



Research paper

Simultaneous purification and modification process for organobentonite production

Z. Yeşilyurt^a, F. Boylu^{a,*}, K. Çinku^b, F. Esenli^c, M.S. Çelik^a^a Istanbul Technical University, Faculty of Mines, Min. Proc. Eng. Depart., Istanbul, Turkey^b University of Istanbul, Engineering Faculty, Mining Eng. Depart., Istanbul, Turkey^c Istanbul Technical University, Faculty of Mines, Geological Eng. Depart., Istanbul, Turkey

ARTICLE INFO

Article history:

Received 15 May 2013

Received in revised form 28 January 2014

Accepted 2 April 2014

Available online 3 May 2014

Keywords:

Na-Bentonite

Purification

Modification

HTAB

ABSTRACT

Bentonites are commonly subjected to a water and energy intensive purification process in order to obtain high-grade montmorillonite, prior to modification to suit technological needs. In this study, the purification and modification processes were combined in order to minimize costs. A method for the production of organobentonite from roughly purified Na-bentonite from Reşadiye, Turkey, was proposed with a quaternary alkylammonium salt, hexadecyl trimethyl ammonium bromide. Further purification and ion exchange reactions were simultaneous within a centrifugal separation process, followed by the removal of excess modifier agent using the flotation method. The parameters of centrifugal force, feed solid content for Falcon concentrator and modification time, and the amount of alcohol for ion exchange reactions were optimized. Ammonium intercalated organoclays were characterized by X-ray diffraction analysis, thermogravimetric analysis, and swelling tests in organic liquids. An optimum flow sheet for the simultaneous purification and modification process yielding a 97% pure organobentonite with a 2.02 nm basal spacing was developed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Na⁺-Bentonites have a wide range of applications owing to their layered structure, high cation exchange capacity, ability to swell, and their high platelet aspect ratio. Inorganic cations are present on the basal plane of montmorillonite layers, which make it hydrophilic in nature. However, cation-exchange reactions have been traditionally employed as a method to replace these inorganic cations with organic surfactant cations, which intercalate into the clay layers leading to an increase in the basal space diameter. This not only changes the surface properties to hydrophobic, but also facilitates penetration of the polymer between the clay layers (Paiva et al., 2008).

Various organoclays are widely used (Paiva et al., 2008) as fillers in polymer nanocomposites (McLauchlin et al., 2011), adsorbents for organic pollutants (Lee et al., 2002), or rheology modifiers (Borah and Chaki, 2012). Quaternary alkylammonium salts are the organic cations most often intercalated into montmorillonites (Paiva et al., 2008). Commonly, purification steps prior to modification consist of dispersion/disintegration methods, sedimentation, centrifugation, and ion-exchange reactions for Ca-bentonites (Patel et al., 2007).

Effective separation of a Na-bentonite sample by multistage hydrocyclone was reported in our earlier study (Boylu et al., 2010). However, few studies have been reported on directly modifying raw clay, then removing impurities and unmodified clay for the production of high purity organoclay. In these applications, delamination in organic solvents and separating settled impurities from organobentonite, which is then subjected to evaporation, is one of the methods. Pure organobentonite was separated from a mixture of organobentonite and unreacted clay minerals and other impurities through delamination in nitrobenzene (Venugopal and Rajamathi, 2008). In addition, some patents have been found in the literature proposing simultaneous purification and modification in non-aqueous solutions in one process. Daren et al. called their application “one-pot purification and modification” and proposed some examples with different surface modifiers (Daren, 2008). These applications can also be achieved in aqueous solutions and some additional stages of the processes, such as evaporation and the utilization of additional organics can be eliminated. With this application (simultaneous purification and modification), it is thought that the dewatering of purified bentonites might be easier by its direct modification, which renders the bentonite surfaces more hydrophobic and results in nature that has better filtering properties.

The aim of this study was to obtain highly pure organobentonite through a simultaneous purification and modification process while reducing water and energy costs. The properties of organomontmorillonite

* Corresponding author at: Istanbul Technical University, Faculty of Mines, Mineral Processing Engineering Department, 34469, Maslak, Istanbul, Turkey.

E-mail address: boylu@itu.edu.tr (F. Boylu).

were investigated using X-ray diffraction (XRD), thermogravimetric (TG), and swelling test analyses.

2. Materials and methods

2.1. Materials

A raw Na-bentonite sample (ROM: Run of mine ore) with cation exchange capacity (CEC) of 78 meq/100 g collected from Tokat-Reşadiye deposit of Turkey was used in the experiments. Swelling index and FANN viscosity values of the sample at 6% solids were determined as 21 mL/2 g and 20 and 35 m Pas (at 300 and 600 rpm), respectively. The raw bentonite sample, 30–35 mm in size, was crushed to 4–5 mm prior to disintegration in water. As Na^+ -bentonite disintegrates naturally in water; no further size reduction was applied.

The representative sample of the raw bentonite exhibited a mineralogical composition of mainly dioctahedral smectite with a mixed layer of illite-smectite of about 10% and small amounts of quartz, feldspar, calcite, and opal-CT (opal-cristobalite/tridymite) (approximately 15% in total) (Boylu et al., 2010; Bulut et al., 2009).

2.2. Methods

Chemical analyses performed at ACME Labs (Vancouver, Canada), established that the bentonite sample contains 57.09% SiO_2 , 16.73% Al_2O_3 , 2.51% Na_2O , 3.18% CaO , and 3.24% Fe_2O_3 with the Loss of ignition (LOI) value of 13.40%. The ratio of 0.68 for $[(\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{CaO} + \text{MgO})]$ seems relatively low compared with the general classification for Na-bentonites. This is caused by the larger proportion of feldspar in the matrix.

Mineralogical compositions of the representative ROM sample and products were analyzed by XRD method using air-dried and ethylene-glycol-treated samples. The Rigaku diffractometer with $\text{Cu}(\text{K}\alpha)$ radiation was used. In addition, mineral contents of the samples were estimated by the quantitative XRD modal analysis method recommended by Chung (Chung, 1974, 1975) and Davis and Walavender (Davis and Walavender, 1982). The highest reflections of the mineral peaks 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 (Boylu et al., 2010; Bulut et al., 2009). Amorphous material contents were estimated from the hump appearing in 20–30° (2 θ) of the XRD patterns.

The differential thermal analysis (DTA) and TG analysis of the 20 mg of ROM bentonite and the products of the simultaneous purification and modification process (organobentonites) were performed at temperatures between 25 and 1000 °C in the presence of nitrogen gas (30 mL/m) using a SEIKO SII TG/DTA 6300. The heating rate was 10 °C/min.

2.2.1. Experimental procedure

2.2.1.1. Rougher purification. The bentonite sample 4–5 mm (d_{90}) in size was added initially to filtered water in required amounts (solid content was around 3%) and then blended for 5 min at 12,500 rpm using a glass jar blender (Arcelik Co., Turkey).

Bentonite dispersions were then left to settle in 1000 ml beakers for 30 min to remove the easy-to-settle non-clay minerals of coarse sizes. The initial removal of coarse gangue minerals hindered the possible deterioration of the sedimentation bed during centrifugation. The dispersed particles in the measured cylinders were then transferred to one-stage centrifugal purification through an L40 model lab-scale Falcon concentrator (Sepro Mineral Systems Co., Langley, BC, Canada) operating with centrifugal forces of up to 300 “g”.

2.2.1.2. Simultaneous purification and modification. Following disintegration, screening (500 μm) and further settlement in beakers (removal of

coarse impurities), the bentonite dispersion without coarse impurities was introduced to the Falcon concentrator to remove possible impurities of very fine sizes. Falcon overflows, including treated bentonite dispersion, were then transferred into a beaker and modified with Hexadecyl trimethyl ammonium bromide (HTAB) (including 10% isopropanol) in amounts of 96% of CEC. Following modification for 30 min (optimum as shown in Fig. 1), the modified organobentonite dispersion was introduced to the purification unit with centrifugal force of 100 “g”, because our experience revealed that modified products can be purified at low centrifugal forces (100 g), and that an increase above this causes deterioration of purification, as shown in Fig. 1.

The purified organobentonite products were then transferred to a Denver flotation cell, in which both further purification and the washing processes can be performed simultaneously. Initial tests on the flotation/washing process revealed that four stages of washing/flotation were required for the complete removal of excess modifier agent (Fig. 2). Thus, the total dissolved solid concentration of approx. 400 ppm in modified bentonite dispersions was reduced to 10 ppm through 4-stage washing/flotation. In addition to the primary impurities that accompany raw bentonite dispersion, the washing/flotation process also provides the removal of possible secondary/external impurities entrained from the mechanical parts of the Falcon concentrator. Following the simultaneous purification and modification, the purified organobentonite dispersion was filtered and dried at 60 °C in an oven. The development of modified and purified bentonite is illustrated in Fig. 3.

3. Results and discussion

The application of the simultaneous purification and modification process is illustrated in Fig. 4 as a flowchart with XRD patterns of the products of each stage. The mineralogical composition of the products from quantitative XRD modal analysis is illustrated in Table 1.

As seen from Table 1, without any purification, unmodified (UM) pristine bentonite contains 25% impurities and 75% smectite, which is reflected as 79% by the modified (M) pristine bentonite. Following the initial treatment of pristine bentonite through screening, only impurities at coarse sizes such as feldspars were removed, without any loss of smectite. Further settling of the disintegrated and screened bentonite dispersion resulted in the removal of predominantly O-CT, quartz, and calcite minerals. Falcon concentration of the roughly purified bentonite dispersion allowed the removal of zeolite and O-CT. Following the removal of coarse impurities through screening, settlement, and Falcon concentration, the complete removal of the illite, quartz, feldspar, and calcite was achieved, leaving the bentonite concentrate that included only 5% zeolite and 9% O-CT. Further simultaneous modification and purification process yielded the purified and modified bentonite product

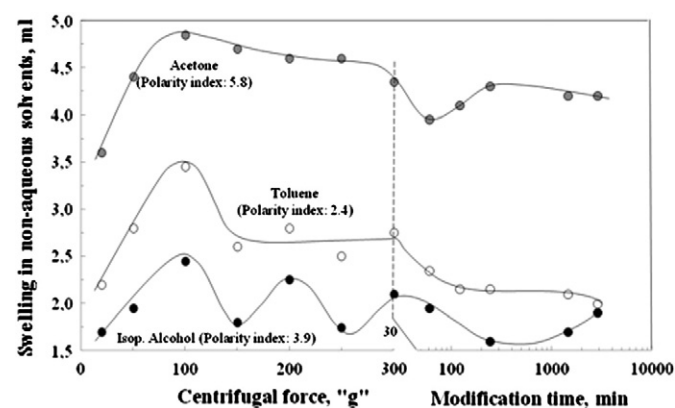


Fig. 1. Effect of centrifugal force and modification time on simultaneous purification and modification process (HTAB in amount of 64% of CEC).

Download English Version:

<https://daneshyari.com/en/article/1694807>

Download Persian Version:

<https://daneshyari.com/article/1694807>

[Daneshyari.com](https://daneshyari.com)