



Significance of particle aggregation in the reverse flotation of kaolinite from bauxite ore



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ARTICLE INFO

Article history:

Received 13 February 2015

Revised 6 April 2015

Accepted 7 April 2015

Available online 16 May 2015

Keywords:

Model surfaces

Pyrophyllite

Gibbsite

Dodecylamine

Contact angle

ABSTRACT

Significant interest has been demonstrated for the removal of kaolinite from bauxite ore by flotation. The reverse flotation of kaolinite from bauxite ore at low pH with dodecylamine hydrochloride collector has been reported. However, resolving the mechanism of the reverse flotation process is largely limited by the misunderstanding of the anisotropic surface properties of kaolinite particles. Based on recent fundamental study of the surface properties of kaolinite particles and their interaction, the significance of particle aggregation in the reverse flotation of kaolinite from bauxite ore has been revealed. The wetting characteristics of the basal plane surfaces of kaolinite with dodecylamine hydrochloride collector have been estimated by contact angle measurements at model surfaces. The improved hydrophobicity of the kaolinite nano-particles is not enough to account for the significant increase in the flotation recovery at low pH when compared to the flotation performance at high pH. Instead, particle aggregation is expected to be the major factor which contributes to the improved flotation response at low pH. Both simulation results and X-ray CT results have demonstrated aggregation and formation of kaolinite clusters at low pH. It appears that these kaolinite clusters have sufficient mass and hydrophobicity to account for the successful reverse flotation of kaolinite from bauxite ore at low pH.

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1. Introduction

Froth flotation has been considered as one of the most widely applied and efficient particle separation processes for the recovery of mineral resources. Kaolinite exists as a common gangue mineral in many valuable ore deposits, including bauxite, potash ore, iron ore, sulfide ores, oil sands, phosphate and rare earth ores. In some cases it is desired to depress kaolinite during flotation while in other cases the kaolinite is removed by reverse flotation. Of particular interest is the development of flotation for the removal of kaolinite from low grade bauxite ores. An important result of recent bauxite flotation research was the opening in 2002 of the first bauxite mineral processing plant in China (and in the world) which uses direct flotation to prepare a bauxite concentrate for the Bayer process (Zhao et al., 2010). One million tons/yr of bauxite ore can be treated at this plant. Now more than 80% of the two billion tons of low grade diasporic bauxite in China can be used instead of being discarded, extending the usable amount of bauxite resources for the China aluminum industry from only about 10 years to more than 50 years. Another significant bauxite reserve

(~10%) is located in Brazil (Bray, 2014). Although extensive research has been done to study the flotation of Brazilian bauxite, the flotation practice is still new and not yet practiced in the Brazilian bauxite industry (Bittencourt et al., 1990; Massola et al., 2007). To understand and develop future industrial practices for bauxite flotation, the surface/colloid chemistry associated with the reverse flotation of kaolinite needs to be considered.

In spite of the difficulty in the development of technology for the flotation of fine particles, such as kaolinite, some success has been achieved. Both direct flotation and reverse flotation processes have been developed for bauxite flotation (Marino, 2012). For direct flotation of low grade bauxite ore, gibbsite or diasporite can be floated with hydroxamate collector at high pH (pH 9–10), in the meantime, the silicate minerals (such as kaolinite) are depressed by sodium silicate and iron oxide minerals are depressed by starch. On the other hand, in the case of the reverse flotation process for low grade bauxite ore, the silicate minerals (such as kaolinite) are floated with amine and the bauxite minerals, gibbsite and/or diasporite, are depressed with starch at low pH (pH 4–5). Recent studies have suggested that reverse flotation is economically favored over the direct flotation process (Xu et al., 2004; Zhao et al., 2010), due to the fact that (1) clays (kaolinite) are more readily liberated than gibbsite/diasporite at a coarse size, thus significant energy for the grinding process is expected to be

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saved in reverse flotation and (2) hydroxamate collectors used for direct flotation are much more expensive than the amine collector used for reverse flotation. In addition, the hydroxamate collector consumption in direct flotation is greater due to the greater amount of gibbsite/diaspore in the bauxite ore when compared to the clay minerals.

Extensive research has been conducted to improve the flotation of kaolinite from bauxite, including the development of new collectors, adjustment of pH and ionic strength, and design of the flocculation–flotation process (Bittencourt et al., 1990; Hu et al., 2004, 2005; Zhong et al., 2008; Ma et al., 2009; Marino, 2012). Yuehua Hu has led his team and made significant contribution to the study of the reverse flotation of low grade bauxite, efforts which include the development of new collectors as well as fundamental studies on the reverse flotation of kaolinite (Hu et al., 2001, 2003a,b, 2004, 2005; Zhong et al., 2008; Liu et al., 2009). Recently, many researchers have been dedicated to developing new cationic collectors which can improve the flotation behavior of kaolinite from bauxite, and a large variety of the collector types have been investigated, such as the primary amine (dodecylamine), tertiary amines (N,N-diethyl-dodecyl amine (DEN), N,N-dimethyl-dodecyl amine (DPN), and N,N-dibenzyl-bodecyl amine (DBN)), quaternary amines (cetyl trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium chloride (DTAC), cetyl trimethyl ammonium chloride (CTAC)), n-(2-aminoethyl)-dodecanamide, n-(3-amino-propyl)-dodecanamide, and N,N-dipropyl-dodecyl amine (PN) (Hu et al., 2003a,b; Zhao et al., 2003a,b Liu et al., 2009, 2011; Xia et al., 2009; Jiang et al., 2011). Primary amines are some of the most common collectors used in reverse flotation, and the recovery of kaolinite from bauxite is ~70%. Newly developed collectors mentioned earlier can improve the recovery to as high as 80–90%. Additionally, it has been demonstrated that the flotation recovery of kaolinite is significantly increased by decreasing the pH of the flotation slurry (Bittencourt et al., 1990; Hu et al., 2003a,b, 2005).

However, the nature of kaolinite flotation using cationic collectors (alkyl amines) is not well understood. The mystery lies in the fact that half of the kaolinite surface is exactly the same as the surface of gibbsite, including crystal structure and composition. Nevertheless, kaolinite particles are able to be separated from gibbsite particles by amine flotation at low pH (pH < 5). Simulation results have suggested that dodecylamine prefers adsorption at the silica face surface of kaolinite over the alumina face surface (Hu et al., 2005). However, a detailed explanation for the better flotation recovery of kaolinite in acidic solution has not been reported in the literature. Only recently has the fundamental surface chemistry of kaolinite particles been established (Gupta and Miller, 2010; Liu et al., 2014). The alumina face surfaces of kaolinite particles are reported to be positively charged, the silica face surfaces and the edge surfaces are negatively charged even in acidic solution. In addition, kaolinite particle interactions have recently been studied (Johnson et al., 1998, 2000; Gupta et al., 2011; Liu, 2014; Liu et al., 2015). These surface chemistry studies of kaolinite particles provide fundamental knowledge for the analysis of the flotation behavior of kaolinite particles with dodecylamine collector.

In order to reveal the nature of the reverse flotation of kaolinite from bauxite ore, the interaction between two basal plane surfaces of kaolinite particles and dodecylamine was investigated in this current research. Due to the difficulty in the study of fine kaolinite particles (~500 nm), model surfaces with similar properties to the two face surfaces of kaolinite have been used to describe the behavior of kaolinite. The basal plane surface of pyrophyllite, a tri-layer phyllosilicate, was selected to represent the silica face surface of kaolinite; gibbsite, an aluminum hydroxide mineral with octahedral structure, was used to represent of the alumina face surface

of kaolinite particles. The pyrophyllite basal plane surface and the gibbsite octahedral surface are good candidates as model surfaces for the silica surface and alumina surface of kaolinite because of their structures. In addition, the surface charge and wettability of the pyrophyllite basal plane surface and gibbsite surface compare favorably to the properties of the silica face surface and the alumina face surface for kaolinite as summarized in Table 1. It is evident that good agreement is found between the model surfaces and kaolinite face surfaces. On this basis, the pyrophyllite basal plane surface and the gibbsite surface were selected to be the model surfaces for the silica face surface and alumina face surface of kaolinite.

Dodecylamine, one of the most common amines used for the flotation of kaolinite from bauxite, has been chosen as collector for this flotation study. The interactions between the model surfaces and dodecylamine collector were studied and based on these results the nature of the interaction of dodecylamine with kaolinite surfaces is suggested. In addition, the flotation mechanism of kaolinite from bauxite was analyzed and clarified based on the kaolinite surface properties, particle interaction, and the interaction between kaolinite surfaces and dodecylamine. These results provide further fundamental information for the future development of new flotation technology, including flotation conditions, control, and evolving new chemicals for the reverse flotation of kaolinite from low grade bauxite ores.

2. Materials and methods

2.1. Materials

A pure and white gibbsite specimen was purchased from Ward's science. The sample was polished to a very smooth surface, with polishing paper, followed by polishing with 0.3 μm and 0.05 μm gamma alumina powders on a polishing cloth. The gibbsite sample was cleaned with ethanol alcohol and high purity Milli-Q water (Millipore Inc.), followed by plasma cleaning for 20 min.

The pyrophyllite sample was obtained from a collection in the Department of Geology, University of Utah. The basal plane of pyrophyllite was polished to a flat surface, and then, a fresh surface was acquired by peeling off several layers of pyrophyllite using adhesive tape.

Table 1

Surface charge and wettability of pyrophyllite and gibbsite as model surfaces to represent the silica face surface and alumina face surface of kaolinite.

Surfaces	Point of zero charge	Cation exchange capacity (meq/100 g)	Wetting characteristics
Pyrophyllite basal plane surface	<pH 3 Hu et al. (2003a)	1.24–1.56 Prasad and Saxena (2008), Desai et al., (2010)	Surface, 40–50° Hu et al. (2003a) Powder, 79.2° Giese et al. (1991)
Silica face of kaolinite	<pH 4 Gupta and Miller (2010)	3–15 ^a Carroll, D. (1959), Bhattacharyya et al. (2008)	Modestly hydrophobic Yin et al. (2012)
Gibbsite surface	pH 7.5–11.3 Jodin et al. (2005), Kosmulski (2009), Adekola et al. (2011)	N/A	Hydrophilic Liu (2014)
Alumina face of kaolinite	pH 6–8 Gupta and Miller (2010)	N/A	Hydrophilic Yin et al. (2012)

^a Note this value indicates the cation exchange capacity for kaolinite surfaces in general.

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