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Amazonian kaolin purification by selective flocculation

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ABSTRACT

The most important kaolin deposit in the north of Brazil presents titaniferous contaminants finely disseminated in the bulk. Those contaminants affect the commercial value of the mineral urging a process for removing them. The removal of those contaminants can not be carried out by conventional techniques, due to the ultra-fine size of the minerals. This paper presents a mineral concentration process based on selective adsorption of soluble polymers. Flocks of considerable sizes and quite consistent are generated by interactions between anionic polyacrylamide molecules and titaniferous minerals which can be separated from a kaolin suspension by sedimentation. The best results were obtained after a polymer, having a weak anionic charge (10%), was used as flocculant for kaolin impurities. The mineral was dispersed in aqueous media using a high concentration of sodium hexamethaphosphate (4.8kg/t) at a pH value around 10. In these conditions, the content of TiO_2 in the sample was reduced from 1.39% to less than 0.5% and kaolin recoveries ranged between 50 and 65%. Sedimentation of the flocks reached rates around 5.2mm/min.

Keywords: Kaolin; Selective flocculation; TiO_2

1. INTRODUCTION

Kaolin is employed as a paper coating due to its high degree of whiteness and brightness when pure. Such a pure mineral is achievable from mineral deposits only after several treatment stages. The treatments aim to eliminate contaminants species, specially colored ones, which affect optical properties of kaolin ores. The main impurities found in such ores are iron, titanium and silica minerals. Among them, titaniferous impurities are the most difficult to remove. The main kaolin deposits in the world, located in the Georgia State (USA) and in the Amazon region (north of Brazil) present those kind of impurities (mainly anatase). Hence, the commercial quality of those kaolin products depends directly on the beneficiation processes employed to remove those impurities.

According to Yoon and Shi (1986), conventional techniques, such as ultra-centrifugation and high gradient magnetic separation, are not efficient for the removal of impurities having very small sizes.

Carrier flotation, on the other hand, which is used for those cases, also presents limitations with respect to material size due to unspecific interactions undergone by the reagents used as collector agents (Wang and Somasundaran, 1980). Recent researches carried out using alkyl hydroxamates as collectors presented promising results (Yoon *et al.*, 1992).

In the last years, selective flocculation has appeared as the most promising technique for treating these type of minerals, particularly those which appear to be too fine to respond to conventional processes. Recent technological advances, in terms of polymer nature, charge density, molecular weight and structure, have shown to produce efficient separations among fine minerals (Marthur *et al.*, 2000). The flocculation technique is an aggregation process which gather several particles through polymers bridging. Bridging occurs when high molecular weight polymers adsorb simultaneously onto two or more particles, leading to physical cross-linkages between them. The links may be established by hydrogen bonding, hydrophobic interactions and/or chemical bonding forces (Orumwense, 1994; Shaning and Attia, 1987).

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The Selective flocculation technique is based on differences among surface properties of two or more components of a suspension. Those differences are responsible for the distinct interactions degrees observed between minerals and polymers. Mineral particles which present more affinity for the flocculant aggregate easily forming the so called flocks. The density of the flocks becomes higher than that of water and hence they settle down.

The process can be divided in five steps (Figure 1): 1. Mineral dispersion in water; 2. Addition of the polymer into the pulp; 3. Selective adsorption polymer/mineral; 4. Formation and growing of the flocks; and 5. Separation flocks/suspension (Somasundaran, 1980; Yarar and Kitchener, 1970; Attia, 1987; Marthur *et al.*, 2000).

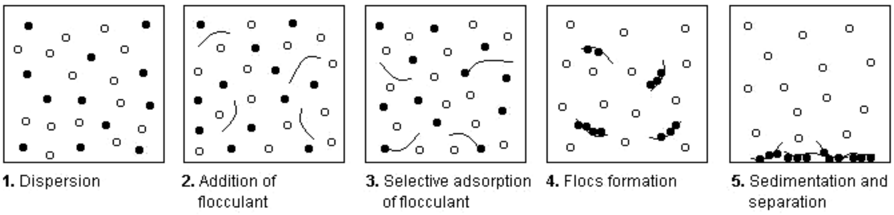

Figure 1. Schematic view of the selective flocculation

Selective flocculation has been studied for more than 30 years for purification of the Georgia kaolin (USA) as an alternative method to remove anatase, a titanium impurity which is refractory to flotation. Very good results were obtained in laboratory tests at bench scale (Yoon and Shi, 1986).

Recently, selective flocculation has been investigated also on the Amazonian kaolin, from the north part of Brazil, to remove anatase impurity (TiO_2) (Larroyd *et al.*, 2002).

This paper presents a study of the effect of a polyacrylamide polymer concentration, its charge density, pH and dispersant concentration on purification of kaolin. The efficiency of the method was evaluated by measuring the degree anatase removal (TiO_2 content). Additionally, microscopic studies of the liberation degree of kaolinite/anatase were also carried out to evaluate separation feasibility. Finally sedimentation velocities of the flocks were determined aiming at industrial applications.

2. MATERIALS AND METHODS

Kaolin samples used in this work came from the north of Brazil. The samples were submitted to dispersion, removal of coarse material, by settling and centrifugation and, magnetic separation, in order to get a homogenous product in terms of composition and size distribution. A pulp having 30% solid was prepared at a controlled pH and dispersant dosages.

The flocculant solution was prepared by dissolving the reagent in distilled and deionized water to make a 0.05% stock. Aliquots of this were added directly to kaolin pulp under agitation (200rpm) and left conditioning for 10min. After ceasing the agitation, the colored flocks formed were removed from the pulp by sedimentation (it took about 15min). The products (kaolin pulp and impurity flocks) were analyzed by x-ray fluorescence for TiO_2 content.

Two different anionic polyacrylamide polymers, partially hydrolyzed, were tested: Superfloc® A-100 and Superfloc® A-150. The charge densities were 10% and 50%, respectively. Despite the high molecular weight (more than 6.0×10^6g/mol) polyacrylamide polymers present high solubility in water. These flocculants, which were co-polymers indeed, were constituted by alternate amido and carboxylic groups in macromolecular structures (Figure 2).

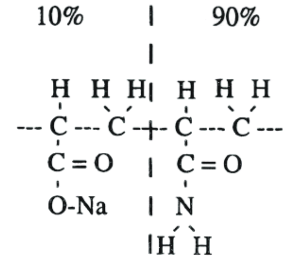

Figure 2. Schematic configuration of a hydrolyzable polyacrylamide (Gary *et al.*, 1997)

Polyacrylamide polymers are soluble in water and appear to have anionic nature due to ionization of carboxylic groups (R-COONa) at pH values above 4.5. The ionic charge (10% or 50%) is calculated as a percentage of monomer units that are hydrolyzed. The different negative charge densities can be explained by the following equilibrium hydrolysis occurring at several parts of the molecules where the –R-COO$^-$ groups appear:

$$\text{R-COOH} \Leftrightarrow \text{R-COO}^- + \text{H}^+ \qquad (1)$$

NaOH solutions were used as pH modifier and sodium hexametaphosphate solutions as kaolin dispersing agent.

A JEOL brand (JEM 2010) scanning electronic microscope (SEM), equipped with energy dispersive spectroscopy (EDS) was used for the investigation of kaolin/anatase liberation degree and for analyzing morphological structures.

The rate of sedimentation and flocks compacting were studied with the use of a Turbiscan®. The measures were taken every minute during 15min (15 measures).

3. RESULTS AND DISCUSSION

The 30% kaolin pulp prepared for this study presented a variable viscosity as a function of hexametaphosphate concentration. Figure 3 shows the rheological behavior of kaolinite suspensions at different dispersing agent concentrations. Comparing the slopes of the stress curves as a function of gradients it can be observed that viscosity decreases as the concentration of sodium hexametaphosphate increases, up to a concentration around 2.8kg/t at which viscosity levels off. The ideal kaolin dispersion is the one which has a maximum fluidity (the lowest viscosity). Hence, the flocculation study was carried out at the lowest viscosity observed.

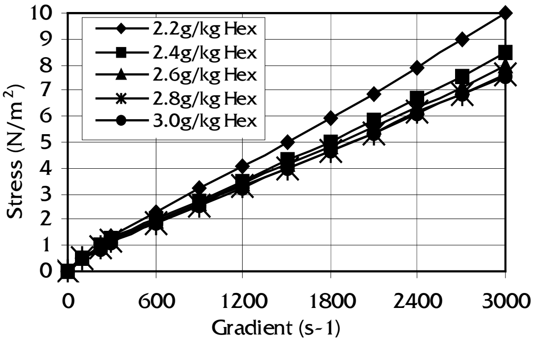

Figure 3. Rheological behavior of the kaolin pulp at different dispersant concentration

Figures 4 and 5 present the effect of charge density of polymers on the grade of TiO_2 and the recovery of kaolin, respectively. From these figures, it can be seen that the polymer SFA-150, which has higher anionic charge density (50%), did not reduce significantly the TiO_2 content of the kaolin pulp, in the pH range studied. On the contrary, the low charge density polymer (10%), in alkaline medium, appears encouraging. The grade of the TiO_2 fell from 1.39%, in the original kaolin sample, to 0.952% in the treated sample, at a pH value around 10 (Figure 4). Unfortunately, the recovery of kaolin also decreases as the pH of the medium increases (Figure 5).

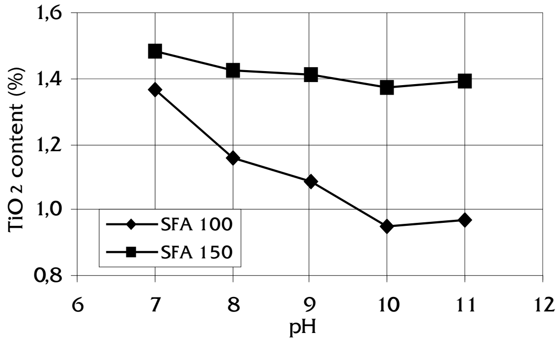

Figure 4. TiO_2 grade vs pH at different polymer charge densities

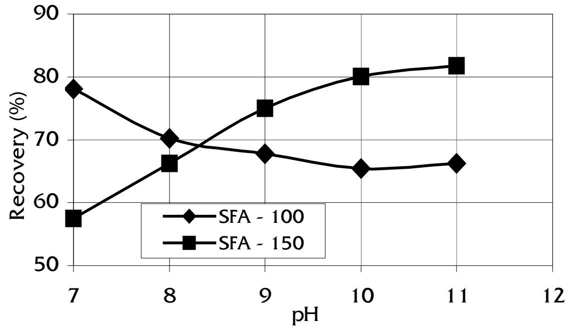

Figure 5. Recovery of kaolin vs pH at different polymer charge densities

In order to improve the efficiency of separation, a series of tests were carried out at higher concentration of hexamethaphophate (1 and 2kg/t over the optimal concentration – 2.8kg/t), at a pH value around 10. In Figures 6 and 7 recovery and grade are plotted, respectively, as a function of polymer concentration for different hexametaphosphate (HMF) dosages. It can be seen that, increasing concentration of flocculant decreases kaolin recovery (Figure 6). On the other hand, increasing the HMF concentration the recovery increases. However, the TiO_2 grades decrease when increasing both, the concentration of polymer and that of the dispersant (Figure 7).

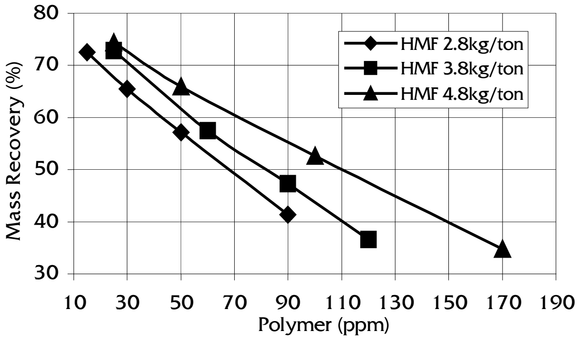

Figure 6. Kaolin mass recovery and polymer concentration for different ionic ambients

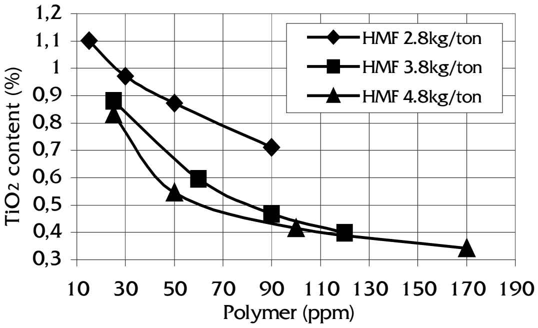

Figure 7. TiO_2 content and polymer concentration for different ionic ambients

In order to shed more light to the data shown in Figures 6 and 7, the same data were plotted in Figure 8 on a recovery/grade graph. From this plot, it can be clearly seen that selectivity increases as concentration of HMF increases, as can be concluded by observing the shifting of the curves toward lower TiO_2 degrees when HMF concentrations increases. On the other hand, the recovery decreases as the concentration of the polymer increases for all testes. However, the recovery is less affected at higher HMF concentrations, as can be seen by comparing points having similar polymer concentrations on different curves.

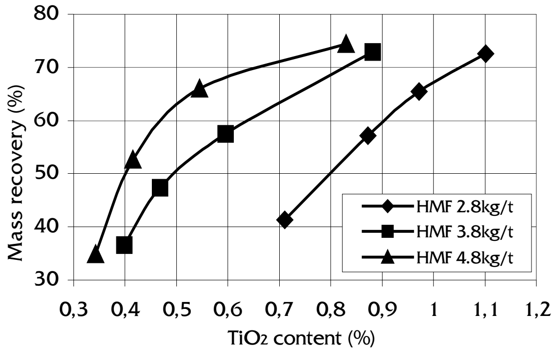

Figure 8. Recovery/grade curves for TiO_2 flocculation from kaolin

A sedimentation study was carried out at different hexametaphosphate concentrations at constant polymer dosage (50ppm) and a pH value around 10. In Figure 9 the height of the layer of flocs settled is plotted as a function of time. It can be seen from the graph that the height increases faster as the concentration of HMF increases. The highest settling rate (height/time) was observed for the highest HMF concentration tested (4.8kg/ton).

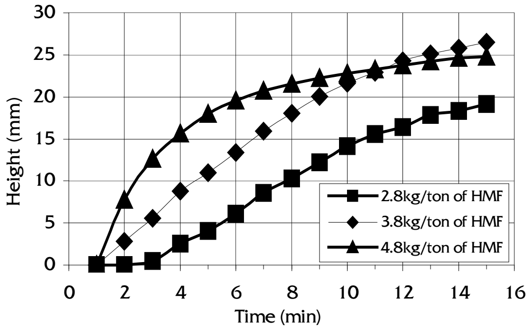

Figure 9. Variation of the height of the solid settled as a function of time

Images of the flocculated material (Figure 10), taken with SEM-EDS, revealed a complete liberation among mineral phases.

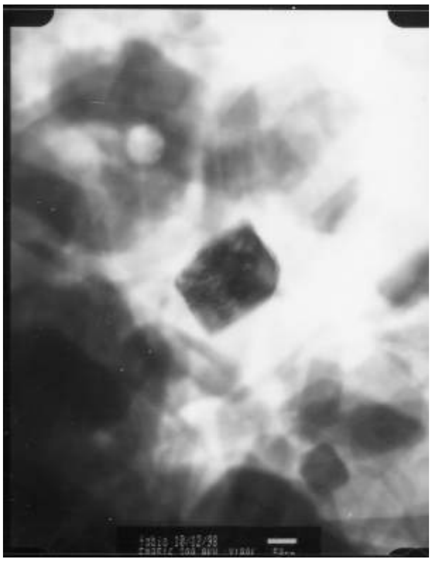

Figure 10. MET image of an anatase crystal liberated from kaolinite (the white bar corresponds to 50nm)

4. CONCLUSIONS

It was shown here that it is possible to carry out kaolinite purification by selective flocculation. The flocculating polymers must have a high molecular weight and a low charge density.

In order to improve the efficiency of the method, it is necessary to increase the stability of the suspension. This was carried out by adding hexametaphosphate to the pulp. This reagent adsorbs onto kaolin particles increasing their charge densities and provoking stronger energy of repulsion among particles and hence stabilizing the suspension.

The addition of HMF additionally improves the rate of sedimentation of the flocculated material, as seen in Figure 9. The increase in the settling rate of the flocs may be due to a combined effect; namely, increase in the density of the formed flocs and/or viscosity decrease of the pulp. The viscosity of the kaolin pulp decreases as the concentration of HMF increases, as it is seen in Figure 3. This effect, though, reaches a maximum at a dosage of 2.8kg/ton of HMF. Beyond that concentration, the viscosity does not appear to have a further decrease, as it is presented on Figure 3. However, the presence of the polymer in the system appears to have a sort of synergistic effect with the HMF on the rheological properties of the pulp because the settling rate does not show such a HMF concentration limiting value observed on Figure 3.

It is suspected that the selectivity of the process is accomplished through Van der Waals forces or hydrogen bonding between the polymer and minerals because, at pH values around 10, both minerals (kaolin and rutile) appear having negative surface charge, as can be concluded by their zero point of charges of 3.4 and 6.7 respectively. Such type of interaction can account for the flocculation behavior observed on Figures 4 and 5. It is seen from those figures that there exist a preferential flocculation of the titaniferous species. In addition, the presence of HMF in the system reinforce the negative electrostatic effect.

The best conditions found to eliminate most of the titaniferous impurities from kaolin mineral was at pH value around 10, 4.8kg/ton HMF and 80 to 90ppm of anionic polymer SFA-100. Hence, kaolin purification results feasible though sacrificing some recovery. Under those conditions, the TiO_2 content was decreased from 1.39%, in the original sample, to less than 0.5% after flocculation. The recovery reached was around 50%.

One of the important conditions to be fulfilled is the complete liberation of the rutile species from kaolin. This was observed to be true in the samples studied as it is seen in the picture shown in Figure 10.

The results given here, are feasible to be applied in plant practice because the settling rates of the flocks are very reasonable.

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