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Research paper

A simple method for physical purification of bentonite

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ABSTRACT

Impurities limit the application of low-grade bentonite, resulting in a large waste of resources. A simple physical method composed of grinding, dispersion and centrifugation was adopted to purify a low-grade bentonite from Zhejiang, China. This experiment increased the montmorillonite content of the bentonite from 44% to 96.5% with montmorillonite yield over 70%. The influence of the grinding time of raw bentonite, the dispersant dosage in bentonite dispersion, and the centrifugal speed on the purification of bentonite were investigated. Results indicate that appropriate grinding is crucial to the dissociation of bentonite aggregates. The particle size of raw bentonite decreases with increasing the grinding time but it is needed to stay within a certain range to avoid excessive grinding that hinders the purification. A suitable amount of dispersant can change the surface potential of minerals and enlarge the flottability and stability differences between montmorillonite and impurities, which is important for their separation by aqueous dispersion. Centrifugal speed is also critical as too low speed decreases the purity level of the purified bentonite and too high speed lowers the yield of montmorillonite.

1. Introduction

Bentonites are used as industrial raw materials for more than 40 applications (Grim and Güven, 1978; Murray, 1999). With the development of modern technology, bentonite application has been transformed from traditional casting, pellet, drilling mud, adsorption agents to some high value-added products like nano materials, medicine, carrier materials and fine chemicals. Bentonite is widely used for the treatment of esophagitis, gastritis, colitis disease and so on based on its strong adsorption, detoxification effect on toxic substances (Shah et al., 2013). Bentonite is also used as a raw material for cosmetics because of its decontamination, detoxification, itching relieving, beauty and moisturizing properties (De Nones et al., 2015). In addition, with adsorption ability and chemical stability, bentonite has been widely used in food processing industry which is closely related to our life and health (Mihaljevic et al., 2006).

Bentonite is generated from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite (Boylu et al., 2010). Besides smectite, bentonite contains a variety of accessory minerals, including quartz, calcite, feldspar, mica, and illite. The presence of such minerals reduces the value of bentonite. So that most of the low-grade bentonite is not suitable for industrial applications, such as water purification (Li et al., 2010), commodity (Bulut et al., 2009), and food industry (Thoruwa et al., 2000). In particular, the quartz and cristobalite which are difficult to remove from bentonite can be a cause of cancer. Strengthen the research on bentonite process-induced mineralogy and bentonite purification technique is very important to improve the quality and performance of bentonite.

Handbook of Clay Science (Bergaya et al., 2006) systematically introduces the method for purification of clay minerals, including decomposition of carbonates, dissolution of (hydr)oxides and oxidation of organic materials. Obviously it is needed to work with the finest grain sizes as possible to get the best degree of liberation of co-existing minerals and reduce the amount of mixed grains. The beneficiation method reported in literatures employed multistage hydrocyclone processing (Schneider and NeeBe, 2004), as well as chemical treatment (Bulut et al., 2009; Carrado et al., 2006). In the study of Selçuk Özgen (Özgen et al., 2009), after hydrocyclone separation the cation exchange capacity (CEC) increased by 138%, the free swelling volume (FSV) by 194% and apparent viscosity (AV) by 325% for bentonites which in their natural state are not suitable for industrial use. Chi-Nhan Ha Thuc applied three different methods (i.e. single centrifugation, sonication coupled with sedimentation, and sedimentation combined with centrifugation and sonication) for the purification of raw bentonites (Thuc et al., 2010). Even so, the above-mentioned purified bentonite could not reach high-purity level, and the yield of montmorillonite was not given. Furthermore, a large amount of chemicals used in the purification of bentonite are harmful to human health and not recommended for application in food, pharmaceuticals, etc. In this experiment, a simple physical purification method composed of grinding + dispersion + centrifugation was adopted. The features of this method are simple in process and only a small amount of dispersant is needed. The bentonite

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purified by this method is of high montmorillonite content and yield, and can be used as raw materials for daily necessities.

2. Materials and methods

2.1. Materials

The raw bentonite was collected from the mining site of Anji Gaoyu, Zhejiang province, China (supplied by Zhejiang Fenghong Industrial Group). Quantitative analyze for the mineral composition of the bentonite is montmorillonite (44%), quartz (33%), calcite (13%), dolomite (5%), and feldspar (5%). Quartz is the main impurity phase. The basal spacing of the montmorillonite is 15.19 Å, confirming the interlayer cation is Ca^{2+} associated with two layers of water (Bergaya et al., 2006). Its chemical composition was found to be as follows: 58.85% SiO_2, 17.16% Al_2O_3, 1.14% Fe_2O_3, 0.026% P_2O_5, 3.4% MgO, 5.44% CaO, 0.054% Na_2O, 1.055% K_2O, 0.126% TiO_2, 0.054% MnO and 12.7% loss of ignition. Sodium hexametaphosphate $(NaPO_3)_6$ (from AR, Beijing Chemical Works) was chosen to be the dispersant.

2.2. Purification of raw bentonite

The purification process includes grinding, dispersion and centrifugal separation. The raw bentonite was ground firstly for a certain time with an universal grinder. Then 3 g grounded bentonite was suspended in 36 g deionized water with about 0–0.06 g $(NaPO_3)_6$, respectively 0%, 0.5%, 1%, 1.5%, 2% of the bentonite mass, and stirred magnetically for 24 h. The supernatant of the dispersion was separated by centrifugation at a certain speed for 2 min. The purified bentonite was obtained after a centrifugation at 4500 r/min for 2 min, followed by drying the solid at 60 °C in an oven. Batch experiments were designed and conducted to find the optimal grinding time, dispersant amount and centrifugal speed.

2.3. Characterization techniques

The chemical composition of the raw and purified bentonite was determined by X-ray fluorescence (XRF). The analysis was performed on a Philips X-ray fluorescence spectrometer, model PW2400.

X-ray diffraction (XRD) was used for mineral phase analysis. XRD patterns were recorded on a Siemens D500 diffractometer equipped with a graphite monochromator, and Cu Kα radiation at 40 kV and 40 mA. For qualitative analysis, oriented samples of raw, grinded and purified bentonite were prepared by deposition of their dispersion on glass slides followed by air drying. The samples were scanned in the angular range of 3–70°2θ with a scan rate of 0.02°2θ/s. For mineral phase quantification, the XRD pattern was recorded under the same condition but in the angular range of 3–40°2θ and counting time of 10 s per step of 0.02°2θ. Packed powder samples and external standard method were used in phase quantification.

Particle size measurements and specific surface area were performed using BT-1500 Particle Size Analyzer. Bentonite powders were added into water in the presence of sodium hexametaphosphate $(NaPO_3)_6$ as dispersant and shaken and ultrasonicated for 24 h before the measurement.

The morphology of the mineral particles for increasing grinding time was observed using a scanning electron microscope (SEM, JSM-6701F, Hitachi Ltd., Japan). And the occurrence of montmorillonite and associated minerals were observed under a Hitachi H-8100 Transmission Electron Microscope (TEM). For TEM analysis, all samples were ultrasonically dispersed in absolute ethanol solution and a small drop of dispersion was placed on a Cu mesh grid which had been coated with carbon. Then, the grids were dried in an oven at 60 °C for 20 min to make sure drying was complete prior to insertion into the instrument.

The Zetasizer Nano ZS90 from Malvern was adopted to fulfill the test of zeta potential. Bentonite suspension was prepared respectively with 0%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3% of $(NaPO_3)_6$ as dispersant. The cell voltage for zeta potential measurement was 29.5 V/cm and temperature was 25 °C.

3. Result and discussion

3.1. Grinding time

As there are many millimeter, micron and nanometer scale particle aggregates in the raw bentonite, which affects the dispersion and purification of the bentonite, crushing and/or grinding processes are required in this study. Experiments were conducted to find the optimal grinding time. The particle size distribution of the purified sample was measured for each grinding time (Fig. 1a). The bentonite particle size is reduced bellow 1 μm with increasing the grinding time from 30 min to 75 min. The initial green-ore particle size distribute between 2 and 6 μm with a median diameter (MD) of 3.79 μm. After 30 min of grinding, particle size distribution left shift to 1–3 μm and MD decreases to 2.57 μm. After 45 min of grinding the particle size decreases slightly, MD is 2.06 μm and quite unchanged compared to 30 min but more particles are smaller than 1 μm in size. When the grinding time is prolonged to 60 min, all the particles have small sizes and MD is remarkably reduced to 0.47 μm. After 75 min grinding MD reduces to 0.28 μm and most of the particles are smaller than 0.5 μm in size. This is decisive for montmorillonite liberation and in good agreement with literature where the particle size of montmorillonite is usually between 0.1 μm and 2 μm with an average diameter of ~0.5 μm (Lagaly and Ziesmer, 2003). Coarse grained minerals in the raw bentonite should be impurities and clay aggregates (Yoon and El Mohtar, 2013).

Concerning the aspect, their contour lines of the particles are of irregular shape, the edges are frayed and turn up and layers or thin flakes of a few layers extrude the packets and enclose cuneate pores. The particles are never true isolated crystals but are more like granular assemblages of silicate layers. They can be compact but, mostly, they look like paper sheets torn into smaller pieces (Lagaly and Ziesmer, 2003). The SEM images showed how the bentonite particles transformed from heterogranular agglomerated to homogenous isometrical dispersed state after grinding and grain size reduction (Fig. 1a).

XRD patterns of the purified bentonites obtained for different grinding time and fixed 1% dispersant dosage have been measured (Fig. 1b). Peaks intensity increased for montmorillonite and decreased for quartz with grinding time increasing from 0 to 60 min, then peaks intensity increased for montmorillonite and increased for quartz with further grinding time increasing to 75 min. This can also be indicated from the graphic summary representing the peaks intensity ratio of montmorillonite relative to that of montmorillonite + quartz versus grinding time (Fig. 1c). The relative XRD intensity for 30 min and 75 min appeared to be similar but the particle size were quite different. This is closely related to flottability differences during the dispersion in water. The hardness of montmorillonite (1–2) is smaller than that of quartz (7), montmorillonite is easier to be broken into fine particles than quartz in the process of grinding. When the bentonite was ground for 30 min montmorillonite and quartz were not well dispersed, because most of the quartz grains still wrapped in between the layers of the montmorillonite flakes and remained as mixed aggregates after the centrifugation. When the bentonite was ground for 75 min montmorillonite and quartz were well dispersed but the particles of quartz become finer. The specific gravity and dispersion property of finer quartz in water approaches that of montmorillonite, so the centrifugation could not separate them and they could only stay together in the upper dispersion. The curves of montmorillonite content and yields (obtained by XRD quantitative analysis) versus grinding time indicated that the yield of montmorillonite increased with increasing the grinding time and the content of montmorillonite in the purified sample reached a maximum of 96.5% at the grinding time of 60 min (Fig. 1d). Particle size distribution plays an important role in determining the efficiency