A simple method for physical purification of bentonite

Zhijin Gong,a,b Libing Liaoa,b, Guocheng Lv ab,c*, Xiaoyu Wanga,b

School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
B Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

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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 and adsorption ability and chemical 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.

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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 (Boylan 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 (Thorwuwa 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 Neele, 2004), as well as chemical treatment (Bulut et al., 2009, Carrado et al., 2006). In the study of Selcuk Ozgen (Ozgen 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
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$_2$O$_3$, 1.14% Fe$_2$O$_3$, 0.026% P$_2$O$_5$, 3.4% MgO, 5.44% CaO, 0.054% Na$_2$O, 1.055% K$_2$O, 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%, 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.

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, ground 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 homogeneous 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 floatability 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
of beneficiation (Sobhy and Tao, 2014). To sum up, appropriate grinding contributes to particle size decrease and efficient mineral dissociation. When grinding is insufficient, the particle size of montmorillonite and associated minerals are not small enough to liberate them from mixed aggregates and they cannot be well separated. Excessive grinding decreases the particle size of all components resulting in ultrafine particles suspension with only small dispersion difference between montmorillonite and associated minerals, which is not conducive to the efficient separation of montmorillonite from the associated minerals either. So the raw bentonite should be ground appropriately to reduce the particle to appropriate size. In this study 60 min is the optimal grinding time.

3.2. Dispersant dosage

When bentonites were dispersed in water, montmorillonite separated into small particles, while the accompanying gangue minerals were accumulated in coarser part. Thus, the difference in dispersion behavior of different minerals of bentonite in water can be utilized for their selective separation, and directly affects the efficiency of purification (Boylu et al., 2010).

Addition of dispersant in bentonite suspension will change the dispersion behavior of minerals. In order to study the effect of dispersant on the purification of bentonite, a batch of purification experiments were conducted with increasing dispersant dosage, respectively 0%, 0.5%, 1%, 1.5%, 2% of (NaPO₃)₆.

With increase of dispersant dosage, XRD peaks intensity increased for montmorillonite and decreased for quartz (peaks for other minerals were very weak), and reached the maximum and minimum respectively when dispersant dosage was 1% (Fig. 2a, b, c, d). A reverse trend was observed when dispersant dosage increased further (Fig. 2e). The montmorillonite content of the purified bentonite calculated from XRD data showed the same variation as illustrated with the graphic summary.
Fig. 2. XRD patterns of purified bentonites obtained for different dispersant dosage and increasing grinding time: 30 min (a), 45 min (b), 60 min (c), and 75 min (d), at fixed centrifugal speed of 700 r/min. A graphic summary of $(M/M + Q)$ XRD intensity ratio as a function of dispersant dosage (e). (f) Montmorillonite content and yield obtained from the bentonite treated with different grinding time for increasing dispersant dosage.
When grinding time was 60 min and dispersant dosage was 1%, the montmorillonite content of the purified bentonite reached the maximum of 96.5%. The montmorillonite yield of the purified bentonite increased with increasing the grinding time and dispersant dosage, and reached 71% when grinding time was 60 min and dispersant dosage was 1%. Both insufficient and excess grinding and dispersant dosage hinder the purification of bentonite.

### 3.3 Centrifugal speed

Based on the optimal grinding time and dispersant dosage, experiments were conducted to find the optimal centrifugal speed. The XRD patterns of the resulting samples were measured at the fixed centrifugal time of 2 min and varied centrifugal speed (Fig. 3a). The peaks intensity increased for montmorillonite and decreased for quartz with increasing the centrifugal speed (peaks for other minerals were very weak), i.e. the montmorillonite content of the purified bentonite increased with increasing the centrifugal speed. However the yield of montmorillonite (Fig. 2f). When grinding time was 60 min and dispersant dosage was 1%, the montmorillonite content of the purified bentonite reached the maximum of 96.5%. The montmorillonite yield of the purified bentonite increased with increasing the grinding time and dispersant dosage, and reached 71% when grinding time was 60 min and dispersant dosage was 1%. Both insufficient and excess grinding and dispersant dosage hinder the purification of bentonite.

![Fig. 3. XRD patterns of purified bentonites prepared with fixed 60 min grinding time and 1% dispersant dosage for different centrifugal speed (a). A graphic summary of (M/M + Q) XRD intensity ratio as a function of centrifugal speed (b). Purified montmorillonite content and yield versus centrifugal speed (c).](image)

![Fig. 4. XRD patterns of raw and purified bentonite (a) and TEM images of raw, grinded and purified bentonite (b). The white arrow points to the quartz, and the black arrow points to montmorillonite.](image)
decreased with increasing the centrifugal speed, especially when the centrifugal speed was higher than 700 r/min (Fig. 3c). So 700 r/min is the optimal centrifugal speed when the duration is 2 min.

3.4. Characterization of purified bentonite

3.4.1. Chemical composition and XRD analysis

Chemical composition of the bentonite after purification changed to: 52.66% SiO$_2$, 19.27% Al$_2$O$_3$, 1.32% Fe$_2$O$_3$, 0.41% P$_2$O$_5$, 3.52% MgO, 2.44% CaO, 0.43% Na$_2$O, 0.047% K$_2$O, 0.089% TiO$_2$, 0.018% MnO and 19.4% loss of ignition. Compared with that of the raw bentonite, SiO$_2$ decreased 10.5% and Al$_2$O$_3$ increased 12.3%. Apparently, most part of silicon impurities has been removed.

In the XRD pattern, characteristic peaks of feldspar, dolomite and calcite disappear for purified bentonite which means feldspar, dolomite and calcite have been removed (Fig. 4a). The diffraction peaks intensity decreases for quartz and increases significantly for montmorillonite compared with that of the raw bentonite. The montmorillonite content obtained from the bentonite was increased from 44% to 96.5% with montmorillonite yield over 70%. The nature of montmorillonite has not changed (basal spacing of montmorillonite remains 1.578 nm).

3.4.2. Transmission electron microscopy analysis

The morphology of montmorillonite in the TEM is as thin lamellae; quartz is as fine grains of a few nanometers in diameter (The arrow points to the quartz, and the black arrow to montmorillonite.). The particle agglomeration in raw bentonite is very obvious. Montmorillonite and other associated minerals are aggregated together in large clusters of a few microns. After grinding, the aggregation and superposition phenomenon decreased, and most of the particles appeared isolated and turned into a few hundred nanometers. But there are still a lot of impurities. After purification compared with the raw and grinded bentonite, the content of quartz is significantly reduced, only a few residual granular quartz sticking to the montmorillonite surface is observed (Fig. 4b). Also agglomeration is reduced, and montmorillonite become well dispersed.

3.5. Discussion

The method adopted in this study combines grinding, dispersion and centrifugal separation.

As discussed in Section 3.1, grinding is crucial to bentonite purification. Appropriate grinding contributes to mineral dissociation and is in favor of mineral dispersion and separation.

In the stage of dispersion, appropriate dispersion of minerals is the most important. To investigate the effect of dispersant on the dispersion of minerals, bentonite suspensions were prepared respectively with 0%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3% of (NaPO$_3$)$_6$ as dispersant and the zeta potential of each sample was tested (Fig. 5a). The zeta potentials of bentonite showed negative values which was consistent with previous observations (Cottet et al., 2014). With increasing the amount of dispersant, zeta potential of samples decreased. When the dispersant dosage was more than 1.5%, the absolute value of the zeta potential tended to be fixed at around 17–18 mV which indicated the dispersion system stabilized. Research has pointed out only when the absolute value of particle’s potential is larger than 15–20 mV can the barrier form

![Fig. 5. Zeta potential (a) and specific surface area (b) of particles with increasing dosage of (NaPO₃)₆ dispersant. Schematic diagram of the dispersion process of montmorillonite and quartz in calcium bentonite(c). The 2 series in (a) are repeated-measures for the same set of experimental data.](image-url)
between particles, and the repulsive force present between particles is in favor of mineral’s dispersion (Li, 1994). So a certain amount of dispersant is necessary to achieve a stable and well dispersed dispersion. The exponential growth of the specific surface area of the suspended particles with increasing dosage of (NaPO₃)₆ also indicated the well dispersion of minerals in the suspension (Fig. 5b). This is because of the breaking down of more and more particle agglomerations with the addition of more (NaPO₃)₆. However excess dispersant hinders the separation of different minerals species because their dispersion differences become smaller.

On the other hand, when dispersant is added in appropriate amount, all particles in dispersion are negatively charged, the face to face FF contact of montmorillonite and the agglomeration of particles caused by electrostatic attraction disappear (Rabaïoli et al., 1993). Compared with face to face contact, edge to surface EF contact is weak (Stein and Fitch, 1996). Under the external mechanical force (ultrasonic vibration and magnetic stirring), the dispersion structure is modified, granular mineral like quartz loses support and then separated from montmorillonite, which is schematically shown in Fig. 5c.

4. Conclusions

A bentonite with 44% montmorillonite from Anji Gaoyu, Zhejiang province, China, was purified adopting a simple method composed of grinding of raw bentonite, dispersion of ground bentonite in water with addition of some dispersant and centrifugal separation. Purified bentonite with montmorillonite content of 96.5% and montmorillonite yield of 71% was obtained under optimized process conditions of grinding time = 60 min, dispersant = 1 wt.% (NaPO₃)₆, centrifugal speed = 700 r/min, centrifugal time = 2 min. The particle size of montmorillonite is usually between 0.1 μm and 2 μm with an average diameter of ~0.5 μm. However the montmorillonite and accompanying mineral usually agglomerate with each other. Coarse grained minerals in the raw bentonite observed from the TEM images should be impurities and clay aggregates. Appropriate grinding of raw bentonite and addition of dispersant in the dispersion can promote the dissociation and dispersion of minerals in bentonite and enlarge their dispersion differences, which is very important for their centrifugal separation. When grinding and dispersant is insufficient, montmorillonite and associated minerals are not well separated. Excessive grinding and dispersant will decrease the particle size and dispersion difference between montmorillonite and associated minerals, which is not conducive to the efficient separation of montmorillonite from the associated minerals either. Both insufficient and excess grinding and dispersant dosage hinder the purification of bentonite. The addition of dispersant make all particles in dispersion negatively charged, the face to face FF contact of montmorillonite and the agglomeration of particles caused by electrostatic attraction is transformed into the edge to face EF contact. Under the effect of magnetic stirring, the edge to face EF combination is easy to collapse. Under the condition of optimal grinding time and dispersant dosage, bentonite with different montmorillonite content and yield can be obtained by adjusting the centrifugal speed. For a fixed centrifugal time, higher montmorillonite content can be obtained by a higher centrifugal speed, and the yield will be lower. If an increased yield is demanded, reduce the centrifugal speed and the corresponding montmorillonite content will be decreased. The purification technique adopted in this study is simple in process and has very good feasibility. Changing process parameters, this method may be used for the purification of other bentonite.

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