



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 3, Issue 3, May 2014

Influence of Different Dispersants in Electrochemical Reduction of Iron Oxides from Kaolin Clay

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Abstract— In the present research work was carried out the study of the electrochemical behavior of iron species in solutions prepared from kaolin and different industrial dispersants. The iron species present different behavior in relation with pH, because that one solution pH was adjusted in order to study electro activity of the species in acid pH. To carry out this study was used a diagram type Pourbaix in order to establish the thermodynamic potentials of oxidation and reduction. These results were compared with kinetic studies by means of cyclic voltammetry. These studies revealed that the species of iron are more electro active in the solutions prepared with sodium hexameta phosphate and sodium polyacrylate and that setting to an acid pH, the electro activity of iron species increases.

*Index Terms—*Electrochemistry, kaolin, iron, pH adjustment.

I. INTRODUCTION

Kaolin clays are widely studied due to their considerable economic and industrial importance. The pure kaolin clay has a white matte color, with a soft and non-abrasive texture, high adhesion, in addition to having other features that make it ideal for several industrial applications [1]. However, the clay exists as much in nature is not presented in its purest form. The main problem is that the impurities in the kaolin clay degrade its properties such as color, smoothness, and adhesion. In countries like the United States of America, Germany and England, various techniques have been developed to reduce these impurities. Especially iron oxides are the main contributors of pigmentation. The main techniques used today are: leaching [2-5], high-intensity magnetic separation [6, 7], flotation and flocculation [1, 8]. The application of these techniques is expensive and in Mexico is not yet systematically applied to benefit kaolin clay [9].

Furthermore, a previous study [10], demonstrated that it is feasible the use of simple techniques for the purification of kaolin such as electrolysis. For application of this technique it is necessary that the solution allows the conduction of electric current. Industrially, various substances are applied during wet processing of kaolin clays, these substances are used as dispersants in aqueous media for processing, handling and preparing slurries during the manufacturing process. That is why in the present research is studied the electrochemical activity of the iron present in these slurries prepared with dispersants commonly used, in order to assess whether during the current industrial processes can be implemented a kaolin clays purification by electrolysis.

II. EXPERIMENTAL

Chemical analysis was carried out with a Perkin Elmer spectrometer Optima 3000XL, ICP-OES; for this study, samples were previously digested in an acid medium of HF and H₃BO₃.

Construction of Pourbaix type diagrams were performed with Outokumpu HSC Chemistry ® for Windows software [11]. Clay solutions were made with commercial beige kaolin clay and dispersed in deionized water by adding separately sodium polyacrylate, sodium hexametaphosphate, sodium hydroxide and calcium hydroxide as dispersants, all reagent grade. Was used for the adjustment of pH reagent grade HCl; the solutions were shaken for 30 minutes with an agitator by convection.



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Cyclic voltammetry and electrochemical techniques were applied with a potentiostat-galvanostat PAR263A, in a typical three-electrode cell. The electrodes used were: as working, a plate of silver 99.9% of purity; a graphite bar as counter electrode and as reference a Calomel electrode (SCE). All the measurements was converted to the standard hydrogen electrode (SHE) for comparative purposes.

III. RESULTS

To confirm the presence of iron in the kaolin used as raw material to prepare the solutions, chemical analysis was performed by ICP-OES, and the results are shown in table 1.

Table 1. Chemical analysis raw kaolin clay

Compound	% Wt.									
	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	MgO	MnO ₂	ZnO	ZrO ₂	TiO ₂	Loi
Kaolin	46.688	37.635	0.212	1.418	0.028	0.028	0.074	0.177	1.035	12.540

The kaolin clay contains impurities such as iron (1.418%) in the form of oxides, in addition to titanium (1.035%). It contains aluminum and silicon, which are part of the kaolinite, the main component of this type of clays.

In order to establish the potential range where takes place the electrochemical reduction of iron according to the pH of solutions, Pourbaix diagram of the system Fe – H₂O was held, which is shown in Figure 1.

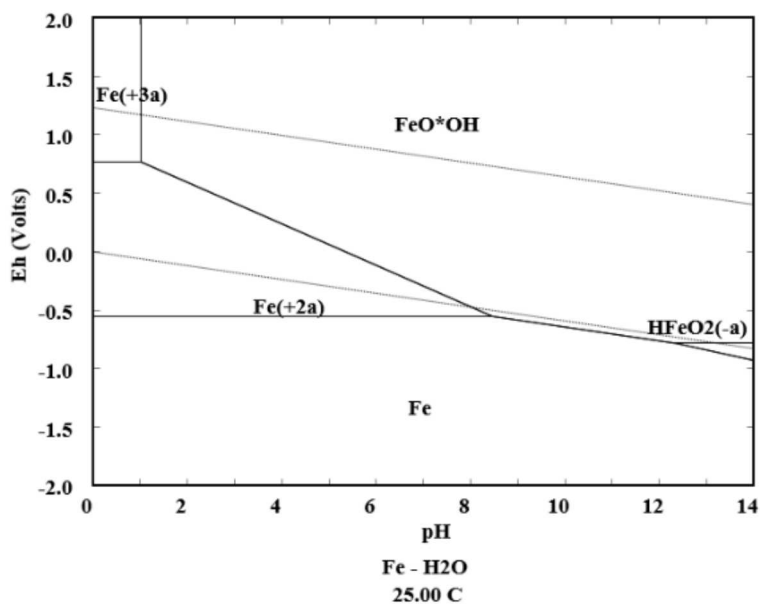


Fig 1. Pourbaix diagram of iron in aqueous medium at 25 °C with Fe 2.35 mM (E vs. SHE)

At a pH between 0 and 1, the soluble Fe³⁺ species are presents in potential range of 0.77 V to 2.0 V, from pH 1 and up to 8.3 can exist a soluble specie of Fe⁺² in a potential range from 0.77 V to - 0. 53V, as shown in the diagram the predominance area, where this specie is present, decreases when the pH increases. One of the species with greater predominance in a wide range of pH (from 1 to 14) is FeOOH, a species of Fe³⁺, the more stable in this system. It is also observed a reduction of Fe²⁺ to Fe⁰ and another of FeOOH to Fe⁰ at potentials lower than - 0.53 V at all pH scale. However, from a pH of 8.53 and until pH 14, Fe⁰ reduction occurs at more cathodic potentials due to the instability of the metallic iron at alkaline pH values. This indicates that in this system may be the thermodynamic conditions to produce metallic iron as a coating and the electro activity of Fe enhances in acidic pH [12]. However, industrial dispersants due to its chemical nature alter the pH of the solutions. As noted in the previous study, the pH of the solution can affect electro activity of iron species. Due this the measurements of the pH of the solutions prepared with industrial dispersants were conducted. These results are shown in Table 2.

Table 2. pH measurement of the solutions prepared with kaolin clay at 25 ° C.

Dispersant	pH
Sodium hydroxide	11.58
Calcium hydroxide	10.76
Sodium polyacrylate	7.98
Sodium hexametaphosphate	7.33

The solutions with alkaline pH are those prepared with hydroxides, with a pH of 11.58 for sodium hydroxide and 10.76 for calcium hydroxide. The corresponding to the polyacrylate sodium and sodium hexametaphosphate, they presented a value of pH more neutral of 7.98 and 7.33 respectively. These results indicate that in these latest dispersants electrochemical iron species increased activity is expected. In order to corroborate these arguments, studies of cyclic voltammetry were conducted, which are presented in figures 2 and 3, the results were grouped according to their pH.

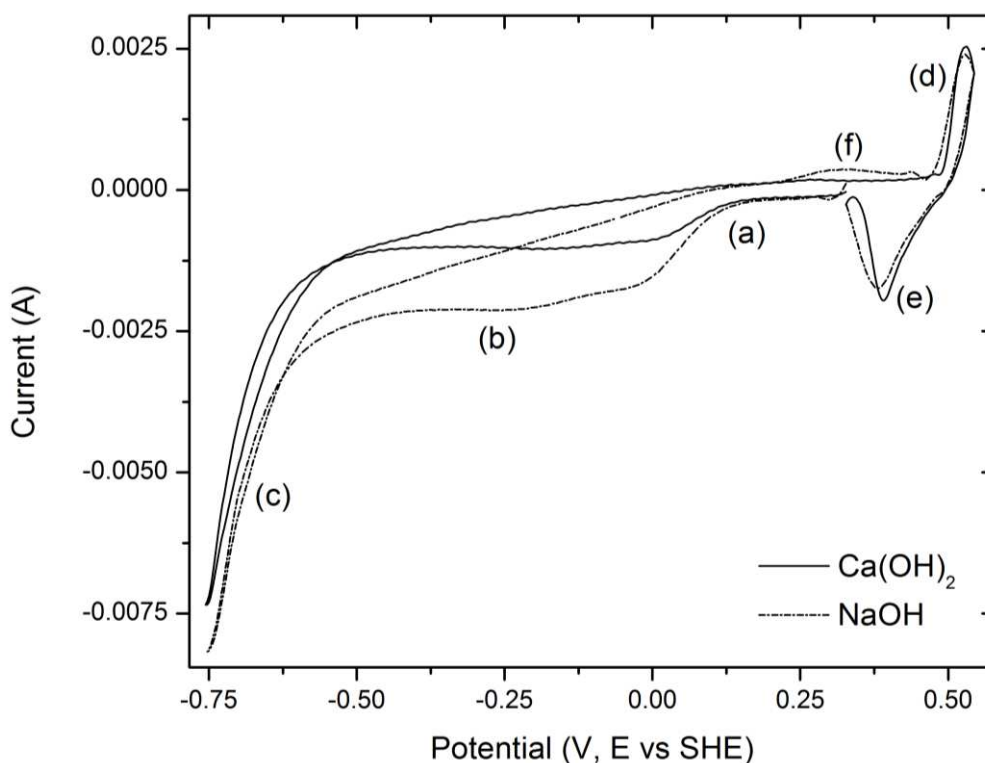


Fig 2. Voltammeteries obtained from kaolin solutions prepared with Ca(OH)₂ and NaOH, at a scan rate of 25 mV s⁻¹.

In Figure 2, on the curve corresponding to calcium hydroxide voltammetric, presents different reduction and oxidation processes. This curve shows a reduction process (a) followed by another process (b) this behavior, attributed to the reduction of the environment since according to the diagram of Pourbaix at a pH of 11.58, reduction of any kind in corresponding to the iron does not takes place in the potential of between 0.3 V and - 0.51 V which is the range of potential corresponding to these processes.

Likewise an increase of cathodic current in the process can be observed in (c) from - 0.51 V, this current increase arises with a sudden drop, which indicates that the evolution of hydrogen is being conducted on the electrode. This last is confirmed by the figure 1 diagram, at a pH near to 11, hydrogen evolution begins at a potential near to - 0.5 V. Likewise, it corroborates that the reduction of Fe³⁺ to metallic iron takes place as a coupled process with the

evolution of hydrogen in the surface of electrode. On the other hand, an oxidation process (d) is observed to reverse scan, which is attributed to the oxidation of the species Fe^{2+} to Fe^{3+} . When the scan is reversed again occurs the process (e) according to the literature which corresponds to a reduction of Fe^{3+} to Fe^{2+} [12].

In the curve corresponding to the solution prepared with sodium hydroxide, arise also processes reduction (a) and (b) in the range of potential between 0.3 V and -0.59 V, which is the reduction of the electrolytic medium. The only difference with the processes corresponding to the prepared solution with calcium hydroxide is arising more cathodic current for the same potential, especially in the process (b). Likewise, the process (c) begins at a potential of -0.6 V which is slightly more cathodic that previous curve, this can be attributed to the chemical nature of this dispersant displaces the evolution of hydrogen toward this potential. In the range of potential of the process (c) carries out the species of iron reduction to metallic iron coupled with the evolution of hydrogen. On the other hand, in the reverse scan, presents a process (f), which corresponds to the oxidation of the species reduced during (a, b or c). Also in this curve are present the processes (d) and (e), which correspond to the change of Fe^{2+} to Fe^{3+} and vice versa [12].

The voltamperometric results corresponding to the solutions prepared with sodium polyacrylate and sodium hexametaphosphate are presented in Figure 3.

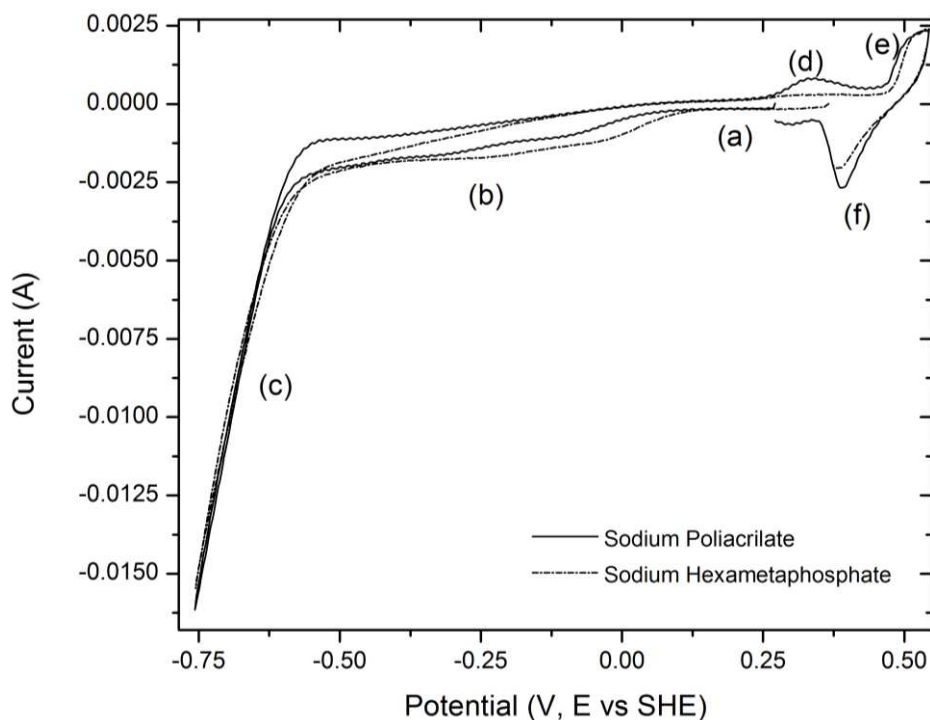


Fig 3. Voltammeteries obtained from kaolin solutions prepared with sodium polyacrylate and sodium hexametaphosphate, at a scan rate 25 mV s-1.

A reduction process (a) is present in curve for sodium polyacrylate (Fig. 3) in a range of potential between 0.27 V and 0.02 V. This process is attributed to the medium reduction since as is confirmed by the diagram of figure 1, in this range of potential, at pH 7.98, no reduction of iron species are present. The curve also presents a reductive process (b) in a range of potential between 0.02 V and -0.57 V, which can be attributed to reduction of $FeOOH$ to a soluble species of Fe^{2+} . In the direction of the scan, is increased the cathodic current from a potential of -0.57 V to -0.75 V called process (c), this process corresponds to the reduction of Fe^{2+} to metallic iron and the hydrogen evolution, this results correspond to the diagram of figure 1. When the scan is inversed a process (d) appears which is attributed to the oxidation of the reduced species in the processes (a, b or c). Also in this curve, the processes (e) and (f) are shown, which correspond to the change of Fe^{2+} to Fe^{3+} , and vice versa [12].

In the curve of the solution prepared with sodium hexametaphosphate (Figure 3), are also presented the reduction processes (a, b and c), similarly to the last one and almost in the same potentials. These processes are attributed to the reduction of the electrochemical medium for the case of (a) and (b) and the reduction of FeOOH to Fe^0 , coupled with the evolution of hydrogen for the process (c). It is also observed that this curve shows a peak oxidation (e) and (f) in the inversed scan.

The similar behavior of these two dispersants can be attributed to the pH in both solutions is very close. These also can be attributed to both dispersants possess sodium in their chemical composition.

When comparing the four solutions was observed that similar oxidation-reduction processes occur in all. However, the main difference is that the current changes to at a same potential; for a potential of -0.7 V at a pH between 1 and 10, Pourbaix diagram indicates that the transformation of iron species to metallic iron is coupled with the evolution of hydrogen. In the case of alkaline pH solutions present a current reduction of -0.0052 A , while the solutions with neutral pH present a current of -0.0107 Amp . The increase of current reduction may correspond to a major transformation of the species of iron in the more acid solutions.

In order to corroborate that the iron species are more reactive in acidic medium, another study was conducted by adjusting the pH at 1.2 in the solution prepared with sodium polyacrylate, the voltammetry results are shown in Figure 4.

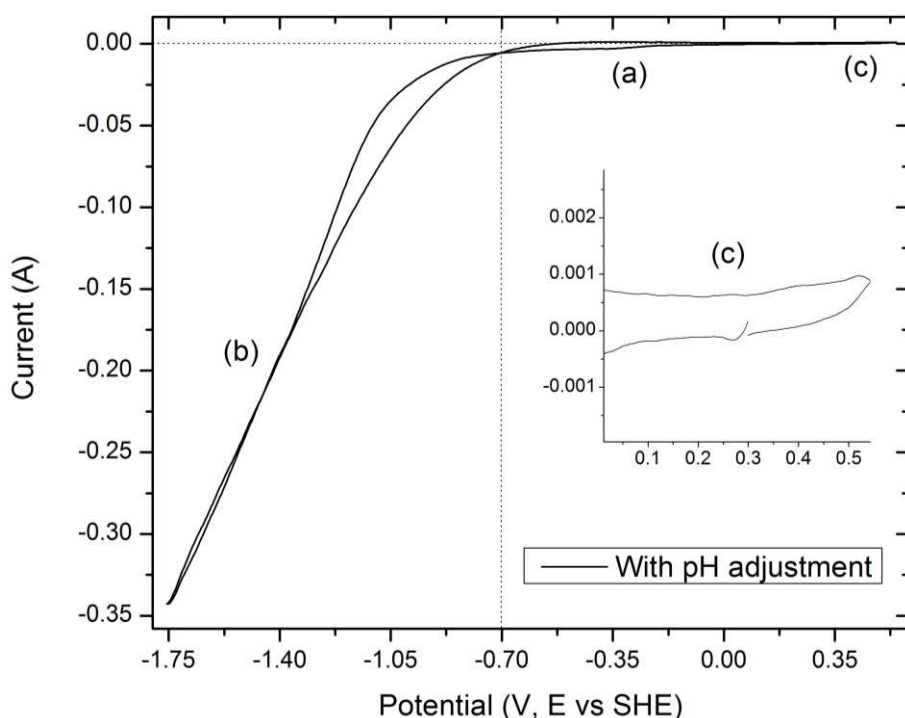


Fig 4. Voltammetry obtained from kaolin solution prepared with sodium polyacrylate and adjusting pH to 1.2, at a scan rate of 25 mV s^{-1} .

In Figure 4, the voltammetry made on acidic pH is shown. In this one have presented a process (a) in a wide potential range between 0.3 V and -0.71 V . This process is attributed to the reduction of medium and further the reduction of Fe^{3+} to Fe^{2+} . These correspond to the diagram of figure 1 in the corresponding pH. Likewise, a reduction process (b) is observed with increasing cathodic current from a potential of -0.71 V , the curve present a drop with a large slope, this is attributed to the evolution of hydrogen at the electrode in a coupled process with reduction of the Fe^{2+} species. When the scan is reversed, no oxidation peak is presented. However, it is important to note that a potential of -0.7 V is shown in an intersection curve with a current close to 0 A , which corresponds to an electro crystallization process, this process could correspond to the redox couple $\text{Fe}^{2+}/\text{Fe}^0$. However, in the diagram of Figure 1, at pH of 1.2 this occurs redox couple at a potential of -0.53 V , and in Figure 4 this is presented



ISSN: 2319-5967

ISO 9001:2008 Certified

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displaced to more negative potential; this may be due to the interfacial conditions are different because solid species (kaolin clay) are present in solution.

IV. CONCLUSIONS

Preparing the solutions was confirmed. By Pourbaix diagram Fe - H₂O was confirmed that exist the thermodynamic conditions to perform the electrochemical reduction of iron species present in the solutions. Furthermore, the electrochemical studies revealed that in the solutions prepared with studied dispersants, iron species exhibit electro activity and can be reduced to metallic iron. The pH conditions of these solutions cause that the reduced species are unstable and reversible, so that the processes are presented with low efficiency. Moreover, it is recommended to adjust the pH to acidic values for reduction processes more efficient. It is recommended to study the energy conditions for metal deposits in order to definitively separate the iron from solution.

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