

# Impact of interfacial Al- and Si-active sites on the electrokinetic properties, surfactant adsorption and floatability of diaspore and kaolinite minerals



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## ABSTRACT

The active sites of mineral surfaces play an important role in many industrial processes, such as mineral flotation and dewatering. This paper was aimed to investigate the effect of Al- and Si-active sites on the mineral crystal faces exposed to water on the electrokinetic properties, surfactant adsorption, and floatability of diaspore and kaolinite, which are, respectively, the valuable and gangue minerals in the processing of diasporic bauxite ores. Specifically, the acid treatment was used to change the physicochemical properties of diaspore and kaolinite minerals for their selective flotation. Microelectrophoresis method was used to determine the zeta (surface) potential of diaspore and kaolinite particles before and after the acid treatment as a function of pH. The change in the surface potential was analyzed applying the theory on the electrical double layers at the solid-solution interface. The proton donor–acceptor reactions occurring simultaneously on amphoteric alumina or/and silica sites of diaspore and kaolinite were considered. The mass balances were applied to link the surface active sites with the minerals charge and potential. Comparing the modeling with the experimental data revealed the significant decrease in the Al-active sites and increase in the Si-active sites by the acid treatment. Single mineral flotation and surfactant adsorption tests of diaspore and kaolinite before and after the acid treatment were carried out using sodium hexametaphosphate (HMP) and dodecylamine hydrochloride (DAH) as a depressant and a collector, respectively. After the acid treatment, the adsorption density of depressant on both diaspore and kaolinite decreased due to the reduced density of Al-active sites on the minerals surfaces. The changes of collector adsorption capacity and floatability of diaspore were very small while those of kaolinite were significantly increased. These changes were caused by decreasing the density of Al-active sites (covered by HMP and thereby preventing DAH adsorption) on both diaspore and kaolinite and increasing the density of Si-active sites of kaolinite (not covered by HMP and thereby facilitating DAH adsorption). The results clearly indicated that the acid treatment was shown to be conducive to changing the active Al- and Si-sites on diaspore and kaolinite and thereby improving their flotation separation.

## 1. Introduction

Interfacial properties of minerals display a governing influence on a wide range of interfacial processes such as adsorption, catalysis, and flotation (Leja, 1982). Change of interfacial active sites on minerals can affect the physical and chemical characteristics of solid/water interface. In many cases, it is particularly important in flotation separation, where adsorbed hydrophobic species to the interfacial active sites can effectively enhance the attachment efficiency of solid particles onto air bubbles. Consequently, a better understanding of the effect of the interfacial active sites on the solid surface properties of solid particles is critical to optimizing the conditions for the more cost-effective flotation separation technology (Hu et al., 2003). Here we investigate the effect

of changing Al- and Si-active sites available on the crystal faces of diaspore [ $\alpha$ -AlO(OH)] and kaolinite [ $Al_2Si_2O_5(OH)_4$ ] on their electrokinetic properties, surfactant adsorption, and floatability. Diaspore and kaolinite minerals are very important because diaspore is the valuable mineral while kaolinite is one of the main gangue minerals in the processing of diasporic bauxite ores which is the main raw material of alumina industry. The upgrading process of these bauxite ores focuses on the separation of diaspore from kaolinite by flotation (Zhang et al., 2017).

Diaspore consists of hexagonal close-packed oxygen sheets with aluminum atoms filling two-thirds of the octahedral interstice sites (Hill, 1979), while kaolinite is a two-layer-structured aluminosilicate which has anisotropic properties. As shown in Fig. 1, kaolinite consists

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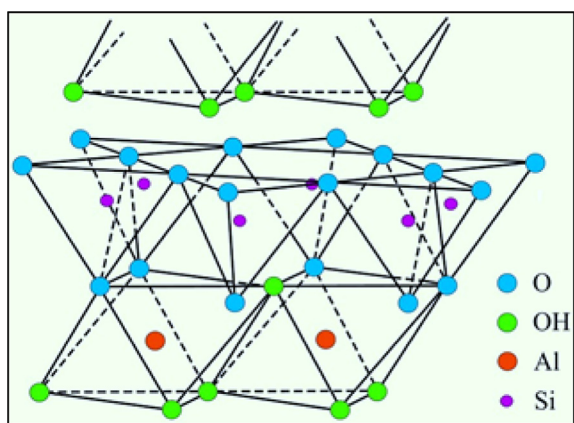


Fig. 1. A schematic diagram of the crystal structure of kaolinite.

of alternating layers (basal surfaces) of tetrahedral siloxane and octahedral aluminum oxy-hydroxides as well as edge surface (Chassagne et al., 2009). When subjected to grinding, the ionic/covalent Al–O bonds of diasporite are destroyed, and resulting in a surface of unsaturated or ionic nature. For kaolinite, the tetrahedral silica sheets and octahedral alumina sheets on the edges are destroyed, and resulting in a surface of broken Si–O and Al–O bonds. The presence of these broken bonds acts as the surface Al-active sites or/and surface Si-active sites, affecting the change in physicochemical properties of the resultant surfaces and their interactions with flotation reagents, which in turn determines flotation separation performance (Hu et al., 2003).

Acid treatment has been reported to be an effective method for the dealumination of kaolinite (Panda et al., 2010) and other minerals such as zeolite (Huang et al., 2016). In addition, the acid treatment can alter the active site density of Al and Si on the surface of clinoptilolite has also been reported (Wang and Nguyen, 2016). Considering that diasporite and kaolinite are also aluminosilicate minerals as well as clinoptilolite-type minerals, we propose a hypothesis that acid treatment also can change the surface active site density of Al or/and Si on the surface of diasporite and kaolinite. If the hypothesis is correct, the physicochemical properties of the surface of diasporite and kaolinite after acid modification can be changed, so that the interaction between them and the flotation reagents can also be changed, resulting in a better separation of the minerals by flotation. However, no related research has been reported, which makes the rationality of the hypothesis undocumented and the related influence unknown.

Under the existing technical means, the direct characterization of the number of broken bonds and active site density of the mineral surface has great difficulties. Fortunately, the change of the active site density can change the electrokinetic properties of the minerals which

can be quantified by measuring the surface potential and analyzing the changes by applying the theory on the electrical double layers (Wang and Nguyen, 2016). In this paper, the effect of acid treatment on the change of the number of Al- or/and Si-active sites on the surface of diasporite and kaolinite was investigated by examining the changes in electrokinetic properties and, thereby, examine the effect of the interfacial active sites on other properties such as the floatability and surfactant adsorption of two minerals. Firstly, the zeta potential of diasporite and kaolinite before and after the acid treatment was examined, and then a simplified Gouy-Chapman-Stern (GCS) model was developed and the change of the surface active site density of Al or/and Si on the mineral surface before and after the acid treatment was determined by using the established model. Finally, the single mineral flotation and surfactant adsorption experiments were carried out, and the change in these properties was explained by the change in the Al- and Si-active sites.

## 2. Materials and methods

### 2.1. Materials

The diasporite and kaolinite samples used in this study were gathered from Gongyi in Henan Province and Suzhou in Jiangsu Province of China, respectively. The mineral lumps were crushed, ground in a porcelain mill, and then sieved to obtain  $-54 + 20 \mu\text{m}$  size fraction for the experiments. The use of the narrow-grained fraction as an experimental sample was designed to reduce the particle size effects on subsequent experiments, especially on flotation experiments (Zhang et al., 2017). The narrower the particle size range, the smaller the flotation difference caused by the difference in the particle size distribution.

The main mineralogical phases and chemical composition of the samples were examined by X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis. The results presented in Fig. 2 and Table 1 showed that the main impurities in diasporite and kaolinite samples were anatase and quartz, respectively. The purities of the minerals were both higher than 90% as the mass contents of  $\text{Al}_2\text{O}_3$  in diasporite and kaolinite samples are 79.53% and 39.05%, respectively.

Analytical grade  $\text{H}_2\text{SO}_4$  (Sigma-Aldrich, Australia) was used for the acid treatment of the diasporite and kaolinite samples. Analytical purity of HCl and NaOH (Sigma-Aldrich, Australia) were used to adjust pH for the zeta potential measurements, surfactant adsorption, and flotation experiments. Analytical grade NaCl (Sigma-Aldrich, Australia) was used as the background electrolyte solution for the zeta potential measurements. Analytical purity of sodium hexametaphosphate (HMP) (Sigma-Aldrich, Australia) was used as a depressant and dodecylamine hydrochloride (DAH) (Sigma-Aldrich, Australia) with a purity of 99.9% was used as a collector. Azure B and Eosin Y of analytical grade (Sinopharm

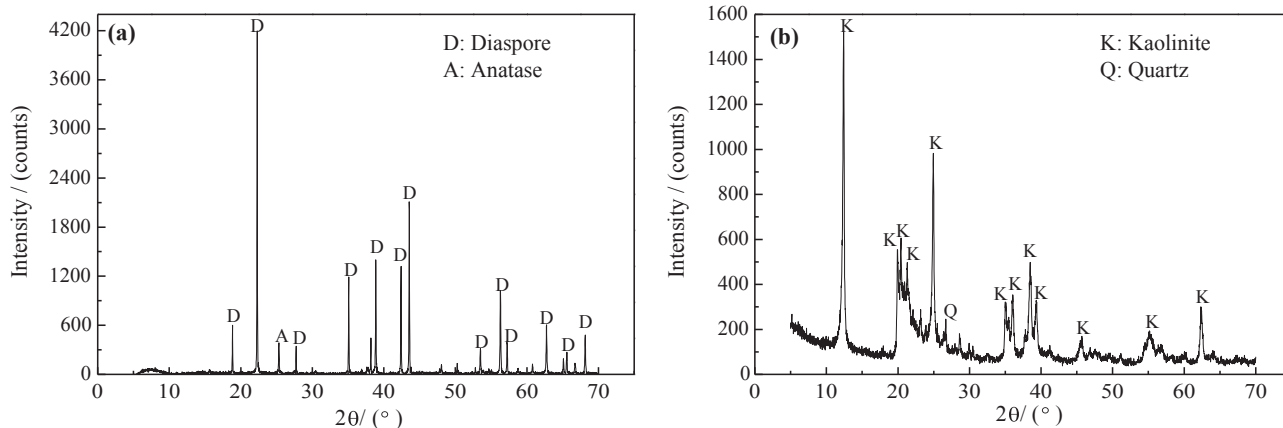


Fig. 2. XRD patterns of the diasporite (a) and kaolinite (b) samples.

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