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

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ABSTRACT

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 (Na_2CO_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.

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 (İpekoğlu 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 cm^3 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, thixotrophy 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; Köroğlu et al., 1998).

The effect of inorganic additives on bentonite dispersions have 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 Mg^{2+} 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 (Alther, 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

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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 Çanbensan 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 $(Na_2O+K_2O)/(CaO+MgO)=0.57$ (Table 2) fall within the classification of mixed bentonites (Günay 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(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 20–30 (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 moisturized bentonite samples and kneaded till all the bentonite had reacted with soda. After soda addition and kneading, the activated samples were left to drying/curing 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
Some characteristics of the bentonites.

Sample	CEC meq/100 g	Swelling index ml	FANN viscosity @ 6 mass %					
			20 min			24 h		
			300 rpm	600 rpm	pH	300 rpm	600 rpm	pH
CGB	65	14.5	3.50	5.50	9.03	5.0	7.0	8.20
CYB	71	15.5	4.50	7.00	8.58	5.5	8.5	8.30

Table 2
Chemical analysis of Run-of-mine (ROM) (Na, Ca)-bentonites used in this study.

Component	CGB bentonite	CYB bentonite
	Content, mass %	
Na_2O	2.3	2.5
MgO	1.9	2.5
Al_2O_3	17.3	15.6
SiO_2	61.9	57.8
P_2O_5	0.1	0.1
K_2O	0.9	1.1
CaO	3.0	2.1
MnO	0.1	0.1
TiO_2	0.3	0.7
Fe_2O_3	3.3	4.9
LOI	7.9	12.5

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.

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 concentrations (ccc) were determined by visual inspection of the settling behavior of 0.025% dispersions after MgO addition.

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