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Research paper

# Removal of fine quartz from coal-series kaolin by flotation

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ABSTRACT

Coal-series kaolin (CSK) in Xuzhou, Jiangsu Province of Eastern China was characterized by chemical analyses, X-ray diffraction (XRD) and zeta potential measurement as well as by scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS). The authigenic ultrafine quartz grains ($d_{90}$ = 15.8 μm) closely associated with this CSK sample was the major impurity mineral, which cannot be separated from kaolin by screening and size classification process. This work investigated the separation of fine quartz from kaolin by flotation. Single mineral flotation tests indicated that effective separation of quartz from kaolin was possible with acidic pH value (pH = 3), depressant of starch and collector of dodecyl amine (DDA). Rougher flotation tests of coal-series kaolin revealed that the $SiO_2/Al_2O_3$ weight ratio of the concentrate was qualified for industrial applications in the presence of 160 g/t starch and 100 g/t DDA, at acidic pH pulp. A specially designed two-stage cleaner flotation flowsheet increased the concentrate recovery from 37.26% to 46.55% compared to a rougher flotation process.

## 1. Introduction

Kaolin, also known as china clay, is a relatively pure clay predominantly consisting of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) having a $SiO_2/Al_2O_3$ weight ratio of 1.18, which is important in geology, agriculture, construction, engineering, process industries, and environmental applications (Jones et al., 1992; Murray, 2000). Kaolin finds application in a variety of industries like paper, ceramics, rubber, plastics, cement, ink, catalyst, fiber glass (Mohammadi and Pak, 2003; Murray, 1963). Kaolin can also be used in the environment as a natural scavenger of pollutants by removing pollutants either through ion exchange or adsorption, which makes it a very promising low cost adsorbent for water treatment (Rafatullah et al., 2010).

Kaolin extracted from commercial deposits contains kaolinite as a major component along with organic material and other minerals, such as quartz, muscovite, limonite, anatase, hematite, and illite (Saikia et al., 2003). These ancillary minerals are deleterious since they adversely affect the properties and make kaolin unsuitable for many applications. Hence, their removal is of prime importance in order to achieve the optimum utilization of kaolin. The methods of beneficiation depend upon the quantity and nature of the impurity minerals associated with the clay. Common techniques involve: (I) size classification for removing coarse minerals and for attaining the specific particle size distribution, (II) magnetic separation of the colored minerals containing iron for improving the brightness, (III) chemical bleaching for removing organic coloring impurities (oxidative) and iron minerals (reductive), and sometimes, (IV) froth flotation to separate micaceous, graphitic and titanoferrous minerals (Jepson, 1988; Liu et al., 2017; Newns and Pascoe, 2002; Raghavan et al., 2004).

Coal-series kaolin (CSK) deposits, found in coal seams of coal mines, are mainly concentrated in northwest China with large reserves found in Shanxi, Sanxi, Inner Mongolia, Xinjiang, Jiangsu and Henan Provinces (Wilson, 2004). Kaolin minerals ($SiO_2/Al_2O_3$ weight ratio < 1.29) are used for coating in the paper industry; and the presence of quartz is undesirable due to the abrasion it causes to the machinery (Ye and Matsuoka, 1993d). Coarser impurities (generally quartz) are easily separated by screening or classification while micron-sized impurities require special treatments (Ediz et al., 2015; Mukai et al., 1974). The authigenic ultrafine quartz grains (around 10 μm) are found in Late Permian coal from Xuanwei, east Yunnan Province, Southwest China (Zhao et al., 2016) and the Early Cretaceous Wulantuga coal, Inner Mongolia, North China (Dai et al., 2012). For this reason, CSK is discarded as a waste in some areas, and its accumulation is creating new environmental problems.

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Froth flotation is well known as the most common process in mineral separation to recover valuable minerals from gangue when dealing with fine particles (Marion et al., 2015; Yang et al., 2010). Flotation is strongly dependent on the degree of adsorption of collectors onto the surface of the mineral. To determine whether the adsorption of the collector is due to the electrostatic force or chemisorption, the characteristics of the surface charge of the minerals is required (Moudgil et al., 1987). The reason why it is difficult to separate quartz from kaolin by flotation is that quartz has a similar surface charge to kaolin (Kosmulski, 2009).

The flotation method for separating fine quartz from dickite (one of the kaolin minerals) was developed by Mukai et al. (1974). They found that dickite could float selectively from quartz by using dodecylammonium acetate (DAA) as a collector in an acidic pH range. The reason for the selectivity was thought to due to the hydrogen ions entering into the interlayer of dickite instead of the $DA^+$; and that the $DA^+$ was adsorbed on the dickite surface that was more negatively charged than that of the quartz. Yoshikawa et al. (1989) separated dickite from quartz finer than 2 μm using a pressure type and a Denver type flotation cell. They activated dickite with calcium chloride, and used sodium oleate as a collector. Dickite has also been selectively floated from quartz at pH of 7 when the mixture of dickite and quartz (coarser than 5 μm) was preconditioned in diluted HCl solution (Ye and Matsuoka, 1993a). In the presence of inorganic electrolyte such as $CaCl_2$ or KCl, the decomposition of dickite during diluted HCl preconditioning is promoted through an ion exchange reaction at short times. Good separation of dickite and quartz can be made for particles coarser than 2 μm, while separation is still unsatisfactory for particles finer than 2 μm (Ye and Matsuoka, 1993b). In order to improve the separation of dickite from quartz finer than 2 μm, selective flocculation with the polymeric flocculant, Separan AP30, was introduced to the flotation process which includes preconditioning in diluted HCl solution containing $CaCl_2$ (Ye and Matsuoka, 1993c). In addition, it was found that dickite was selectively flocculated and depressed by corn starch and satisfactory separation between quartz and dickite was obtained (Ye and Matsuoka, 1993d).

In this study, the mineralogical composition of coal-series kaolin from Xuzhou, Jiangsu Province of Eastern China was studied using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersion spectrometer (EDS) and chemical analyses. The flotation performance was investigated for pure mineral samples with conventional depressants (hydrofluoric acid, sodium silicate and starch). In order to meet the requirements for high quality of $SiO_2/Al_2O_3$ weight ratio, flotation experiments were also performed to effectively separate quartz from dry rod mill output coal-series kaolin. The results from the study highlight the potential benefits of applying flotation technology to increase the utilization of coal-series kaolin deposits. In addition, zeta potential measurements were employed to explain the mechanism of the effect of reagents on minerals.

## 2. Experimental

### 2.1. Materials

Pure kaolin (< 10 μm) used in single flotation tests was obtained from a kaolin mine of Suzhou, Jiangsu province, PR China. Pure quartz, having a $SiO_2$ grade higher than 99.8%, was purchased from Suqian (Jiangsu province, PR China). In order to obtain a fine size fraction of quartz the sample was passed through a hydrocyclone with a cut size of 10 μm. The hydrocyclone overflow was used directly for single mineral flotation experiments.

The coal-series kaolin (CSK) sample, was supplied by Jiahe mine in Xuzhou (Jiangsu province, PR China). For chemical analysis and X-ray diffraction (XRD, Bruker D8 Advance, Germany) measurements, the CSK sample was ground and milled to pass through a 320 mesh screen. Polished thin-sections and block samples were prepared for scanning electron microscopic (SEM, FEI Quanta 250, US), coupled with an EDAX energy dispersive X-ray spectrometer (EDS, JEOL Ltd., Japan), observations. Following analysis, the CSK sample was crushed and ground to a size fraction with 90% of the material being < 10 μm. The material was then used for the flotation experiments.

**Table 1**
Flotation reagents (analytical quality) used in this study.

| Reagent name | Molecular formula | Reagent type | Manufacturer |
|---|---|---|---|
| DDA | $C_{12}H_{25}NH_2$ | Collector | Sinopharm Group |
| Hydrofluoric acid | HF | Depressant | Zhongtai chemical |
| Sodium silicate | $Na_2SiO_3$ | Depressant | Sinopharm Group |
| Starch | $(C_6H_{10}O_5)_n$ | Depressant | Sinopharm Group |
| Hydrochloric acid | HCI | pH modifier | Aladdin Bio-Chem. Tech. |
| Sodium hydroxide | NaOH | pH modifier | Aladdin Bio-Chem. Tech. |

Flotation reagents used in this study are shown in Table 1. DDA can adsorb at the air/aqueous solution interface and obtain fine size bubbles, which has been employed in kaolin flotation (Hu and Liu, 2003; Hu et al., 2005; Ma et al., 2009) and the reverse flotation of quartz for the concentration of iron ores (Corona-Arroyo et al., 2015). In this study, a stable froth can be obtained in the presence of DDA, therefore the function of conventional frother reagent was replaced with DDA.

### 2.2. Chemical analysis, XRD, SEM-EDS and zeta potential measurement

The CSK sample was initially characterized in terms of the mineralogical composition by chemical analysis and X-ray diffraction (XRD). Chemical element analysis of the CSK was tested using chemical titration method based on the Chinese standard GB/T 14563, 2008 (Liu et al., 2017; Zhu et al., 2014). X-ray fluorescence spectrometry (XRF) was used to validate the chemical element results determined by this chemical titration method. The difference of the oxides of mayor elements between XRF and chemical titration techniques was ignorable. XRD patterns were collected using a D/MAX-2500 pc powder diffractometer equipped with Cu-Kα (λ = 1.54 Å) radiation which was generated at 40 kV and 40 mA in China University of Mining and Technology. The samples for XRD analysis were measured from 5 to 80° (2θ) with a step size of 0.02° (2θ) and a counting time of 0.2 s per step.

Morphology of minerals in the CSK sample were investigated using and electron microscope equipped with an energy dispersive spectrometer (SEM-EDS) in China University of Mining and Technology. The selected polished thin-sections and sample blocks were coated before SEM observation. The SEM was operated with a beam voltage of 20.0 kV, working distance ~10 mm, and a spot-size of 5.5, while for the Hitachi-S3400 X/I the accelerating voltage was 20 kV and the beam current was 40–60 mA during SEM operation. The energy dispersive spectroscopy (EDS) was taken at a vacuum of $10^{-4}$ Pa using an accelerated voltage of 20 kV to investigate the arrangement of the present phases.

The zeta potential measurement was carried out by standard procedures on a Brookhaven Zeta Plus Zeta potential meter. The sample having 0.02% solid concentration was added into a 100 mL beaker. The suspension was agitated for 2 min and transferred to the testing vessel, after which the zeta potential measurement was made. The suspension pH was modified with the addition of HCI and NaOH and measured by REX Model PHS- 3C pH meter.

### 2.3. Single mineral flotation

Flotation tests were undertaken on both pure kaolin and quartz. All flotation tests were conducted in a 1.5 L mechanical laboratory flota-