



KAOLINITE MICROFLOTATION AND ZETA POTENTIAL MEASUREMENTS IN THE PRESENCE OF AMMONIUM QUATERNARY SALTS

Otávia M. S. Rodrigues¹, Armando C. Araujo², Antônio E. C. Peres³,
Júnia S. Alexandrino¹, Gilmar M. Lopes¹

¹ Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas
Universidade Federal de Minas Gerais
Avenida Antônio Carlos, 6627, Pampulha, 31270-901 Belo Horizonte, MG, Brazil
otaviamartins@yahoo.com.br

² Mining and Mineral Processing Research Center
BP 30320, F-57283 Maizières-lès-Metz Cedex France
armando.correa@arcelormittal.com

³ Associate Professor, Departamento de Engenharia Metalúrgica e de Materiais
Universidade Federal de Minas Gerais
Avenida Antônio Carlos, 6627, Pampulha, 31270-901 Belo Horizonte. MG, Brazil
aecperes@demet.ufmg.br (corresponding author)

ABSTRACT

Studies on kaolinite flotation are being driven by Chinese bauxite characteristics, presenting low alumina:silica weight ratios. This paper addresses the effect of the presence of cetyl pyridine chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB) on kaolinite floatability and zeta potential. The reagents were dosed at three concentrations and the best floatability results were achieved at the highest concentration level (1×10^{-4} mol/L). Zeta potential determinations showed that both quaternary salts (CPC and CTAB) shift the kaolinite zeta potential to more positive values the specific collectors adsorption onto the mineral surface.

Keywords: Kaolinite, flotation, zeta potential, ammonium quaternary salts.

1. INTRODUCTION

Bauxite is an essential raw material for alumina and, consequently, aluminum production. The aluminum bearing minerals are digested in the Bayer process, resulting in alumina production. According to Constantino et al. [1], the major aluminum bearing minerals present in bauxites are gibbsite (abundant in Brazilian bauxites), diasporite (abundant in Chinese bauxites), and boehmite (abundant in European bauxites). Some gangue minerals present in bauxites decrease the Bayer process efficiency. Kaolinite is an example, for adding reactive silica to the ore.

Reactive silica is the ore fraction that reacts with caustic soda in the Bayer process digestion stage without increasing the alumina production. The presence of reactive silica results in higher and energy and reagents consumption and does not bring gains to the process. The amount of reactive silica in the ore is indicated by the weight ratio alumina:silica (A/S). Higher kaolinite or other aluminosilicates contents result in lower A/S ratios. Some authors [2,3] suggest A/S ratios between 8 and 10.

Brazilian bauxites, on the other hand, present chemical characteristics that meet the feed standards required by the Bayer process. Nevertheless, as occurred in China, the trend is towards the scarcity of the above mentioned reserves, adding relevance to studies aiming at kaolinite removal from bauxite ores.

Froth flotation has been the most widely used method for kaolinite separation. Amines [4,5,6] and quaternary ammonium salts [7,8,9,10,11] are usually employed as collectors.

The target of this paper is to evaluate the effect of the presence of cethyl pyridine chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB) on kaolinite floatability and zeta potential, as a function of pH and reagent concentration.

2. EXPERIMENTAL

The kaolinite sample came from Vila Munguba, Almerim district, Pará state, Brazil. Wet chemistry was used for the sample chemical characterization. The mineralogy was determined by X-ray-diffraction (Philips diffractometer, model PW1710, CuK α radiation, graphite monocromator crystal, scanning speed 0.06°2 θ /s, counting time 1s, scanning interval from 3° to 90° (2 θ)).

Two quaternary ammonium salts were used as collector: cetyl pyridine chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB). As all quaternary ammonium salts, both reagents present positive charge in the full pH range. Both possess 16 carbon atoms in the hydrocarbon chain which constitutes the non polar portion of the molecule. The difference stays in the structure of the polar portion. The CPC polar head is constituted by the pyridine group (C₅H₅N) and that of CTAB e a do CTAB contains one nitrogen atom bound to three methyl groups (C₃H₉N).

In the microflotation experiments the pH was adjusted with sodium hydroxide (NaOH) and hydrochloric acid (HCl). In the zeta potential determinations, potassium hydroxide (KOH) and nitric acid (HNO₃) were used for pH control and potassium nitrate (KNO₃), at the concentration of 1x10⁻³ mol/L, was utilized as supporting electrolyte.

The microflotation experiments were performed in a modified Hallimond tube adapted with an extension to prevent fine particles entrainment. The kaolinite sample weight was 2 g, in the size range between 45 μ m and 300 μ m. Nitrogen gas was used for bubbles generation at the flow rate 50 mL/min. The collector concentrations employed were 1x10⁻⁴ mol/L, 5x10⁻⁵ mol/L, and 1x10⁻⁵ mol/L, conditioned during 1 min, and the pH was set at the values 2, 4, 6, 8, 10, and 12. The flotation time was set at 10 min, as suggested by kinetic studies.

Zeta potential determinations were performed in the ZM3-D-G, Zeta Meter systems 3.0+ apparatus, with direct video image, manufactured by Zeta Meter, Inc, EUA, using the electrophoresis technique.

The supporting electrolyte KNO_3 was used in all measurements. The pH was set at 4, 7, and 10 and the zeta potential was determined in the presence of collectors at three concentrations (1×10^{-4} mol/L, 5×10^{-5} mol/L, and 1×10^{-5} mol/L), and also in the absence of collectors, at different pH values.

3. RESULTS AND DISCUSSIONS

The x-ray diffractogram of the kaolinite sample is illustrated in figure 1 and the results of chemical analysis are presented in table 1.

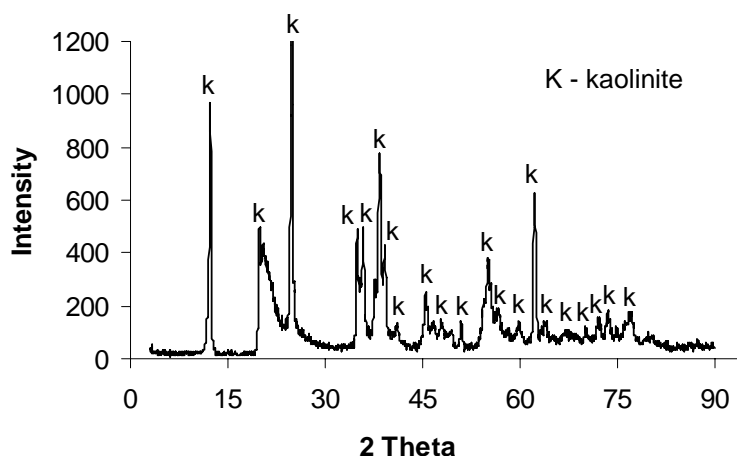


Figure1: X-ray diffratogram of the kaolinite sample.

Table 1: Results of the kaolinite sample chemical analysis and expected composition from the mineral stoichiometric formula.

Grade	Theoretical (%)	Analysed (%)
LOI	13.96	13.40
SiO_2	46.54	44.80
Al_2O_3	39.50	38.33
TiO_2	0.00	1.3
Fe_2O_3	0.00	1.9
Cr_2O_3	0.00	0.01
MnO	0.00	0.00
CaO	0.00	0.00
MgO	0.00	0.07
Na_2O	0.00	0.00
K_2O	0.00	0.01
P_2O_5	0.00	0.06
ZrO_2	0.00	0.05

The analyzed loss on ignition (LOI), silica (SiO_2), and alumina (Al_2O_3) contents were, respectively, 4.0%; 3.6%, and 3.0% lower

than the theoretical values, suggesting that the sample purity is equal to or higher than 96%. The X-ray diffractogram did not present

any peaks that might indicate the presence of impurities.

Figure 2 illustrates the best results of kaolinite floatability with CPC and CTAB. The curves show the same trend for both reagents. At the concentration 1×10^{-4} mol/L both perform well the collector role in the pH

range between 4 and 10. At the concentration 5×10^{-5} mol/L the highest floatability level is achieved at pH 4, the recovery decreasing for higher pH values. At the concentration 1×10^{-5} mol/L the highest floatability achieved by both reagents was low, reaching only 30%. As a general trend, CPC was slightly more efficient than CTAB.

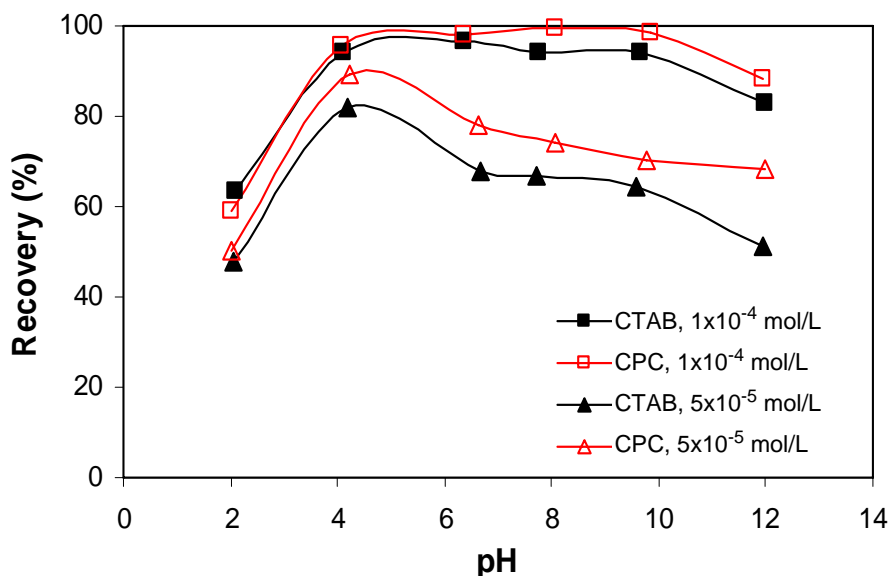


Figure 3 presents kaolinite zeta potential curves in the presence and absence of CPC and CTAB.

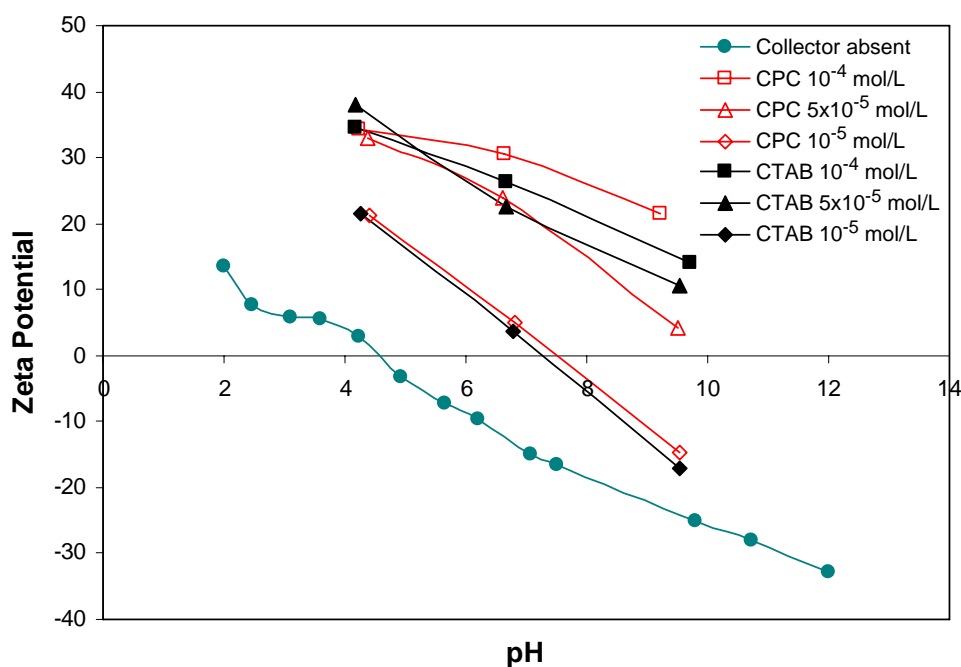


Figure 3: Kaolinite zeta potential in the absence and presence of CPC and CTAB.

In the presence of the supporting electrolyte and collectors absence, the isoelectric point was observed at pH = 4.6, in agreement with reports in the literature [7,12,13]. The presence of both salts shifts the kaolinite zeta potential towards more positive values, the increase being proportional to the reagent concentration, indicating adsorption in the full pH range. It may be observed from figure 3 that the zeta potential shift caused by CPC is slightly higher than that due to CTAB, what might be an explanation for the better floatability in the presence of CPC.

4. CONCLUSIONS

At the concentration 1×10^{-4} mol/L, CPC and CTAB performed well the collector role in the pH range between 4 and 10. The kaolinite isoelectric point was observed at pH = 4.6. The presence of both salts shifts the kaolinite zeta potential towards more positive values, indicating adsorption in the full pH range.

ACKNOWLEDGEMENTS

The authors are grateful to CNPq for the financial support.

5. REFERENCES

[1] Constantino, V. R. L.; Araki, K.; Silva, D. O.; Oliveira, W. Preparation of aluminum compounds from bauxite: consideration of some aspects involved in a teaching experiment. *Química Nova*, v. 25, p. 490-498, 2002. (In Portuguese)
[2] Cao, X. F.; Liu, C. M.; Hu, Y. H. Research on the relationship of three amine collector's structure and their flotation performances on three aluminosilicate. In: *INTERNATIONAL MINERAL PROCESSING CONGRESS*, n. 24, 2008b, Beijing, China, Proceedings..., p. 1513-1517.
[3] Zhang, Y. H.; Wei, D. Z.; Zeng, K. W.; Ren, A. J.; Zheng, G. B.; Liu, S. H.; Chen, D. Z.; Application and development of depressant BK501 in the desilication from bauxite by reverse flotation. In: *INTERNATIONAL MINERAL PROCESSING CONGRESS*, n. 24, 2008d, Beijing, China, Proceedings..., p. 1563-1567.

[4] Yuehua, H.; Wei, S.; Haipu, L.; Xu, Z. Role of macromolecules in kaolinite flotation. *Minerals Engineering*, v. 17, p. 1017-1022, 2004.
[5] Cao, X.; Liu, C.; Hu, Y. Flotation of kaolinite with dodecyl tertiary amines. *Journal of Central South University Technology*, Changsha, China, v. 16, p. 749-752, 2009.
[6] Liu, C.; Hu, Y.; Cao, X. Substituent effects in kaolinite flotation using dodecyl tertiary amines. *Minerals Engineering*, v. 22, p. 849-852, 2009.
[7] Hu, Y., Jiang, H., Wang, D. Electrokinetic behavior and flotation of kaolinite in CTAB solution. *Minerals Engineering*, v. 16, p. 1221-1223, 2003.
[8] Li, Z.; Gallus L. Adsorption of dodecyl trimethylammonium and hexadecyl trimethylammonium onto kaolinite - Competitive adsorption and chain length effect. *Applied Clay Science*, n.35, p. 250-257, 2007.
[9] Zhao S.; Zhong, H.; Liu, G. Effect of quaternary ammonium salts on flotation behavior of aluminosilicate minerals. *Journal of Central South University Technology*, Changsha, China, n. 4, p. 500-503, 2007.
[10] Wang, Y.; Hu, Y.; Liu, X. Flotation desilicating from diasporic-bauxite with cetyl trimethylammonium bromide. *Journal of Central South University Technology*, Changsha, China, v. 10, n. 4, p. 324-328, 2003.
[11] Köster, R.; Schreck, B.; Rybinskii, V.; Dobias, B. New reagent systems for the flotation of kaolinite. *Minerals Engineering*, v.5, p.445-456, 1992.
[12] Zhao, S. M., Wang, D. Z., Hu Y. H., Liu B. D., Xu J. The flotation behaviour of N-(3-aminopropyl)-dodecanamide on three aluminosilicates. *Minerals Engineering*, v.16, p.1391-1395, 2003.
[13] Yuehua, H., Wei S., Haipu L., Xu Z. Role of macromolecules in kaolinite flotation, *International Journal of Mineral Processing*, v.76, p.163-172, 2005.