appearing at 2θ = 30 (2θ).

CGB contained 55% montmorillonite, 10–15% feldspar, 10% amorphous material, 10% quartz, 5% calcite and 5–10% opal, while CYB contained 50% montmorillonite, 15% feldspar, 10–15% amorphous material, 15% quartz, 5% calcite, 5% gypsum, and <5% opal.

Run-of-mine (ROM) bentonite sample ground into <150 µm was used in all tests. Activation was performed using soda and MgO. Because the bentonite samples were stored for over a year, the moisture content remained around 10%. Therefore, the bentonite was moisturized to reach the required levels prior to soda addition. MgO addition, however, was performed without any moisturizing. The optimum moisture of the bentonite samples for soda activation was found to be 40% in our preliminary activation studies on viscosity, swelling, and filtration loss. In soda activation, soda ash powder was added to the initially moistened bentonite slurries of 6% by mass in compliance with the API standards. The bentonite slurries were mixed at 11,000 rpm using a kitchen type blender for 10 min and transferred to sealed beakers to prevent evaporation of water in the pulp for 24 h. The FANN viscometer was utilized for measuring viscosities at 300 and 600 rpm. Following viscosity measurements, the slurries were transferred to the API filtration loss test equipment and filtration losses at 7.5 and 30 min were recorded but only those at 30 min were considered in the analysis.

Filtrates of filtration loss tests were collected and transferred to the zeta potential cell into which a small amount of bentonite particles from the filter cake was added to measure the electrokinetic properties of the activated bentonites. Electrokinetic measurements were carried out using the Zeta Meter 3.0 equipped with a microprocessor unit (Sabah et al., 2007).

The presence of heterocoagulation between MgO and bentonite particles was tested through coagulation tests following the procedure given by Lagaly and Ziesmer (2003). The critical coagulation concentration of MgO (C). While the swelling index is 28 ml, filtration loss and viscosity are 12 ml under sunlight for a month to complete the activation process (Harvey and Lagaly, 2006).

Following activation and drying/curing period for a month, the activated samples were crushed to its original size of >150 µm using mortar and pestle.

### Table 1

<table>
<thead>
<tr>
<th>Component</th>
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<th>CYB bentonite</th>
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<tr>
<td>Na$_2$O</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>MgO</td>
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<td>2.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
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<td>15.6</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>61.9</td>
<td>57.8</td>
</tr>
<tr>
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<td>0.1</td>
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<tr>
<td>K$_2$O</td>
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<td>MnO</td>
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<tr>
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<td>0.7</td>
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<tr>
<td>Fe$_2$O$_3$</td>
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<tr>
<td>LOI</td>
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Swelling tests were performed in 100 ml graduated cylinders using 2 g bentonite dried at 105 °C using halogen driers. After slowly feeding the bentonite, the mixture was left for settling for 5–6 h before the sediment volumes were recorded.

Viscosity measurements were carried out with the activated bentonite slurries of 6% by mass in compliance with the API standards. The bentonite slurries were mixed at 11,000 rpm using a kitchen type blender for 10 min and transferred to sealed beakers to prevent evaporation of water in the pulp for 24 h. The FANN viscometer was utilized for measuring viscosities at 300 and 600 rpm. Following viscosity measurements, the slurries were transferred to the API filtration loss test equipment and filtration losses at 7.5 and 30 min were recorded but only those at 30 min were considered in the analysis.

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3. Results and discussion

3.1. Viscosity, swelling and filtration loss of the activated CGB Bentonite

The combined activation of soda and MgO (Fig. 2) led to higher viscosities while samples activated with soda or MgO individually showed no significant change on viscosities. Also, lower filtration losses were obtained with the combined activation of soda and MgO. Although soda only activation did not yield high viscosities, it produced the lowest filtration losses (Fig. 3).

Swelling properties of the activated bentonites (Fig. 4) confirm the positive effect of the soda–MgO combination. The highest swelling indices were obtained with the formulation of 2% soda + 3% MgO, though this does not comply with the drilling mud requirements (Çinku and Bilge, 2001; Malayoğlu and Akar, 1995). When the soda–MgO combination is considered, soda concentrations >0.5% in the formulation deteriorated the technological properties of the activated products (Çinku and Bilge, 2001).

If the results presented in Figs. 2–4 are considered for drilling mud applications, activation with 2–3% soda + 0.5%MgO yielded suitable filtration loss, viscosity and swelling data (Fig. 5A–C). While the swelling index is 27–28 ml, filtration loss and viscosity are 12–14 ml and 40–60 cP, respectively. These results clearly show that CGB activated with the combination of soda and MgO can be used as a drilling mud in accordance with the API and TS EN ISO 13500 standards. Erdoğan and
Demirci (1996) studied the same sample with a \((\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{CaO} + \text{MgO})\) ratio mass ratio of 0.76. Their study indicated that addition of inorganic salts developed viscosity insufficient for the use as drilling mud. However, they determined that the use of Na–CMC, polyacrylamide and polyacrylic acid (PAA) can approach the drilling mud standards. Monovalent ions may exert unfavorable effects on rheological characteristics since they cannot form network links between layers as opposed to multivalent ions such as Ca\(^{++}\) and Mg\(^{++}\). However, above a certain level of multivalent ion concentration, because of their strong coagulant effect, a decrease in viscosity through hampering the network structure and in turn causing face/face combination may lead to the coagulation of suspensions (Abend and Lagaly, 2000; Colic et al.,

Fig. 1. A. XRD pattern of CYB. B. XRD pattern of CGB.
Fig. 2. Viscosities of CGB dispersions activated with soda and MgO.

Fig. 3. Filtration loss characteristics of CGB activated with soda and MgO.

Fig. 4. Swelling characteristics of CGB activated with soda and MgO.

Fig. 5. A. Optimum additive level (dotted line) based on viscosity of CGB. B. Optimum additive levels (dotted line) based on filtration loss of CGB. C. Optimum additive levels (dotted line) based on swelling index of CGB.
1997; Ece et al., 1999; Güven, 1992a,b; Hiemenz, 1986; Lucham and Rossi, 1999). These effects of Na\(^+\) and Mg\(^{2+}\) can be clearly observed in Fig. 2.

3.2. Viscosity, swelling and filtration loss of the activated CYB bentonite

Fig. 6 demonstrates the highest viscosity values in the range of 30–45 mPa s of the products activated only with soda or MgO. The optimum additive dosage is 2% for soda and MgO (Fig. 7A–C). If the additive dosage was >2%, the suspension viscosity either remained constant or decreased. Thus, the viscosities could not be improved unless a combined activation was applied. Fig. 6 indicates that a viscosity of 150 mPa s was reached by the use of a combination of soda (>1.5%) and MgO. The most convenient combination was 2% soda. The enhanced effects of soda–MgO were reduced with soda addition. When mixed bentonite was activated with soda–MgO, viscosity values suitable for the paint industry were produced. However, for drilling fluids the filtration loss (Fig. 8) of the suspensions becomes more crucial. Further MgO addition seemed to reduce the network structure. Similar results had been obtained for the Reşadiye Na-bentonite (Çinku, 2008). For the drilling industry, a combination of 2% soda + 0.5% MgO provided an adequate product with the appropriate properties giving filtration loss and viscosities at the levels of 15–16 ml and 65–70 mPa s.

While the swelling values increased to 26–27 ml with only 2% soda addition (Fig. 9), they decreased to 18–19 ml with the use of MgO alone. However, similar to viscosity data, the swelling values increased to 45 ml with the use of soda and MgO together. With 2% soda and 0.5% MgO the swelling values increased to 31–32 ml.

When the activation characteristics of the two (Na, Ca)-bentonite were combined, our results generally indicated higher viscosities. This is frequently attributed to both ion exchange and heterocoagulation of oppositely charged MgO and clay mineral particles (Fig. 11). Lower viscosities and higher swelling indices are usually ascribed to ion exchange alone. MgO appears to control the activation of bentonite through heterocoagulation but soda activation is primarily governed by ion exchange.

3.3. Electrokinetic properties of activated CGB and CYB bentonites

Electrokinetic properties of the bentonites play an important role in controlling the characteristics of the dispersions and also in explaining the mechanism responsible for the development of viscosity, filtration

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**Fig. 6.** Viscosities of CYB dispersions activated with soda and MgO.

**Fig. 7.** A. Optimum additive level shown in dotted line based on viscosity of CYB. B. Optimum additive level shown in dotted line based on filtration loss of CYB. C. Optimum additive level shown in dotted line based on swelling index of CYB.
loss and swelling index, particularly those obtained with soda and MgO activated samples. The results of electrokinetic measurements are shown in Fig. 11.

As it is well documented in the literature, Mg salts in aqueous solutions may be present in various species with pH. In bentonite suspensions, the addition of MgO results in various ion forms such as Mg$^{+2}$, MgOH$^+$ and Mg(OH)$_2$(S) depending on the pH. Increasing the value above pH 9.5 converts Mg$^{+2}$ ions into MgOH$^+$ and Mg(OH)$_2$(S) depending upon the concentration of total Mg in the solution (Moriyama et al., 2009; Obut and Girgin, 2005; Sasaki et al., 2009). The formation of MgOH$^+$ may impart higher viscosities by forming gel-like structure while Mg(OH)$_2$(S) formed at high pH is precipitated and forms heterocoagulates with the clay mineral particles and in turn destroy the network structure. Both these mechanisms adversely affect the viscosity, and swelling and also filtration losses. On the other hand, Na and Mg carbonates may be formed in the suspension. However, these compositions are not expected to change much the system. The higher Mg addition in our system corresponded to a $10^{-1}$ mol/l base addition which also increased the pH due to Mg(OH)$_2$(S) precipitation (Fig. 10). It became evident that Na$^+$ ions clearly affected the system; the viscosity and swelling index increased with increasing Na$^+$ ion concentration whereas the filtration losses decreased. On the other hand, divalent cations restrict the swelling to the formation of four-water layer complexes (Lagaly, 2006). This situation was observed in the two swelling tests activated with soda and MgO. Sufficient swelling was only observed with simultaneous soda and MgO.

In clay mineral suspensions, generally edge/edge or face/face interactions are referred to as coagulation whereas edge/face interactions are called heterocoagulation both of which are controlled by the DLVO theory. Heterocoagulation which can also occur between the oppositely charged minerals can be expressed as heterocoagulation, which was encountered in this study, as agglomeration of positively charged MgO particles and negatively charged clay mineral particles. In the pH range of 6–12, bentonite and MgO (solid) particles carry opposite charges giving rise to the iew at about pH 12 (Fig. 11); this is in line with
the reported values in the literature (Roncari et al., 2000; Sadowski and Polowczyk, 2004). At this condition, aggregation and/or coagulation between MgO and bentonite particles are expected to lead to heterocoagulation. Coagulation test results seen in Fig. 12 reveal that in the presence of either 1.5% (ccc: critical coagulation concentration) of MgO only or MgO + soda, the bentonite particles start to settle; this represents the onset of heterocoagulation. While the ccc values of MgO for MgO only and MgO + soda combination were found as 1% and 2% ccc values (for MgO only and MgO–soda combination) remained the same (ccc = 1%) for CGB. Although for MgO the ccc corresponds to 1% addition of soda increased the ccc value due to the dispersing effect of Na+ ions released from soda. The difference in ccc values of MgO for CGB and CYB is attributed to the differences in MgO, Na2O and CaO contents of the bentonites.

Coagulation tests were performed at the solid concentration of 0.025% for appropriate visual inspection while viscosity tests were performed at 6% solids concentration. The lower ccc values observed for coagulation tests were explained with the differences in solids concentrations. Lagaly and Ziesmer (2003) also reported similar findings where the higher solid ratios yielded higher ccc values.

4. Conclusions

Activation of two Turkish bentonites with soda and MgO mimicking industrial applications influenced the viscosities, swelling indices and filtration losses.

The tests revealed that the two raw bentonites did not fulfill the drilling mud standards. However, the addition of 1.5–3% soda and 0.5% MgO brought the sample to the required standards. Finally, in addition to their applicability in drilling, these samples can be used as thickeners or viscosity modifier in the paint industry due to their viscosity and swelling characteristics.

References

