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Study of Electrometalurgical Parameters of the Kaolin Bleaching Process

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Abstract: The objective of this study is to present the methodology and results of the study of chemical bleaching process of kaolin from potentiometric measurements in experimental systems. The bleaching of four kaolin samples, from La Union municipality in the department of Antioquia (Colombia) was studied at laboratory level, considering as main variables, the reducing agent percentage involved (Sodium Dithionite, $Na_2S_2O_4$) and the process time. The Electrochemical potential (Eh) and pH of the system were evaluated with a 692 pH/Ion Meter Metrohm equipment, the amount of dissolved iron as Fe^{3+} measured at the end of each test using Atomic Absorption Spectrophotometry (AAS) and the whiteness index calculated by Calorimetry. The Electrochemical potential (Eh) variation of the system, the changes in Fe^{2+}/Fe^{3+} ratio with the increase concentration of reducing agent as well as the variation of whiteness index W (Whiteness %) with processing time are a first approach to the understanding of bleaching kaolin phenomenology.

INTRODUCTION

Is known as kaolin, the group of silicates with a structure constituted by tetrahedral layers of SiO_4. In general terms the basic structure of this group is constituted by a series of sheets that are stacked successively in each sheet can be distinguish five planes that contain the different ions as detailed below:

- OH plane 5
- Al^{3+} o Mg^{2+} plane 4
- O, OH plane 3
- Si plane 4
- O plane 5

The oxide and hydroxide ions are arranged in such a way that they generate octahedral holes where the Al^{3+} or Mg^{2+} cations are located. Consequently, the general formula of the kaolin minerals group corresponds to next composition:

$$X_n(Y_2O_5)(OH)_4$$

Where:
X = The ion that occupies the octahedral position
Y = One that occupies the tetrahedral position (generally, Si^{4+}, although, it can be Al^{3+} and rarely Fe^{3+})

The most representative mineral of the kaolin group is known as kaolinite and it is a fundamental constituent

Table 1: Contributing minerals

Minerals	Structure
Anatase	TiO_2
Goethite	FeO (OH))
Hematite	Fe_2O_3
Ilmenite	$FeTiO_3$
Magnetite titaniferous	$Fe_{3-x}Ti_xO_4$
Biotite	$K_2[Mg.Fe^{2+}]_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH, F)_4$

of most clays used in manufacture of fine and refractory ceramics. Its composition is obtained from the subgroup general formula by making n = 2 which therefore, turns to be:

$$Al_2\ (Si_2O_5)(OH)_4$$

The structure is based on a sheet containing tetrahedrons of SiO_4, forming a composition layer $(Si_2O_5)^{2-}$ and joined through common oxygen to Al^{3+} ions with gibbsite structure which complete its coordination index up to six with OH^- groups[1].

Kaolin white color is one of the main characteristics for which it is used in many industrial applications and its use requires in some cases, brightness and whiteness specifications.

The kaolin whiteness is affected by the presence of colloidal and/or nanometric minerals of iron (Fe) and Titanium (Ti) adsorbed by kaolinite surface[2], some of which are shown in Table 1.

In general, the industrial use of kaolinite, in many cases, implies the separation of this type of contaminants by methods of extractive metallurgy. Industrially, the most used method is a chemical method that through of inorganic leaching agents produces the selective dissolution of minerals color contributing.

A classical conception of chemical bleaching, stablish the formation of ferric iron complexes in aqueous medium through an imposition of the system pH and the subsequent reduction of this ion present in kaolin as hematite (Fe_2O_3) and/or goethite using a reducing agent. The commonly used reducing agent is sodium dithionite ($Na_2S_2O_4$), a water soluble salt.

The use of a reducing agent in bleaching process involves the coupling of two processes, one anodic and other cathodic.

Anodic process:

$$S_2O_4^{2-} \leftrightarrow SO_3^{2-} + e^- \quad (1)$$

Catodic process:

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \quad (2)$$

Oxide-reduction reactions in Eq. 1 and 2 or coupled anodic and cathodic processes, admit the formation of ferrous iron complexes in aqueous solution which places these extractive metallurgy processes into electrometallurgy area.

Thus, reactions involved in bleaching process can be characterized by the potentiometric study of the system. Potentiometry is an electroanalytical technique with which the concentration of an electroactive species in a solution can be determined using a reference electrode (an electrode with a constant potential in time and known) and a working electrode (an electrode sensitive to electroactive specie).

Potentiometry of platinum electrode has proven to be a valuable tool for investigating the leaching reaction between sodium dithionite and ferric iron in clays[3]. By potentiometry the electrochemical potential of the system is measured from which it is possible to construct phase diagrams. These diagrams allow to visualize the conditions of thermodynamic stability of minerals in contact with solutions of a determined composition, the solution properties in which a metal or compound is unstable and should be decompose, the decompose products and its precipitation conditions.

The system equilibrium potential is determined by the thermodynamic equilibrium condition which according to Nernst equation[4]:

$$Eh = E^0 - \frac{RT \ln Q}{nF}$$

Where:

- Eh = Solution potential
- E^0 = Standard equilibrium potential of the system that is its equilibrium potential if all substances involved in reaction are in their standard state
- Q = Electrochemical reaction constant
- F = Faraday constant (23.060 cal/volt)
- n = Electron number

In the equilibrium Eh = 0 and Q = K, last one known as the equilibrium reaction constant. Potentiometric measurements are sensitive to the variation of bleaching process parameters. The working kaolin crystallinity, the percentage of solids and the average size distribution of suspended particles, mineral and ionic impurities, the process time, concentration of reducing agent and the temperature are variables that control the bleaching process and therefore can infer in the potentiometric analysis results[5].

In a first approach to the study of thermodynamic variables (Eh and pH) of the kaolin bleaching process, the study described, here, developed at CIMEX Minerals Institute of the National University of Colombia, Medellín, evaluates, the influence of three variables in the efficiency of bleaching process. The contact time, percentage of sodium dithionite and the type of clay are variables inspected in the experimental process described below.

MATERIALS AND METHODS

Experimental process

Potentiometric measures: A 692 pH/Ion Meter Metrohm brand equipment was used in Electrochemical potential (Eh) measurements following the process described below:

A kaolin pulp was prepared in demineralized water with a percentage of solids not exceeding 20%. The system pH was regulated with H_2SO_4 to a strongly acidic pH. The reducing agent (sodium dithionite, $Na_2S_2O_4$) was added in three different concentrations varying between 0.0045 and 0.1 M.

- Concentration 1: between 0.0068 and 0.0088M
- Concentration 2: between 0.0048 and 0.0068M
- Concentration 3: between 0.0028 and 0.0048M

Four samples of kaolin, described as A, B, C and D with the characteristics mentioned below were used: samples A and C are kaolin of different origins and without any treatment, B is the result of a delamination process of sample A and sample D is a kaolin that was subjected to whiteness.

Dissolved iron (Fe) in bleaching process: Once, the bleaching test was finished, dissolved iron was measured in proportion Fe^{3+}/Fe^{2+} present in the solution. This measurement was made by atomic absorption spectrophotometry with a Thermo Scientific-iCE 3000 series spectrophotometer from the chemical laboratory at the I.M. CIMEX.

Whiteness index: The samples at the end of each test were filtered and dried at a temperature not exceeding 100°C to then analyze their whiteness index through the datacolor microplast equipment. In this kind of analysis four color parameters are measured:

- Whitness (W)
- Color purity (L)
- Level of red (a)
- Level of yellow (b)

The specifications, for a kaolin of optimum whiteness of each of these parameter are detailed in Table 2.

Table 2: Color index for a white kaolin

Index	Expected values
W	≥60
L	93.2-95.5
a	(-0.2)-(-0.45)
b	3.5-4.5

RESULTS AND DISCUSSION

Potentiometric measurements

Electrochemical potential (Eh) in bleaching process: Next is shown the change of potential (Eh) in time for the bleaching test of sample A (Fig. 1).

In previous graph, time at 0 min marks the stable potential of the kaolin pulp, equivalent to 0.25 V, the initial 10 min record the change of potential which reaches 0.46 V in minute 10 with pH adjustment. The first recording after sodium dithionite addition is made at min 11 (1 min after the addition of the reducing agent) with a potential of -0.23 V and finally, a potential equivalent to -0.004 V is recorded in min 30 (20 min after the addition of sodium dithionite) at this moment bleaching test is considered finished (Fig. 2).

Kaolin effects on the reduction potential of the sodium dithionite ($Na_2S_2O_4$): Next graph shows the change of potential in two systems after the addition of sodium dithionite, first system without kaolin and second with the same percentage of solids as sample A in previous test.

Dark line, with a minimum at -0.31 V, shows the change of potential (Eh_1) of a system without kaolin, acidic pH and sodium dithionite concentration between 0.0045 and 0.1 M, on the other hand, red line shows the effect that the presence of kaolin A has on potential (Eh_2) in a curve with a minimum of -0.23 V. At the end of the test (30 min) Eh_1 = -0.028 V and Eh_2 = -0.004 V.

Electrochemical potential variation in bleaching with concentration of ($Na_2S_2O_4$): Whiteness test was repeated for three different concentrations of sodium dithionite and kaolin A in each case (Fig. 3).

Dark line shows the change in potential measured in the system of concentration 1 of dithionite, red line the concentration 2 and blue line concentration 3. Figure 4 also shows the potential measured in each case at 10, 11 and 30 min of the test.

Nature clay and the Electrochemical potential (Eh): The variation in raw material, particularly in particle size and iron content can have a substantial effect on potentiometric measurements of the bleaching process. Graph shown below such behavior is compared under the same concentration of the reducing agent -0.0045 and 0.1M using four types of sample A-D.

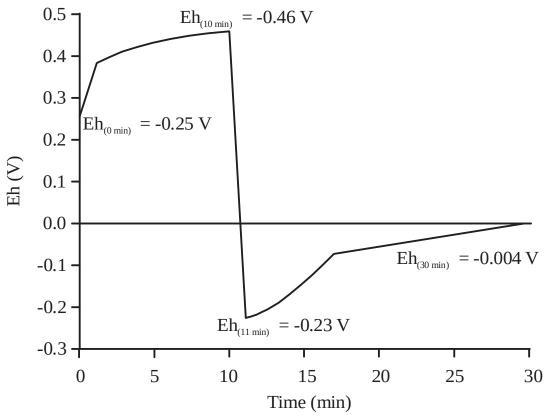

Fig. 1: Eh vs t in the complet process, sample A

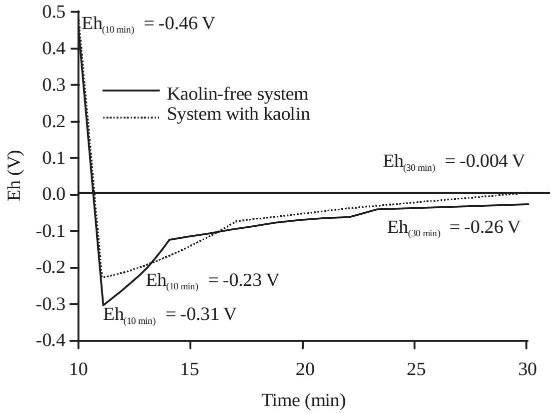

Fig. 2: Eh vs. t for two systems with and without kaolin

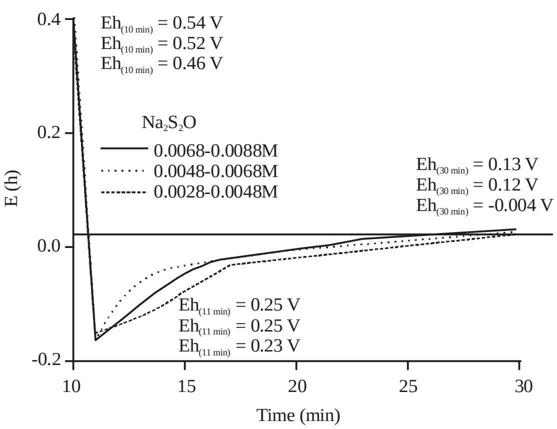

Fig. 3: Eh vs. t concentration effects of ($Na_2S_2O_4$)

Disolved iron (Fe) in bleaching process: Following graph shows, in a log-log scale, the amount of dissolved iron (Fe^{2+}/Fe^{3+}) as a function of sodium dithionite concentration in the bleaching test with four types of clays, A-D. Each clay was subjected to bleaching using three different concentrations of sodium dithionite (Fig. 5).

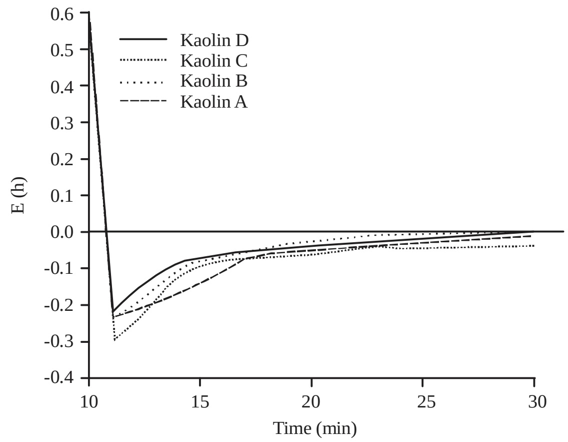

Fig. 4: Effects of clay type on potentiometric measurements of the system

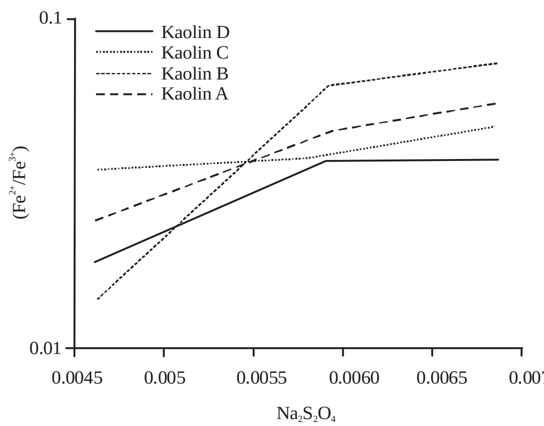

Fig. 5: Dissolved iron (Fe^{2+}/Fe^{3+}) as a function of sodium dithionite

Table 3: Parameter W of each simple without bleaching test

Types of kaolin	Whiteness (%)
A	38.56
B	45.66
C	61.10
D	30.51

Table 4: Parameter W of each simple after bleaching test at concentration 1 of $Na_2S_2O_4$

Types of kaolin	Whiteness (%)
A	58.11
B	63.40
C	68.30
D	46.10

Whiteness index: The whiteness parameter W (Whiteness) of each kaolin, measured before bleaching test is mentioned next (Table 3).

At the end of each bleaching test, whiteness analysis was made. Next, results of each clay are compared with the concentration 1 (0.0068-0.0088M) of sodium dithionite (Table 4).

Table 5: Parameter W measured at different times in the kaolin bleaching A-D

Kaolin	W(%) (9 min)	W(%) (15 min)	W(%) (20 min)	W(%) (25 min)	W(%) (30 min)
A	50.11	58.50	58.11	59.96	58.19
B	62.65	63.66	63.40	63.61	63.61
C	43.76	46.05	46.10	46.14	45.96
D	65.70	67.24	68.30	66.61	66.61

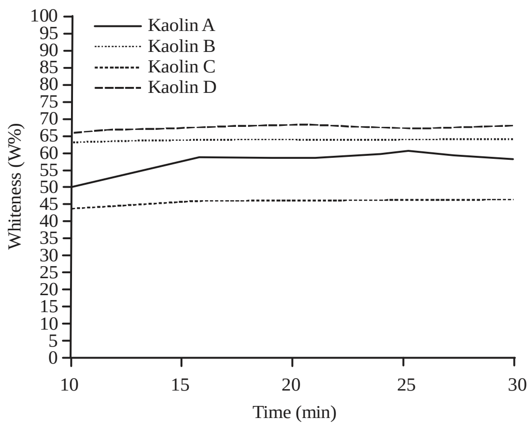

Fig. 6: Whiteness parameter W% in bleaching process of kaolin A-D

In the experimental bleaching process mentioned before (concentration 1 of $Na_2S_2O_4$), 5 samples were taken for whiteness analysis. The first sample after 9 min of the test (before the addition of the reducing agent), second at 15 min (5 min after the addition of the reducing agent), the third at min 20, fourth at 25 and fifth at min 30. These results are shown next and compared in Fig. 6 for samples A-D (Table 5).

In electrometallurgical terms, kaolin bleaching by the process expose here and as shown in Fig. 1 can be understood as a two-stage process. First one, an oxidation stage (slight increase in Eh after the addition of H_2SO_4) in the first 10 min and second a stage (after the addition of sodium dithionite) of strong reduction in which values of around -0.25 V in the electrochemical potential of the system are reached. The process first stage (oxidation stage) can be understood as the preparation of the kaolin mineral surface before the reducing agent attack on iron impurities adhered to mineral surface.

As shown in Fig. 2, maximum potential reached with the addition of dithionite is for A sample, -0.23 V and for the solution without kaolin of -0.31 V, difference that is due to a retarding effect created by the clay in the dithionite dissolution in aqueous media.

CONCLUSION

The dithionite concentration is proportional to the amount of ferrous iron (Fe^{2+}) in solution, a direct measure of the W whiteness index increase. Thus, it can be thought that the efficiency of bleaching process (increase in whiteness) is directly related to the increase of ferric iron in solution at the expense of a decrease in ferrous iron that could be adhered to the mineral surface as hematite and/or goethite.

The type of clay is also an important factor on the average electrochemical potential in each case as well as the amount of dissolved iron and the measured whiteness parameter W. Granulometry and the amount of iron in the original material are fundamental factors for the process efficiency.

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