

## Study of Clays Electrochemical Purification

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Clays, are usually accompanied by other minerals as impurities such as quartz, anatase and especially iron as hydrated oxides or as intercrystalline replacement element. The presence of this iron affects clays in some industrial applications such as in production of ceramics, paper, refractories, etc. Then, its removal is necessary and beneficial. In this work an electrochemical study of two samples of clay from the state of Hidalgo, is presented. The two types of clay were characterized by the technique of mass spectrometry with inductively coupled plasma (ICP). The samples were also studied by electrochemical techniques such as cyclic voltammetry and cathodic inversion voltammetry which showed the energy potential conditions where impurities removal is possible. Samples tested were characterized by scanning electron microscopy (SEM) before and at the end of the process.

### 1. INTRODUCTION

Mexico is a country that has a lot of both metallic and non-metallic mineral resources. In the Mexican state of Hidalgo the importance is higher since there are many non-metallic mineral deposits such as clays. These deposits extend their presence to the Mexican state of Veracruz. (Departamento de Estadística Minera 2010).

Clays are one of the most commonly used minerals in the ceramic industry, in addition this mineral has got a large number of applications such as in the paper industry, paints, cements, pesticides, pharmaceuticals and cosmetics. Most of the deposits arise as alteration of igneous rocks by decomposition of feldspars rock and they are found in nature accompanied by impurities; then, for its industrial use concentration and purification techniques are required (Norton, 1983). These techniques are basically the physical ones such as washing, magnetic separation, elution, sieving etc. (Raghavan, 1997; Chandrasekhar, 2002; Maurya, 1990). However, chemical and microbiological techniques have been proposed for the removal of pollutants such as oxides of iron and titanium. On the other hand, it is important to mention that although these techniques can be effective, their application represents high investment costs and they are inadequate to other contaminants. In this regard, iron content, which is in form of rust, gives these minerals an undesirable colour ranging from white, beige to red.

Colouring of the clays is one of the major problems to solve in the industry and hence the importance of researching the way to purify them with the goal of setting these clays in the characteristics demanded by the industry and thereby increasing their economic value.

In this work, the problem of purifying clays is addressed through electrochemical studies in two different types of clays (different colour) in which the removal of impurities such as iron and titanium oxides will be observed and analysed. Results obtained with this research will allow designing of an optimal process for the purification of the Hidalgo's clays, which will increase the amount of useful clays applied to various industrial sectors.

## 2. EXPERIMENTAL METHODOLOGY

Two types of clays were studied: a yellow clay (AAM) and kaolinitic clay X (CX)), which were characterized by ICP with a spectrophotometer model ICP -OES Perkin Elmer Optima 8300. The samples were prepared as aqueous suspensions 20%w/v with a density of  $1.14 \text{ gr ml}^{-1}$ , according to the specifications of (Flores-Segura 2013). Electrochemical study was performed using the techniques of cyclic voltammetry, cathodic inversion voltammetry and chronopotentiometry using an electrochemical cell with a typical arrangement of three electrodes. These electrodes were a silver plate as working electrode, a graphite rod as the counter electrode and saturated calomel (SCE) as the reference electrode; all of them coupled to PC and a potentiostat-galvanostat PAR263A. Finally, characterization of deposits adhered to the working electrode was performed using the technique of Scanning Electron Microscopy (SEM) with a scanning electron microscope JEOL JSM 6300.

## 3. RESULTS AND DISCUSSION

Initial quantitative characterization by ICP of the two clay samples was performed to determine the main pollutants content. The results are shown in Table 1.

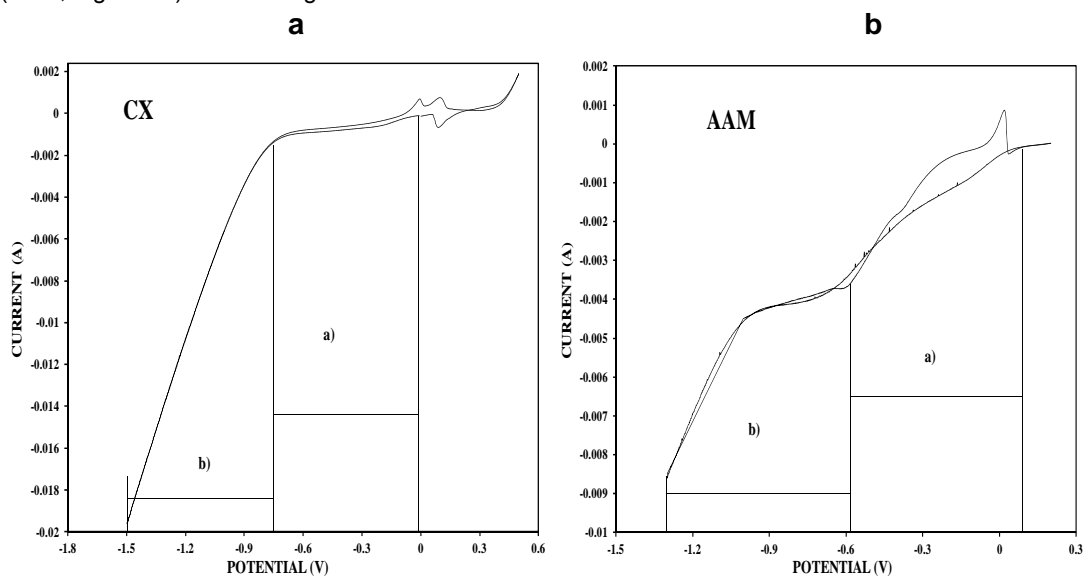
**Table 1. Chemical Composition of AAM and CX clays**

Sample	%Weight	
	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
AAM	21.52	1.25
CX	5.93	7.82

AAM clay sample has a higher content of iron oxides, which provokes many limitations in industrial applications to this clay because of its yellow coloration. The clay sample CX also has iron oxides in a small amount, but significant for some industrial applications such as ceramics, paintings, paper, etc. Finally it is appreciated that the titanium oxide content is lesser in the AAM than in CX clay sample.

## 4. VOLTAMMETRIC STUDIES

Figure 1 shows voltammograms of the two clay samples: kaolinitic clay X (CX, Figure 1a) and yellow clay (AAM, Figure 1b). Voltammograms are initiated in the cathodic direction to a scan rate of  $25 \text{ mVs}^{-1}$ .



**Figure 1.** Voltammograms obtained in suspensions of CX and AAM clay respectively. Scan rate of  $25 \text{ mVs}^{-1}$ . Sweep started in cathodic direction.

In Figure 1a, the voltammetric response of the CX clay suspension shows a cathodic process in the interval from 0 to -0.75V vs SCE (a), which is attributed to the reduction in the aqueous medium. Other reduction process is also observed in the interval of -0.75 to -1.5V vs SCE (b), which is attributed to the reduction of Fe or Ti oxides. By reversing the potential sweep, two oxidation processes can be distinguished, one in the range of -0.095 to 0.02V vs SCE and the other in the range of 0.05 to 0.15V vs SCE. These two peaks can be attributed to the oxidation of the titanium and iron species, respectively; reduced on the forward scan.

In Figure 1b, the response of the clay AAM also presents two reduction processes, one in the interval from 0.14 to -0.59V vs SCE (a) and the other in the range from -0.59 to -1.3V vs SCE (b); they are attributed to the reduction of the medium and the reduction species of iron and titanium, respectively. In reversing the potential sweep, the graph do not shows the two corresponding oxidation processes; instead, there is only one peak that is attributed to the oxidation of the iron reduced in the forward scan.

A cathodic inversion voltammetry study was performed maintaining the cathodic potential inversion during 240 s in order to verify and refine the energy conditions of potential and / or current where the reduction of the impurities in the clays is performed and where the medium is reduced.

## 5. CATHODIC VOLTAMMETRIC INVERSION STUDY

Figure 2 shows cathodic voltammograms where the inversion cathodic potential is maintained during 240 s min on the two clay samples studied (CX Figure. 2a and AAM Figure. 2b). It is noteworthy that each voltammetric curve was obtained on a freshly polished silver electrode.

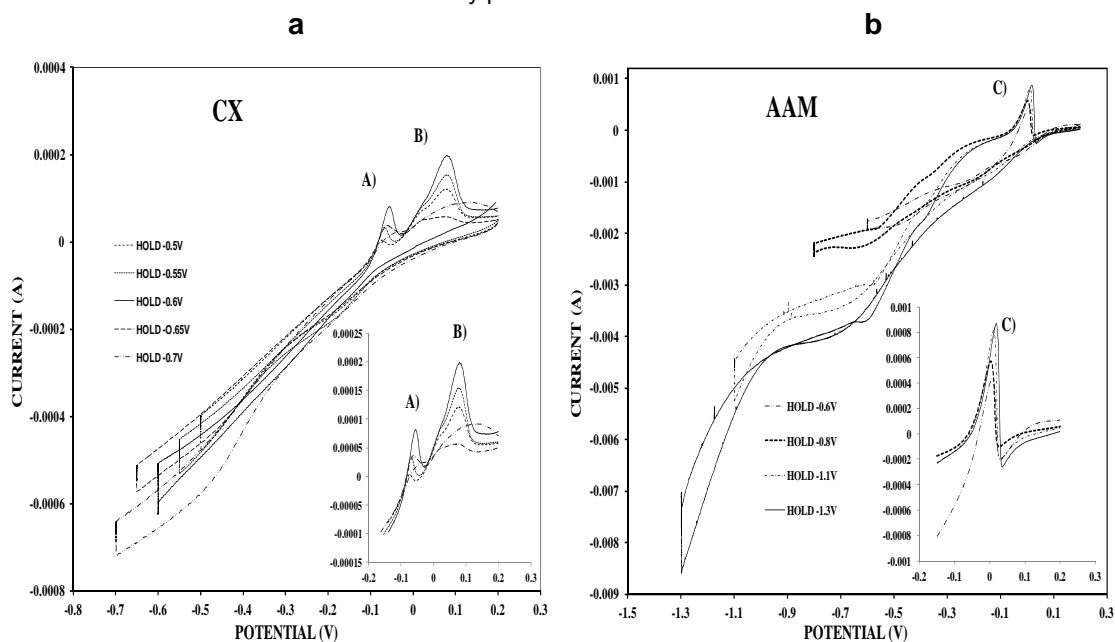


Figure 2. Voltammograms obtained in suspensions of CX and AAM clays respectively. Scan rate of  $25 \text{ mVs}^{-1}$ . Sweep started in cathodic direction.

In Figure 2a, it is observed that as the reversal potential is more negative (from -0.5 to -0.6V vs SCE) the oxidation peak current for Ti and Fe species (A and B, respectively) is increased. This occurs until the inversion potential of -0.6V vs SCE (see enlargement). The figure also shows that oxidation current peaks A and B decreases at higher potentials than -0.65V vs SCE. This behaviour is attributed to the fact that there is less deposit on the silver electrode because the hydrogen evolution reaction is happening on it. Furthermore, it is observed on the graphic that the peaks are shifted to more positive potentials; which is the typical behaviour of the oxidation process of a metal that is being concentrated at the electrode surface [4, 5], according to the corresponding Nernst Law.

In figure 2b, only one peak (C) appears as the inversion potential becomes more cathodic (-0.6 to -1.3V vs SCE) and oxidation current increases. This oxidation process is attributed to the dissolution of the co-deposit Ti / Fe formed on the surface of silver electrode in the forward scan. This proposal is done because the oxidation process occurs at an intermediate potential between -0.1V and 0.1V vs SCE.

It is noteworthy that the current of the oxidation peaks A, B and C is higher and the peaks are better defined when the reversal potential is maintained in a value greater than that of Figure 1. This behaviour is attributed to the fact that there is higher transformation of reduced mass in the forward sweep.

Results of the techniques indicate that the potential range to carry out the reduction of Ti are between -0.5 and -0.6V vs SCE for CX clay and the reduction of the Fe is performed between -0.6 and -1.3V vs SCE for AAM clay.

A chronoamperometric study was performed in order to corroborate the reduction process of the iron and titanium content in the samples with higher concentrations. This study was carried out during 3600s.

## 6. CHRONOAMPEROMETRIC STUDY

In figure 3, the chronoamperometric transients obtained with clays solutions (AAM and CX, respectively) are shown. These transients were obtained by imposing a potential of -1.3 V vs SCE on the Ag electrode and the AAM clay and a potential of -0.6V vs SCE with the Ag electrode and the CX clay, during 3600s.

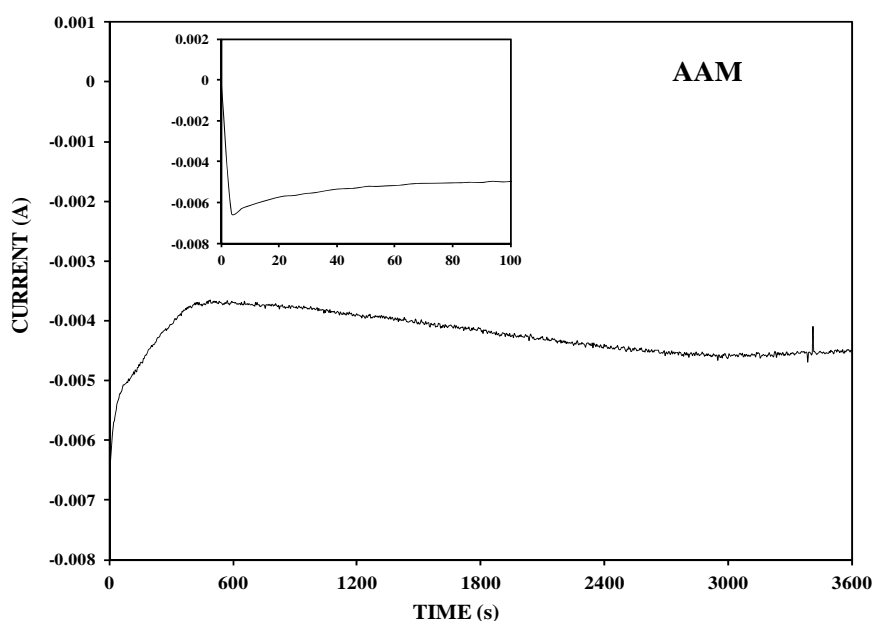


Figure 3. Chronoamperometric transient obtained with the AAM clay, using a three electrode cell and by imposing a potential of -1.3V vs SCE during 3600 s.

The charge of the double layer is observed in figure 3 in the range of 0 to 20 s. After 20 s there is a diminishing of the cathodic current until the experiment has achieved 550s. This diminishing can be attributed to the co-deposit Ti/Fe on the Ag electrode surface. Also, from 550s and after the cathodic current increases indicating the presence of the Ti/Fe co-deposit coupled with the hydrogen evolution.

This behaviour is very important because in the industrial processes hydrogen evolution has to be avoided in order to optimize the energetic conditions and the time to achieve the deposit with the desired properties.

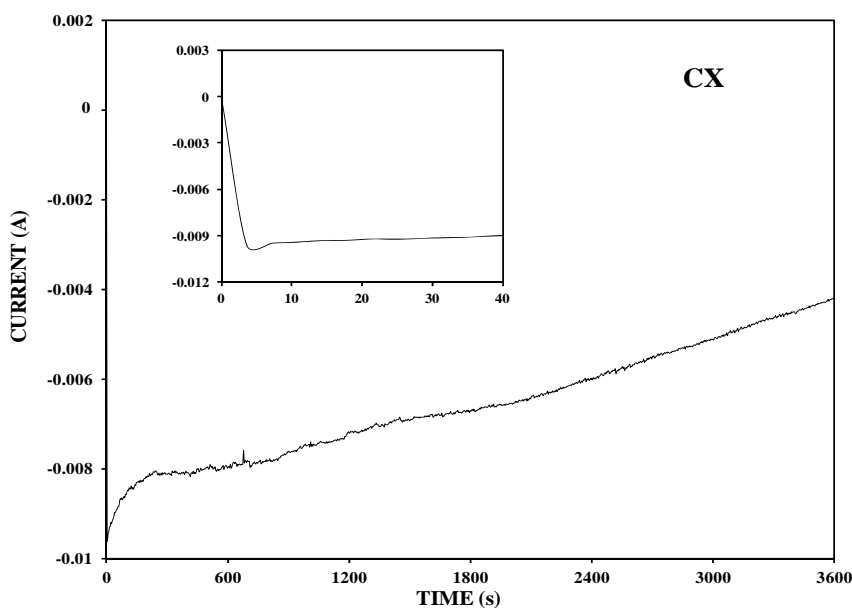


Figure 4. Chronoamperometric transient obtained with the CX clay, using a three electrode cell and by imposing a potential of  $-1.3\text{V}$  vs SCE during 3600 s.

Finally, figure 4 shows that the charge of the double layer is carried out to a shorter period from 0 to 8 s. After that, there is a diminishing in the cathodic current during the experiment, i.e. 3600s. This behaviour could be attributed to the Ti/Fe co-deposit that requires less current due to the modification of the Ag electrode Surface and the change in the energetic conditions.

Also these results are very important because they show that there is a relationship between the Fe and Ti content that allows optimizing the energetic conditions and then diminishing the costs in purification processes.

## 7. CHARACTERIZATION OF MINERAL OUTPUT

The deposit adhered onto the silver electrode surface when a potential of  $-0.6$  and  $-1.3\text{V}$  vs SCE with CX and AAM clays, respectively, was verified by the technique of Scanning Electron Microscopy (SEM) coupled with microanalysis of energy dispersive X-ray (EDS).

Figure 5 show the micrographs of Ti and Fe deposits obtained on the silver electrode surface using low-resolution SEM.

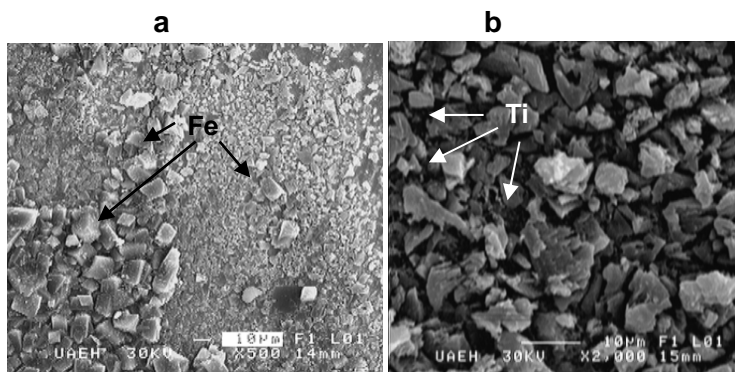


Figure 5. Micrographs of the clay samples AAM (a) and CX (b) obtained by low-resolution SEM.

In Figures 5a and 5b, the micrographs of the massive deposits of the metal cores of Fe and Ti from the surface of the silver electrode are observed. They do not present homogeneous crystal form, since there are different sizes. This result could corroborate the microanalysis study of X-ray energy dispersive (EDS) (Figure. 6a and Figure 6b) where the corresponding peaks of Fe and Ti are observed in the samples of the electrochemically treated clays.

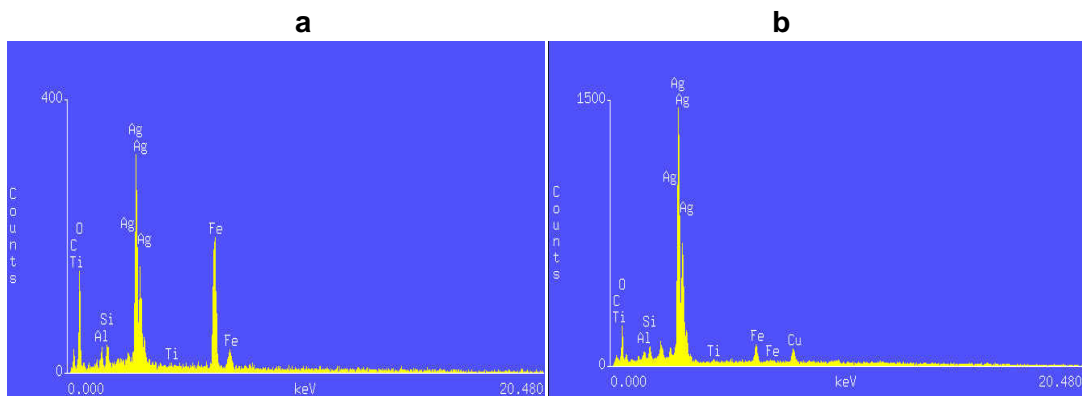


Figure 6. Diffraction graphs of the clay samples AAM (a) and CX (b) obtained with EDS.

## 8. CONCLUSIONS

Voltammetric studies indicated that potential ranges where the purification of the CX and AAM clays can be carried out are from -0.75 to -1.5V and from -0.59 to -1.3V vs SCE, respectively. The cathodic inversion voltammetry study served to precise the potential where the reduction of the Fe and Ti oxides occurs (-1.3 and -0.6V vs SCE, respectively). The deposit of Fe and Ti was corroborated by EDS; however, studies with clays of different composition are being conducted to confirm the results presented here.

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