

REOXIDATION STUDIES OF IRON-BEARING KAOLIN

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ABSTRACT

Reoxidation studies of iron-bearing kaolins have been carried out in order to stabilize the ferrous ions content in solution from kaolin bleaching. This has shown the possibility of minimizing the loss of kaolin brightness when used as paper coating. A kaolin clay from northern Brazil has been studied. Mineralogical characterization has shown that its composition presents more than 90% of kaolinite, being hematite, quartz and rutile/anatase the main contaminants. The results obtained in the present work are quite promising. Within the different complexing agents used for the ferrous ions stabilization, sodium citrate and phosphoric presented the best results. Products of kaolin obtained in this study were prepared in paint form and applied to a polypropylene surface. When using sodium citrate and phosphoric acid as a complexing agent for ferrous ions, the surface where paint was applied presented 77.9% and 79.3% brightness, respectively. When comparing these results with those obtained just applying kaolin without complexing agent, this has resulted in a gain of 2.5% brightness for using sodium citrate and 3.9 for using phosphoric acid.

INTRODUCTION

Kaolin is the commercial name of a white clay, composed mainly of kaolinite mineral. According Grim (1958), kaolin is constituted of clay material, with low iron content, white color or nearly white. Kaolins are hydrated aluminum silicates which chemical composition is closely $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, containing other elements as impurities. Kaolins are resulted of aluminum silicate weathering, mainly feldspar. There are two types of kaolin deposits: primary or residual and secondary. The kaolins from Rio Capim and Jari are examples of secondary deposits in Brazil. These deposits are located in the Pará and Amapá States, respectively. Kaolins produced in those mines have been exported mainly to Europe and Asia to be used by the coating paper industry.

Kaolin presents a vast industrial application, such as paper, paint, plastic, rubber, ceramics, refractories etc. (Bordonalli, 1995). The paper industry is the main kaolin market with a consumption of 45% and then comes the refractory industry with 17% (Roskil, 1996). This vast field of industrial applications can be attributed to its physical properties such as: chemically inert; white; high coating capacity when used as pigment; low thermal and electric conductivity and low abrasion (Murray, 1986).

There are large reserves of kaolin in northern Brazil and great part of them, after beneficiation, presents specifications required for the paper industry. 78% of the Brazilian kaolin reserves are located in the Pará and Amapá States.

The Brazilian production of beneficiated kaolin accounted 1.517 million of metric tons in 1999. The world production of kaolin has been dominated by United States of America, United Kingdom and then comes Brazil occupying the third place.

Kaolins occur in association with impurities like quartz, feldspar, iron oxide, mica, organic material, rutile/anatase and as a such do not present specification required to be used by the industry. Those impurities strongly influence the kaolin properties such as brightness, abrasion, viscosity etc. Kaolins have to be wet processed for removing those impurities. This process consists mainly of dispersion, degritting, storage and blending, classification, delamination, high intensity magnetic separation, flotation, selective flocculation, bleaching, dewatering, redispersion, drying or calcination. (Prasada et al., 1991; Yoon and Shi, 1986).

Chemical bleaching is the most important step in kaolin processing because higher kaolin brightness increase the aggregated value of the product. The chemical bleaching has been performed by doing an oxidizing or reductive leaching. In the first case the reaction is irreversible and in the last one the reaction could be reversible by the oxygen action (Suss, 1986).

Coloring impurities, generally are present in kaolin as organic matter, titanium minerals and iron

bearing minerals. The process for removing organic matter from kaolins consists of its oxidation with a hydrogen peroxide solution at pH 2. The reductive leaching is the most used process for kaolin bleaching. The method consists of removing iron oxide from kaolins by the reduction of trivalent iron to its divalent form, using sodium dithionite, metallic zinc and aluminum Stock et al. (1979). Luz et al. (1995a 1995b 1995c 1995d) have studied and compared the results of kaolin bleaching by using sodium dithionite, metallic zinc and metallic aluminum. Luz and Chaves (1998) developed a kaolin beneficiation process with stabilization of ferrous ions oxide which can be industrially used for kaolin from Northern of Brazil.

Brearley et al. (1952) have described that 30 % of the Fe^{3+} which has been taken into solution during the kaolin bleaching will be dried back as ferrous iron into the clay in the drying pans. The ferrous iron will oxidize in the air to ferric oxide, and so give a discolored clay. When kaolin cake is dried, the soluble iron salts migrate to the evaporating surfaces. In this case, the iron salts which are exposed to the atmosphere revert to ferric oxide during the drying process and a reddish-brown film forms on the surface of the dried clay. The kaolin cake could be washed for removing the ferrous iron but unfortunately the ferrous ions are strongly adsorbed on kaolin clay in acid medium.

When kaolin is applied as a paper coating, its brightness generally decreases between 5 and 12%. For example, if a kaolin product has 86% brightness, when applied to a surface, its brightness dropped to 78%. It is very important to minimize this brightness drop, to enhance one of the most important properties of kaolin (Luz, 1998a,1998b).

The reduction/oxidation reactions have a strong influence on the dissolution of the iron bearing minerals. The reductive dissolution of iron (III) hydroxide can occur with several organic and inorganic reducers, such as ascorbate, phenol, dithionite, HS^- etc. Fe^{2+} in the presence of complex formers can promptly dissolve Fe^{3+} hydroxides (Stumm, 1992). According to Suter (1988) et al., the dissolution of the Fe^{3+} hydroxides is usually enhanced by H^+ ions, complex-forming substances (ligands) and by reductants. According to the same author, Fe^{2+} is released into the solution more easily than Fe^{3+} because the bonds between the reduced iron and its neighbor irons are weakened.

Nowack et al.(1996) describe that , Ethylenediaminetetracetic acid (EDTA) is one of the most widely used industrial complexing agents (photographic, textile and paper manufacturing industry).

According to Charlot (1957), cited by Pourbaix and Zoubov (1966), divalent iron forms complexes as follow: amine, oxalate, hipophosphate, cyanide.

OBJECTIVE

To immobilize ferrous ions content in solution from kaolin bleaching, in order to minimize the losses of brightness after its industrial use as a paper coating.

EXPERIMENTAL METHODOLOGY

Several experiments have been conducted using a kaolin sample from northern Brazil. These experiments consisted of physical beneficiation, bleaching, iron stabilization, preparing kaolin in paint form and applying it as a coating, according to the flowsheet presented in Figures 1 and 4.

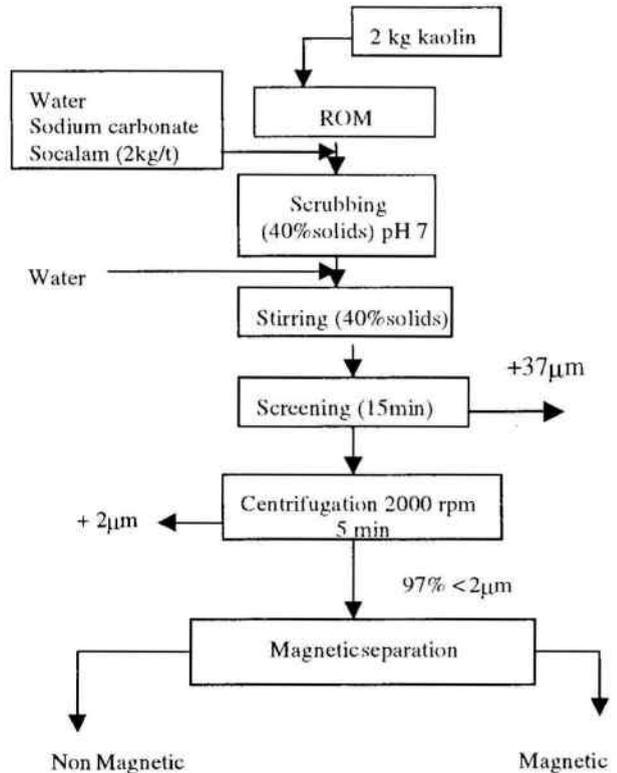


Figure 1 – Flowsheet used in first step of kaolin beneficiation

a) Bleaching

The non magnetic product (<2µm) goes to the bleaching step. The water/kaolin suspension is put into a

reactor (Figure 2) with controlled agitation. Then the pulp is adjusted to 4.5 pH by using $\text{Al}_2(\text{SO}_4)_3$, added 2 kg/t of sodium dithionite and stirred (90 rpm) for 1:00h. At the end of the bleaching test, a pulp sample is taken, filtered and dried at 105°C. A sample of kaolin was prepared for brightness determination, using the Photometer Zeiss, Elrepho type. In this case it was used the 457 nm filter, according to TAPPI T534 om-86 procedure.

After the bleaching step, immobilization of ferrous ions was performed for 60 minutes by using different types of complexing agents such as: Trilon B, Phosphoric Acid, Ammonium Oxalate, EDTA, Oxalic Acid and Sodium Citrate.

At the end of the ferrous ions's stabilization, the kaolin suspension was adjusted for a 4.5 pH by using sulfuric acid or sodium carbonate. The suspension was poured into a Buckner funnel, filtered, dried and measured the brightness by using the same procedure already mentioned.

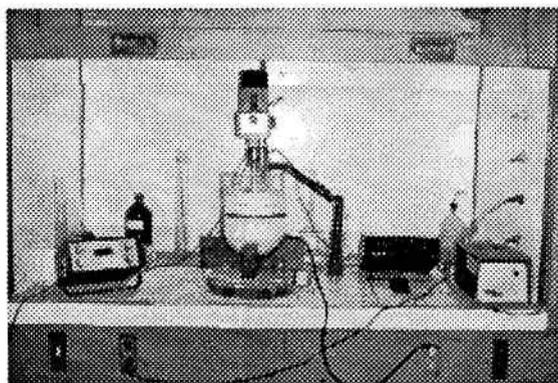


Figure 2 – Reactor used in bleaching and immobilization experiments

b) Coating Application

Products of kaolin resultant of ferrous ions immobilization and products of kaolin just bleached were prepared as a paint and then applied to a polypropylene surface (Figure 3), according to the standard procedure. This paint is based on a mixture of water, kaolin, dispersing agent, pH modulator, synthetic binder (Styronal BD-711, BASF) and anti-froth (Afranil ST, BASF). This paint was applied to the mentioned surface by using a cylinder bar (number 40). After paint application to a polypropylene sheet, this was dried at 80°C temperature. This resultant surface was then submitted to brightness measurement by using the same procedure of TAPPI T 534 om-86. See in Figure 4 flowsheet of the whole process.



Figure 3 – Show the device used for coating application

RESULTS AND DISCUSSION

Within the complexing agents used for ferrous ions immobilization, phosphoric acid and sodium citrate presented the best results (Tables 1 and 2).

Table 1-Influence of phosphoric acid concentration on brightness of polypropylene surface coated with kaolin

Test	Kg/t(*)	1	2	3	4
1	0.00	84.43	-	75.42	9.01
2	0.25	84.43	83.87	69.75	14.42
3	0.75	84.43	85.05	78.56	6.42
4	1.25	84.43	85.65	79.30	6.35
5	1.75	84.43	84.75	75.92	8.88

(*) Phosphoric acid concentration

- 1) Brightness of kaolin just bleached
- 2) Brightness of kaolin bleached and Fe^{2+} stabilized
- 3) Brightness of polypropylene surface coated with kaolin
- 4) Drop of brightness

Table 2 - Influence of sodium citrate concentration on brightness of polypropylene surface coated with kaolin

Test	Kg/t(*)	1	2	3	4
1	0.00	84.43	-	75.42	9.01
2	0.25	84.43	85.00	77.67	7.33
3	0.75	84.43	83.90	75.50	8.40
4	1.25	84.43	86.00	77.90	8.10
5	1.75	84.43	85.48	76.93	8.55

(*) Phosphoric sodium citrate

- 1) Brightness of kaolin just bleached
- 2) Brightness of kaolin bleached and Fe^{2+} stabilized
- 3) Brightness of polypropylene surface coated with kaolin

4) Drop of brightness

a) When using phosphoric acid

It can be seen from Table 1 that the brightness of kaolin product when the ferrous ions have been immobilized by using phosphoric acid as a complexing agent is superior to the brightness of the just bleached kaolin.. The combination of sodium dithionite and phosphoric acid has contributed to improve the iron reduction process as well promoted its immobilization.

The best results were obtained by using 1.25 kg/t of phosphoric acid. The brightness reversion dropped from 9.01 when no complexing agent has been used to 6.35 % points (Table 1).

b) When using sodium citrate

It can be observed from Table 2 that the brightness of kaolin product when the ferrous ions have been immobilized by using sodium citrate as a complexing agent is also superior to the brightness of just bleached kaolin. This suggests that the combination of sodium dithionite with sodium citrate has increased the reduction dissolution of Fe^{3+} . This may explain the promising results obtained by using dithionite and sodium citrate.

The best results were obtained by using 1.25 kg of sodium citrate/t of kaolin processed. In this case, the polypropylene surface where kaolin has been applied presented a brightness of 77.90%. Comparing this result with those obtained with just bleached kaolin, it represented a gain of 2.48% of brightness.

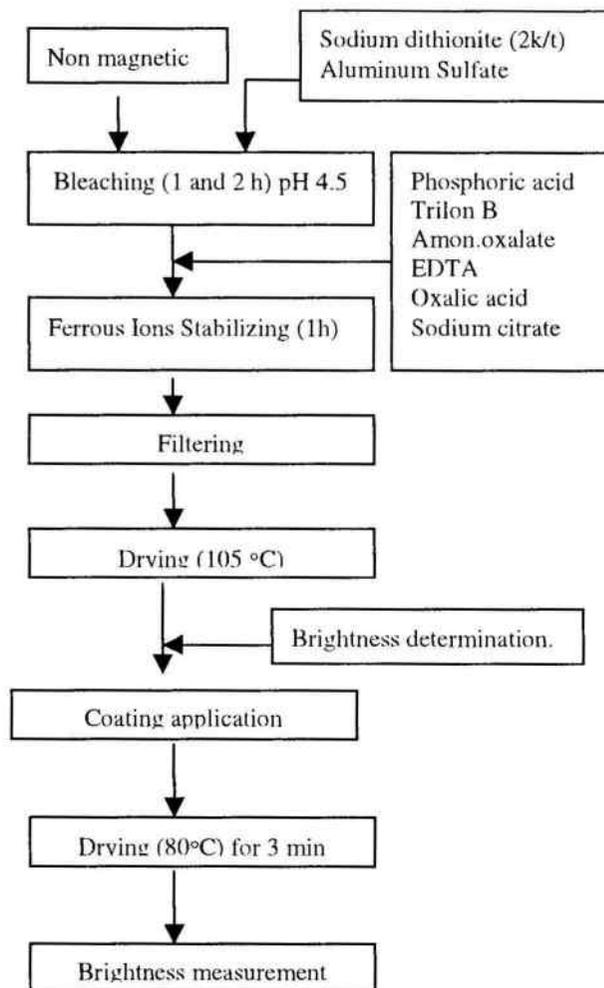


Figure 4 – Flowsheet used in the kaolin beneficiation and ferrous ions immobilization

CONCLUSIONS

a) Mineralogical Characterization

The main contaminants of kaolin from northern Brazil are: hematite, quartz and rutile/anatase. Some image obtained by Scan Electron Microscope-SEM have shown that hematite is altering to limonite which is covering the hematite itself, rutile/anatase and kaolinite.

c) Ferrous Ions Immobilization

Within the five complexing agents studied in the present work aiding immobilization of ferrous ions in a kaolin from northern Brazil, sodium citrate and phosphoric acid presented the best results for 1:00 h of bleaching and 1:00 h of ferrous ions immobilization.

In the case of using sodium citrate as a complexing agent for ferrous ions, the kaolin product

presented 86% brightness, superior to 84.43% brightness which was obtained for just bleached kaolin. It is well known that the combination of a complexing agent and a reductant favored the reduction dissolution of Iron (III) hydr(o)xides). This can explain the promising results obtained when combining sodium dithionite reductant with sodium citrate complexing agent.

When using 1.25 kg/t of sodium citrate as a ferrous ions complexing agent, the surface where kaolin was applied presented 77.9% brightness. If this result is compared with a kaolin product just bleached, it resulted in a gain of 2.48%. This is an indication that the ferrous ions have been stabilized.

In the case of using phosphoric acid as a complexing agent, the best results were obtained for a concentration of 1.25 kg/t. The surface where kaolin was applied presented 79.30% brightness. Comparing these results with those of kaolins just bleached, brightness reversion dropped from 9.01 to 6.35.

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