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Physical and Electrochemical Parameters Study in Kaolin's Processing

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Abstract: In this research, a characterization of the chemical bleaching process of Colombian kaolin by potentiometric an galvanometric measures is shown. Three samples from La Unión, Antioquia (Colombia), were tested in laboratory taking into account the effect of the amount of reducing agent (Na_2SO_4) and the resident times. Phenomena description such as the variation in electrochemical potential, iron concentration in solution and the whiteness index evolution, contributes to the phenomenological analysis of kaolin processing. These results are important for future research works appointing to efficiency of Colombian kaolin blenching that make possible a reduction in precipitated iron species in mineral surfaces.

INTRODUCTION

Kaolin is an industrial mineral[1] widely used in Colombia as raw material in ceramic industry, paint and cement among others, it is composed by Kanditas mineral group mainly kaolinite and some impurities which limit its applications, this is the case of some iron oxides, iron hydroxides and iron titanium oxides such as hematite (Fe_2O_3), goethite (a-FeO(OH)) and ilmenite ($FeTiO_3$)[2], chromophores minerals with nano-colloidal size which adhered to the mainly mineral affecting its whiteness and important feature of this industrial mineral applications [3, 4], consequently impacting its commercial value[5].

In general, the industrial use of kaolin in many cases involves the separation of contaminants by methods from the extractive metallurgy. The mainly industrial method used is a chemical one known as "chemical bleaching" that through inorganic leaching agents is achieved by selective dissolution of minerals color contributors[3]. The Colombian industry use this method to achieve contaminants dissolution, but with limited yields due to strong reversibility couple Fe^{3+}/Fe^{2+} evidenced by adsorption on the mineral surface of the iron compounds in solution[4]. Classically this process has been conceived as a hematite and/or goethite leaching process through a pH strongest system regulation and its subsequent reduction of iron ferric with the addition of sodium dithionite[5] as showed in Eq. 1:

$$Na_2S_2O_4+6Fe_3+4H_2O \rightarrow 2NaHSO_4+6Fe^{2+}+6H^+ \quad (1)$$

The change in the oxidation state of the participating species generates a redox couple as shown below in Eq. 2 and 3, respectively[4]:

Anodic process

$$2H_2O+S_2O_4^{2-} \leftrightarrow 2SO_3^{2-}+4H^++2e^- \quad (2)$$

Cathodic process

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

The oxidation-reduction reactions in Eq. 2 and 3 or anodic processes and cathode processes coupled; support complex formation of aqueous ferrous iron, for these reason these extractive metallurgy processes taken place in the field of electrometallurgy[4].

Thus, the reactions involved in the bleaching process may be characterized by studying the potentiometric system, these reactions are sensitive to changes in operational parameters of kaolins bleaching process. The kaolin crystallinity, the percentage of solids and the Size Average Distribution (SAD) of particle in suspension, minerals and ionic impurities, the process time, the reducing agent concentration and temperature are variables that control the bleaching process and therefore, may interfere in the results of the potentiometric titration analysis[5].

In a first approach to the study of physical and electrochemical parameters of kaolins bleaching process in Colombian, this research evaluates the influence of three variables: the contact time, the sodium dithionite percentage and clay species.

MATERIALS AND METHODS

Experimental procedure

Sample preparation and characterization: Three samples of kaolin from La Union Antioquia (Colombia) with difference in susceptibility to bleaching (Table 1) was selected, this property related is response to industrial chemical bleaching process under operational conditions referred in the local industry.

Table 1: Sample list

Samples	Description
A	Normal susceptibility
B	High susceptibility
C	Low susceptibility

Each sample was dissolved in water and filtered using a No. 325 mesh (43 µm, tyler scale) in order to isolate the larger sizes to 43 µm, composed mainly by quartz and other large mineralogical species of interest in this kind of study. Nominal size particles 4 µm were dried at room temperature after being passed by press filter, then the chemical composition of each sample was measured by X-Ray Fluorescence (XRF) using X-ray Spectrometer PHILIPS PW 2400. The mineralogical composition was measured using a X-ray diffractometer Panalytical X'Pert PRO MPD with Cu anode and Ni filter and finally, the whiteness index was calculated measuring the reflectance spectrum in each sample using a Spectrophotometer Microflash 45.

Conventional characterization for chemical bleaching process: After compositional and mineralogical characterization, a conventional laboratory chemical bleaching process was carried out where was prepared a slurry of each mineral with a percentage of solids between 18-20% in a stirred reactor at 120 rpm, after a conditioning time of 10 min with continuously added sulfuric acid (H_2SO_4) 1%. Finally, 20 min after process was initiated is added the reducing agent, sodium dithionite ($Na_2S_2O_4$), varying its concentration between 2.1×10-3 and 8.1×10-3 M; the concentration range considered economically viable for the local industry.

After the addition process of reducing agent, an aliquot of the sample was extracted from the suspension and subsequently iron content measured in solution by atomic absorption spectrophotometry using a Spectrophotometer Thermo-Ice Scienhfic 3000 Series. The total iron content in solids by XRF and whiteness index (Whiteness, W%) as a control process, it is expected, that the higher the ratio, the bleaching process efficient increases. This procedure was repeated for each test at 5, 10, 15 and 25 min after the addition process of reducing agent. Simultaneously to the above procedure, the pH records and Electrochemical potential (Eh) were taken at all stages of the process, using a pH electrode and a Platinum (Pt) wire counter electrode combined, taking a dual output signal.

Electrochemical kinetic process: Kinetic measurements were made at each stage of the process with linear and cyclic polarization curves using a potentiostat/galvanostat AUTOLAB Model PGSTAT302N, both in potentiostatic mode with the following operational variables: linear and cyclic voltammetries with scanning time 5 sec, speed 0.1 V/sec, initial potential -1.0 and 1.0 V as final potential in each stage, before and after the addition of each reagent was performed an a linear polarization curve, few minutes after the addition of the reducing agent were performed linear and cyclic polarization curves, this measure was repeated 5, 10, 15, 20 and 25 min after initiating the reduction step.

RESULTS AND DISCUSSION

X-Ray Fluorescence (XRF): The weight percent of each element present in the samples were obtained, the results are shown in Table 2.

It is very important to consider the differences in XRF iron (Fe_2O_3) present in all samples. Sample C, low susceptibility kaolin, showed the highest iron content (1.33%) while in the opposite case, the sample B, high susceptibility kaolin, showed less iron contamination (1.2%), not least is the small amount of Titanium (TiO_2)

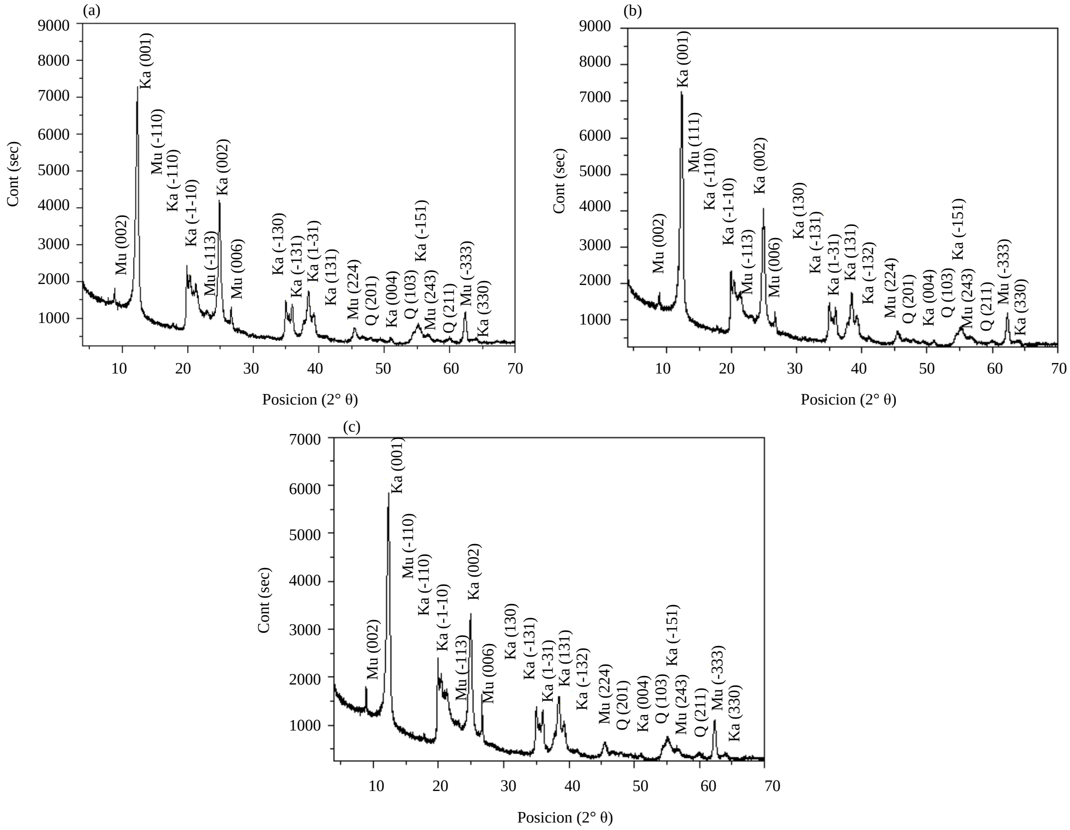

Fig. 1(a-c): X-ray diffraction patterns samples A (a), B (b) and C (c)

Table 2: Chemical characterization by XRF

Samples	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	BaO	P_2O_5	PPI 100-1000℃
A	45.9	37.7	1.26	0.56	0.028	0.15	ND	0.45	0.06	0.008	0.03	13.9
B	45.8	37.6	1.20	0.56	0.002	0.14	ND	0.42	0.26	0.004	0.029	14.2
C	46.9	36.8	1.33	0.39	0.009	0.20	0.03	0.39	0.05	ND	0.012	13.2

and therefore, the sign of its little contribution as a color contaminant. Furthermore, no significant differences are in silicon (SiO_2) and (Al_2O_3) total average and as expected, these are the common elements in the samples, putting kaolinite, an aluminosilicate hydrated as predominant mineral, confirmed by the XRD patterns.

The PPI measured in each sample, reveal a low volatile organic and inorganic compounds, besides, no substantial differences are between samples.

X-Ray Diffraction (XRD): The XRD equipment used in this study has a generator of Cu Ka X-rays with wavelength λ of 1.5406 Å and the results were obtained under conditions of grazing incidence angle of 3°, 2Θ range of 2-70°, increase of 0.02° and 2 sec/step speed with the aim of observing the phases present and crystallographic orientations. The X-ray diffraction patterns are shown in Fig. 1 and identified mineralogy species listed in Table 3.

Table 3: Mineralogy species DRX

Symbols	Description	Chemical
Ka	Kaolinite	$Al_2Si_2O_5(OH)_4$
Mu	Muscovite	$KAl_3Si_3O_{10}(OH)_2$
Q	Quartz	SiO_2

The results show a highly crystallinity and relative abundance of kaolinite $Al_2Si_2O_5(OH)_4$ with less important species as muscovite $KAl_3SiO_{10}(OH)_2$ and Quartz (SiO_2). While Muscovite can get to play an unfavorable role in bleaching kaolin was not possible in this first inspection the identification of hematite and/or goethite, responsible for unwanted coloration kaolin raw materials, one of the answers to this problem is the low amount of total iron as measured by X-Ray Fluorescence (XRF) revealed an average in the study samples of 1.26% by weight. On the other hand, an inspection of these diffraction patterns reveal no difference in crystallinity between samples, for that reason, this is not an influential parameter in the sensitivities above mentioned.

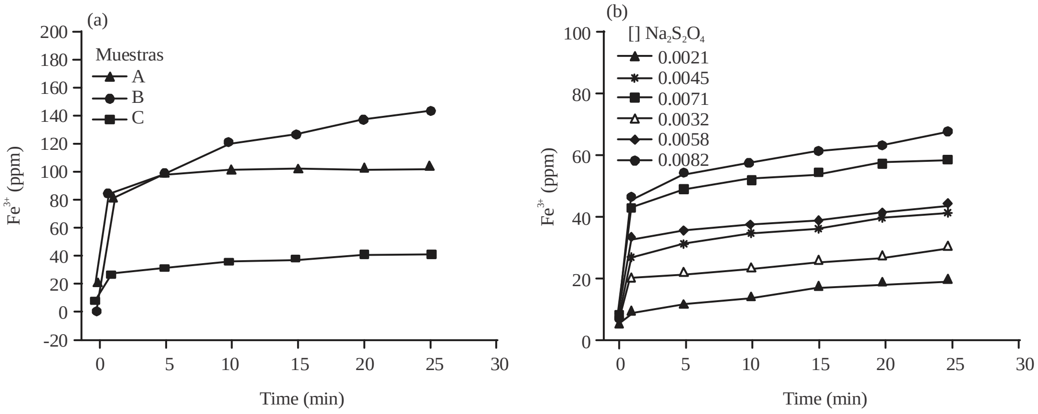

Fig. 2(a, b): Iron concentration in solution (a) Samples A, B and C processed at 4.5×10^{-3} M reducing agent and (b) C samples processed under varying the reducing agent concentrations

Whiteness index related to the total iron content in each sample: Starting spectrograms obtained using a reflectance spectrophotometer with D45 standard illuminant and adapting these results with ASTM E313-05 were calculated CIELAB colorimetric coordinates. Below (Table 4) lists the percentage of Whiteness (W%) and the total iron content in each sample.

The iron content and whiteness index in the samples are inversely related variables, namely, increasing of iron in a sample of kaolin implies lower whiteness index.

Iron in solution measured by atomic absorption spectrometry: In order to establish the role of reducing agent in bleaching kaolin, an experimental methodology that allowed evaluation of the processing step of the samples using a concentration of 4.5×10-3 M Na$_2$S$_2$O$_4$ was proposed (Fig. 2a). They describe the kinetics of iron dissolution during 25 min until after addition of the reducing agent also that this measure is greater for the sample A (145 ppm), less for Sample C (26 ppm) and observed an intermediate value for Sample B (100 ppm). Therefore and according to the scale bleaching susceptibility mentioned previously, this parameter can now relate to the measurement of iron dissolution, it is also important to stress in each of these curves, the growing trend in the first minutes and further stability, however, the sample A retains a slight upward trend to the end of the experiment.

On the other hand, Fig. 2b relates the concentration of iron in solution measured in ppm for each step of the experimental procedure with Sample B above but this time, the concentration of Na$_2$S$_2$O$_4$ was varied in 2.1×10^{-3}, 3.2×10^{-3}, 4.5×10^{-3}, 5.8×10^{-3}, 7.1×10^{-3} and 8.0×10^{-3} M. This sample is chosen as a reference for study because of its less susceptibility to bleaching.

Table 4: Relationship between the whiteness index (W%) and Fe$_2$O$_3$% the kaolinites

Samples	Whiteness (W%)	Fe$_2$O$_3$%
A	43.44	1.26
B	51.18	1.20
C	32.77	1.33

Table 5: The extracted iron percentage measured by XRF in the Samples B and C based on the total iron in the raw material. Coalition reducing agent 4.5×10^{-3} M

	Sample B		Sample C	
t (min)	Fe extracted (%)	W%	Fe extracted%	W%
Raw material	0	51.18	0	32.77
Begin	0.004	51.22	0.071	41.47
0	0.01	62.65	0.23	43.76
5	3.69	63.66	1.075	45.96
10	4.57	63.40	1.21	46.05
15	4.8	63.61	1.25	46.01
20	5.19	63.43	1.38	46.14
25	5.42	62.86	1.42	46.49

Total iron measured by XRF related whiteness index (W%): Table 5 shows the relationship between the iron extracted percentage at each stage of the bleaching process of the Samples B and C using a concentration of no >4.5×10^{-3} M reducing agent, these measurements were made with the XRF technique and related with whiteness index (W%) achieved. It is important to rule out these results, little or no extraction of iron in the first two stages of the experimental process of Sample B, i.e., the point "initial" or pulp and "0 minute" or revealing pH conditioning the walking action of sulfuric acid in the dissolution of hematite, following stages, 5-25 min after the addition of the reducing agent exhibit a uniform relationship Fe-W%.

Hydrometallurgical study from kaolin bleaching: Considering the hematite color, after dilution in water reducing agent, this mineral adhered to the surface of kaolinite is dissolved in water in a leaching process whose mechanism is summarized as:

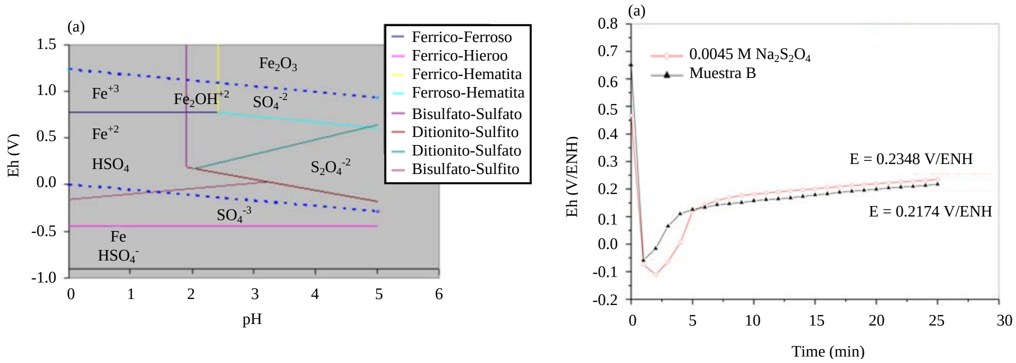

Fig. 3(a, b): (a) Thermodynamic stability diagram of the bleaching process and (b) The redox potential of the sample processing B

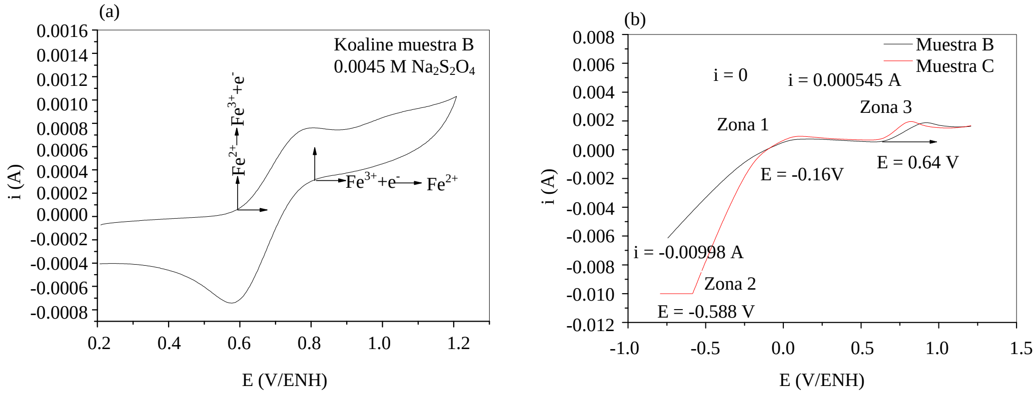

Fig. 4(a, b): Linear voltammetry (a and b) Cyclic potentiostatic mode in bleaching clay B using an equivalent concentration of 4.5×10^{-3} M Na$_2$S2O$_4$

$$3H_2SO_4 \rightarrow 6H^+ + 3(SO_4)^{-2} \quad (4)$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \quad (5)$$

It was built with the HSC Chemistry® thermodynamic the stability diagram, Fe-S-H2O, shown in Fig. 3a in which conditions are established thermodynamic stability of the species involved in the bleaching process. In this diagram, also known as Pourbaix diagram can be deducted stability regions of the most important species in the bleaching process, as are the pairs Fe^{+3} and Fe^{+2} (Ferric-Ferrous), Fe^{+3} and Fe$_2$O$_3$ (Hematite ferric), among others. These regions of stability can be deduced from the expression of the equilibrium constant, calculating the ratio of concentration of the species to a specific pH.

In these diagrams construction should be noted that a vertical line is a balance type acid/base between the two species in question and is therefore dependent only on the pH. For example, the balance Fe^{+3}/Fe$_2$O$_3$, Fe$_2$O$_3$ direct step to ferric iron in solution is achieved by lowering the pH below 2.43, on the other hand, horizontal lines redox processes are totally independent of pH and, in the Fe^{+3} can only Fe^{+2} pass through a pure reduction process requiring a reduction potential (E°) equal to 0.77 V. Diagonal lines are monitored by the Nernst equation, dependent as separate processes both the redox potential and pH, in the case of stability limits of water. Thus, hematite water insoluble is dissolved by sulfuric acid generating species Fe^{3+} and promoting redox balance Fe^{3+}/Fe^{2+} with thermodynamic stability under standard conditions at 0.77 V/NHE, finally, the reducing agent involved in the bleaching process causing reduction Fe^{3+}/Fe^{2+}, seen experimentally reducing potential increased (Fig. 3b) and the solution concentration of Fe^{2+} (Fig. 2).

Approaching the electrochemical kinetics of chemical bleaching process: By linear and cyclic voltammetry techniques was effective the identification of redox reversibility at different stages of the bleaching process as shown in Fig. 4a, b, respectively. It was important to determine the thermodynamic and kinetic factors that control the balance in iron oxidation-reduction in the processing of the Sample B, used as reference in this study due to its low susceptibility to bleaching (Table 5).

CONCLUSION

The differences in the concentration of dissolved iron and its relationship with the whiteness index is an important factor to define the susceptibility to bleaching as the degree of dissolution of the iron comprises a sample of kaolin. It is clear from the results, that even for the sample A is reached the total iron extraction and further that few percentage figures in the extraction of this element implies chromophore substantial gains in Whiteness index a factor symptom of process efficiency. This efficiency will be higher, since, it is considered a method and/or mechanism to decrease the reversibility of dissolved iron species (see, cathodic process 2a) which although not published in this paper a calculation related to the topic reversibility, is sufficient to compare the concentration of dissolved iron in the minute with iron reported in the study to identify the presence of this defect. The post-bleaching stage should be evaluated as it is subject to a serious problem of species re-precipitation dyes, acid washing to ensure the ferric-ferrous thermodynamic stability is a possible short-term solution In the next stage of this study is necessary to determine what fraction of the total iron reported herein corresponds to inside of the structure of kaolinite and that amount is adhered to the surface of the mineral, the latter report important because in theory is part of mineralogical species susceptible to being dissolved by the traditional chemical bleaching process.

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