

http://dx.doi.org/10.1590/0370-44672014690093

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1. Introduction

Chinese bauxite ores have required more elaborated beneficiation processes than the Brazilian bauxite ores. This fact is a consequence of the low alumina/silica (Al/Si) mass ratio in currently mined Chinese ores (Xu et al., 2004). Despite Brazil having some reserves with high-grade alumina, the tendency towards the shortage of rich reserves has been discussed (Rodrigues, 2009; Massola et al., 2009; Marino et al, 2012).

There are many studies addressing the concentration of Chinese bauxites (Hu et al., 2003; Zhao et al., 2003; Yuehua et

from bauxite by flotation **Abstract**

Kaolinite removal

This paper presents a potential condition to separate kaolinite through flotation when it is present in bauxite ore. This research anticipates a Brazilian industry requirement, considering the tendency towards the need for aluminosilicates removal from bauxite ores, as has already occurred in China. Kaolinite is the most abundant aluminosilicate, and gibbsite is the main aluminum bearing mineral in Brazilian bauxite ores.

The first step was a fundamental study involving microflotation experiments with pure samples of kaolinite and gibbsite. Ammonium quaternary salts and amines were used as the collector and corn starch as the depressant.

In a fundamental study, the best conditions determined in the first step were evaluated for the flotation of kaolinite from bauxite ore using laboratory scale experiments. Tests with AQ142/starch (pH 10) and CTAB (pH 7) led to satisfactory results. In general, the highest values of alumina/silica mass ratio were obtained with AQ142/starch and the highest values of mass recovery and metallurgical recovery were achieved with CTAB.

Keywords: froth flotation, flotation collectors, kaolinite, bauxite.

al., 2004, Wang et al., 2004; Xu et al., 2004; Zhang et al., 2008; Zhang et al., 2008b). The main aluminium-bearing mineral in Chinese ores is diaspore. Brazilian bauxites differ from Chinese bauxites in that Brazilian ores have gibbsite as the main aluminium-bearing mineral. Also, the gangue minerals present in those two types of ore are different. Iron and titanium oxides can be present in both types of deposits. Illite, pyrophyllite and kaolinite are the main silica bearing minerals in Chinese ores. Kaolinite and quartz are the main silica bearing miner-

als in Brazilian bauxites.

Brazil holds two types of deposits. The bauxite reserves in the north region present high-grade of Al₂O₂ and kaolinite is the main gangue mineral; the deposits from the central-south region contain not only kaolinite, but also quartz as a silicate gangue and lower Al₂O₃ content, if compared with those from the north region.

One of the objectives in bauxite beneficiation is to reduce the content of aluminosilicates. The presence of aluminosilicates, such as kaolinite, illite and pyrophyllite, decreases the alumina/silica

mass ratio, and, consequently renders unfeasible the utilization of the bauxite in the Bayer Process to produce alumina. Kaolinite in the Bayer Process is known as a reactive silica because it increases the consumption of NaOH and energy in the digestion stage without resulting in alumina formation.

Amines and ammonium quaternary salts are well-known potential collectors to float aluminosilicates. Dodecylamine (DDA) is one of the most used collectors to float aluminosilicates. Xia *et al.* (2009) affirmed that its adsorption onto kaolinite occurs by an electrostatic mechanism and, under acidic condition, addition-

ally by hydrogen bonding. Apart from Xia *et al.* (2009) Rodrigues (2009) also showed, in her microflotation study, that dodecylamine adsorbs onto the kaolinite surface enabling its flotation. Rodrigues (2009), also, tested, with success the etheramine Flotigam EDA, manufactured by Clariant.

Ammonium quartenary salts, for example cetyl trimethyl ammonium bromide, cetyl pyridine chloride, dodecyl trimethyl ammonium chloride and octadecyl dimethyl benzyl ammonium chloride have a good performance when used to float aluminosilicates as shown by Zhong *et al.* (2008), Wang *et al.* (2003),

Zhao et al. (2007).

This article presents a study of kaolinite flotation with Brazilian bauxite from the north region using amines and ammonium quaternary salts. Firstly, a fundamental stage was performed with tests in a Hallimond Tube. Then, the most selective conditions were evaluated in laboratory scale flotation. The results presented in this article are of great relevance for the reason that the flotation of Brazilian bauxite has not been effectively studied, since Brazil still has some reserves with high grade of alumina. In other words, this article anticipates a Brazilian demand.

2. Methodology

Microflotation tests were conducted in a Hallimond tube using pure mineral samples (kaolinite and gibbsite) to evaluate the performance of collectors and depressants in the system.

The samples were carefully ground, avoiding fines production and contamination, using agate mortar and pestle. The particle size of the samples was adjusted between 75 μ m and 212 μ m.

The agitation in the Hallimond tube causes further comminution of the already fine kaolinite particles. Because of this, an extension was adapted to the apparatus to prevent entrainment. N_2 was the gas used to produce the bubbles, at a flow rate of 60 mL/min.

Throughout this study four amines and four ammonium quaternary salts were tested. This article just presents the results with the collectors that showed the highest selectivity at the microflotation stage. The best collectors were cetyl trimethyl ammonium bromide (CTAB)

and Tomamine Q-14-2 PG (AQ142). CTAB is a pure reagent (ammonium quaternary salt) produced by Aldrich Chemistry. AQ142 is a commercial ammonium quaternary salt produced by Pietsch Chemicals. Gelatinised corn starch was used as depressant.

The collectorsCollector performance was evaluated at three concentrations: 1x10⁻⁴ mol/L, 5x10⁻⁵ mol/L, and 1x10⁻⁵ mol/L. The collectors conditioning time was one minute. The performances of corn starch and sodium hexametaphosphate were checked at a concentration range between 10 mg/L and 400 mg/L. The depressant conditioning time was 2 minutes. The froth collection time was determined after kinetic experiments, and was established at 5 min for the tests using CTAB, and at 2 min for the tests using AO142. These experiments were done at pH values close to 4, 6, 8 and 10.

Bauxite ore was carefully prepared,

by comminution operations and size separations, specifically to minimise fines generation. After that stage the ore was deslimed. The final size range of the bauxite sample was: -150 μ m + 15 μ m. The preparation of bauxite caused an increase in the alumina/silica mass ratio from 7.30 to 11.05.

Subsequently, laboratory scale flotation tests were conducted to verify the reproducibility of the results indicated in the microflotation stage.

Laboratory scale flotation tests were done in a Denver machine using a 900 mL cell. Each test was fed with 200 g of bauxite ore and 700 mL of water, the % solids of the pulp being 22%. The gas flow rate was 6 NL/min. These experiments were done at pH values close to 7 and 10. Bench scale tests were conducted in two size ranges. Both stages, microflotation and laboratory scale, were conducted with distilled water.

3. Results and discussion

3.1 Microflotation experiments

Hu et al. (2003) showed that cetyl trimethyl ammonium bromide (CTAB), in the concentration of 2x10⁻⁴ mol/L, works as collector of kaolinite, especially at pH 4, at which the recovery reaches 80%. The results obtained in this research are slightly better than those presented by Hu et al. (2003). Figure 1 shows the recovery of kaolinite and gibbsite with CTAB. One can observe high flotability of kaolinite in the pH range between 4 and 10, except for the lowest concentration of CTAB tested. The same conclusion cannot be

extended to gibbsite. The highest recovery of gibbsite was 37%. These results indicate that kaolinite and gibbsite can possibly be separated by flotation using CTAB as a collector in absence of depressant.

Figure 2 presents the results of recovery of kaolinite and gibbsite, at the pH range between 4 and 10, with the ammonium quaternary salt Tomamine Q-14-2 PG (AQ142).

The presence of the collector AQ142, at concentrations of $1x10^{-4}$ mol/L and $5x10^{-5}$ mol/L, results in val-

ues of recovery for both minerals above 50%. One can observe that increase of pH results in an increase of recovery for both minerals. In conclusion, there is no selectivity window to separate the two minerals. Sodium hexametaphosphate (HX) and corn starch were tested to provide selectivity for the separation.

Figure 3 shows that the introduction of the depressant starch, at pH value 10 and concentration of 400 mg/L, provides a selectivity window of approximately 50%. The use of HX did not make the separation possible.

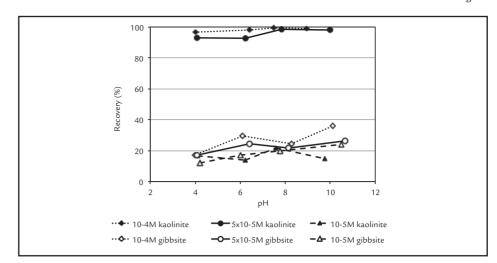


Figure 1 Flotability of kaolinite and gibbsite as a function of pH and CTAB concentration.

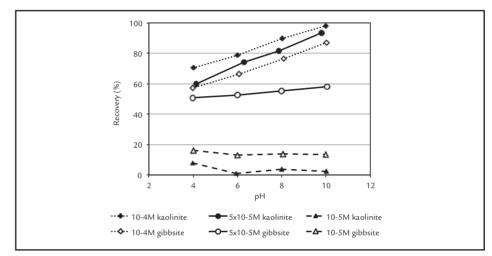


Figure 2 Flotability of kaolinite and gibbsite as a function of pH and AQ142 concentration.

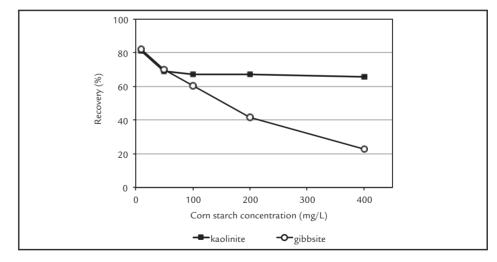


Figure 3 Floatability of kaolinite and gibbsite, as a function of starch concentration, with AQ142 (1x10⁻⁴ mol/L) at pH = 10.

3.2 Laboratory scale flotation tests

Figure 4 shows the best results for the laboratory scale flotation tests of bauxite sample. Laboratory scale tests reproduced the tendency shown in microflotation experiments.

The best result obtained with CTAB was achieved at neutral pH and collector concentration of 400 g/t (test B9); the Al/Si ratio changed from 11.06 to 26.56 and the metallurgical recovery achieved was 78%, the mass recovery being 72.1%.

In general, the combination of Tomamine AQ142 (AQ142) and corn starch provided good results in terms of selectivity of the laboratory scale flotation tests. Figure 4 indicates that the Al/Si ratio hit values between 24.2 and 25.9 (the initial Al/Si ratio was 11.06). The increase in starch concentration did not further improve the selectivity, but resulted in an increase of mass and metallurgical recovery (tests B13, B14 and B15). Using AQ142, the presence

of the depressant was crucial to ensure the selectivity in the stage of laboratory scale flotation tests.

In general, the highest values of the Al/Si ratio were obtained when the reagents used were the collector AQ142 and the depressant starch. However, values of mass recovery and metallurgical recovery obtained when AQ142 was used as collector were lower than those achieved when the collector used was CTAB. In both

cases the increase in concentration of collector was inversely proportional to the recovery values.

For tests done with AQ142 and starch, the highest value of metallurgi-

cal recovery was 71.3%. In this test the mass recovery and the Al/Si ratio obtained were respectively, 24.2 and 64.1.

The laboratory scale flotation tests were only conducted in a rougher

stage. Insertion of scavenger and cleaner stages could improve the results in terms of mass recovery, metallurgical recovery, and alumina/silica mass ratio in the concentrate.

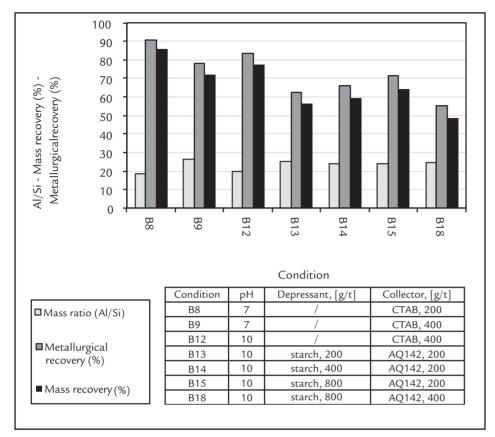


Figure 4
Best results of laboratory scale flotation tests.

4. Conclusions

The microflotation stage indicated two conditions of selectivity to separate kaolinite and gibbsite by flotation: (i) use of CTAB, and (iii) combination of AQ142/starch.

Laboratory scale flotation tests performed with AQ142/starch and

CTAB led to satisfactory results. In general, the highest values of alumina/silica mass ratio were obtained with AQ142/starch and the highest values of mass recovery and metallurgical recovery were achieved with CTAB. At pH 7 and high concentration, 400

g/t, CTAB yielded the highest Al/Si ratio, at reasonably high metallurgical and mass recoveries of 78.0% and 72.1% respectively.

The use of the collector AQ142 is a novelty in this system.

5. Acknowledgements

The authors are grateful to CAPES PROEX, CNPq and FAPEMIG for the financial support.

6. References

HU, Y., JIANG, H., WANG, G, D. Electrokinetic behavior and flotation of kaolinite in CTAB solution. *Minerals Engineering*, v. 16, p. 1221-1223, 2003.

MARINO, S., WANG, X., LIN, C., MILLER, J. The flotation of a gibbsite bauxite ore. In: INTERNATIONAL ALUMINA QUALITY WORKSHOP, 9., 2012, Perth. Proceedings... Londres: International Aluminium Institute, 2012. p. 345-350.

MASSOLA, C. P., CHAVES, A. P., LIMA, J. R. B., ANDRADE, C. F. Separation of silica from bauxite via froth flotation. *Minerals Engineering*, v. 22, p. 315-318, 2009.

RODRIGUES, O. M. S. *Study on kaolinite flotation*. Belo Horizonte: Curso de Pós Graduação em Engenharia Metalúrgica, Materiais e de Minas, Universidade Federal de Minas Gerais, 2009. 96 p. (Dissertação de Mestrado).

WANG, Y., HU, Y., LIU, X. Flotation de-silicating from diasporic-bauxite with cetyl

- trimethylammonium bromide. *Journal of Central South University Technology*, Changsha, v. 10, n. 4, p. 324-328, 2003.
- WANG, Y., HU, Y., HE, P., GU, G. Reverse flotation for removal of silicates from diasporic-bauxite. *Minerals Engineering*, v. 17, p. 63-68, 2004.
- YUEHUA, H., WEI, S., HAIPU, L., XU, Z. Role of macromolecules in kaolinite flotation. *Minerals Engineering*, n. 17, p. 1017-1022, 2004.
- ZHAO, S. M., WANG, Y. H., BAO, S. X., XU, J. Flotation of aluminosilicates using N-(2-aminoethyl)-1-naphthaleneacetamide. *Minerals Engineering*, v.16, p. 1031-1033, 2003.
- ZHAO, S., ZHONG, H., LIU, G. Effect of quaternary ammonium salts on flotation behavior of aluminosilicate minerals. *Journal of Central South University Technology*, Changsha, n. 4, p. 500-503, 2007.
- ZHANG, L. M., HU, Y. H., CAO, X. F., OUYANG, K. Study on mechanism of N,N-alkyl dodecylamine in flotation of kaolinite and diaspore. In: INTERNATIONAL MINERAL PROCESSING CONGRESS, 24. 2008, Beijing. Proceedings... 2008. p. 1580-1586.
- ZHANG, L. X., CHEN, X. Q., LIU, X. Review of flotation desilication on diasporic bauxite. In: INTERNATIONAL MINERAL PROCESSING CONGRESS, 24. 2008b, Beijing. Proceedings... 2008. p. 1485-1490.
- ZHONG, H., LIU, G., XIA, L., YIPING, L., HU, Y., ZHAO, S., YU, X. Flotation separation of diaspore from kaolinite, pyrophyllite and illite using three cationic collectors. *Minerals Engineering*, n. 21, p. 1055-1061, 2008.
- XU, Z., PLITT, V., LIU, Q. Recent advances in reserve flotation of diasporic ores A Chinese experience. *Minerals Engineering*, v. 17, p. 1007-1015, 2004.
- XIA, L., ZHONG, H., LIU, G., LI, X. Electron bandstructure of kaolinite and its mechanism of flotation using dodecylamine as collector. *Journal of Central South University Technology*, Changsha, v. 16, p. 73-79, 2009.

Received: 2 June 2014 - Accepted: 5 May 2016.