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EFFECT OF ORGANIC ACIDS ON IRON DISSOLUTION FROM KAOLINITIC CLAY

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Abstract

The aim of the paper is to study the dissolution capacity of iron from an iron-stained kaolinitic clay, using two organic acids (oxalic and citric acids) at two different concentration (0.1M and 0.01M, respectively) and at room temperature, to improve kaolin's whiteness. The influence of pH on dissolution is also studied. The results show that, for both acids, the diluted solutions (0.01M) solubilize more iron from the mineral structure, comparable with the concentrated (0.1M) solutions of acids. Among these two acids, the oxalic acid is capable of dissolving large amounts of iron from kaolin and is suitable to use it on a large scale of applications. The effect of these two acids on iron dissolution was investigated at pH between 2 and 5 and the experiments show that the maximum dissolution corresponds to the pH between 2.0 and 3.0 and decrease after pH = 3.

Keywords: kaolin, iron dissolution, oxalic acid, citric acid.

Introduction

The problem of iron dissolution is of particular interest for the industrial minerals like kaolin, since many deposits are contaminated by iron oxides. Clays and clay minerals are very important industrial minerals, with numerous practical applications: in the industry or agriculture, in engineering and construction, in environmental remediation, in geology and in many other miscellaneous applications (Veglio et al., 1998; Lee et al., 2007). Their variety of uses is largely dependent of their mineral structure and composition. The clay minerals are hydrous aluminum silicates and in

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some cases there are alkaline or alkaline earth silicates. As a particle size term, the size fraction comprised of the smallest particles is called the clay fractions. For special applications, some complex structural clays, such as sodium montmorillonite, are processed to become organophilic and/or hydrophobic clays (after Pribylov et al., 2010). Clay minerals of the size of micrometric particles are the most abundant minerals at the earth surface and a major constituent of sedimentary rocks and practically of all soils and paleosoils.

Clay is also a rock term and has no genetic significance, because it is used for residual weathering products, hydrothermaly altered products and sedimentary deposits. As a rock term, kaolin is predominantly formed by kaolinite and/or one of the other kaolinitic minerals. As a mineral term, kaolinite is a clay mineral, part of a group of industrial minerals, which have a layered silicate structure, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra. Kaolinite is by far, the most common kaolin mineral. Organic or inorganic material in clay affects the color and the other physico-chemical properties. In agriculture, knowledge of clay minerals is necessary to understand the structure of soils, the weathering processes that form them, and the nutrients exchanged or extracted from them (Murray, 2007). Exploration geologists know that clay minerals can be used as stratigraphic markers and environmental indicators. Understanding the diagenetic changes in clay minerals is essential to reconstruct the temperature history of potential petroleum basins. Clay minerals are catalysts in the origin of petroleum and play a role in the study of shales or source rocks for petroleum (Murray, 2007). There are numerous classifications of clay and clays minerals.

In some industrial applications, the presence of iron is disadvantageous because it affects the brightness and/or whiteness of kaolin clays. The amount of iron (and also of titanium) coloring oxides is often decisive to evaluate the quality of raw minerals in some industries. Dissolution of iron from kaolinitic structures to improve it´s whiteness is called deferrization and can proceed by a variety of pathways (Ambikadevi and Latithambika, 2000). Low whiteness kaolin appears due to the presence of high iron content (up to 1%), but whiteness can be enhanced by adopting various physico-chemical processes, like magnetic separation, leaching of iron with various reagents, dissolving iron-bearing phases to lower iron content of the kaolin or removing-reduction of iron (Tarjan, 1986). Nowadays, the most iron leaching may be carried out “in situ” by growing of microorganisms in the presence of kaolin. The efficiency of the processe is largely dependent on the biological strain used in the experiment, the pH value and the ratio of culture medium to mass of kaolin (after Cameselle et al., 2002). The most important industries where low whiteness kaolin is used are ceramics and porcelains, white cements, paper industry and medical industry. Although about 80% of all kaolin production is used for paper obtaining, other uses include fillers for rubbers, pigments, textiles, plastics, paints or adhesive materials. The ferric iron content gives a brown-yellowish color to kaolin, which limits its applications. Some physico-chemical methods used for kaolin deferrization are listed in Cameselle et al. (1997).

In the present work a preliminery study of iron chemical dissolution (using oxalic and citric acids, in normal conditions) and the influence of pH on dissolution process from kaolin were performed.

Materials and method

A complete chemical analysis of kaolinite sample (Aghireş, Romania) used in experiment is reported in tab. 1 (Gavriloaiei and Gavriloaiei, 2009).

Tab. 1 Content of the main oxides of kaolin used in experiment (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	L.O.I.
57.10	32.18	1.29	0.65	0.37	0.45	0.10	0.22	5.53

L.O.I. – loss on ignition, 900^0C

Kaolin is basically composed of kaolinite and muscovite; iron is present as magnetite and as amorphous oxides/hydroxides. The amount of iron can vary from kaolin to kaolin, depending on the origin of rock and the geologic processes. The total iron content is more than 1% and it usage in industrial applications involves a low ferric iron content.

The amount of iron which can be removed by leaching process was determined by treatment with oxalic and citric acid solutions. The leaching experiments were carried out in Erlenmeyer flacks, where 5 g kaolin (fine particle size) were suspended in 100 mL of leaching solution of oxalic and citric acid, at different concentrations (0.1 M and 0.01 M, respectively) on a magnetic stirrer and at room temperature.

Other experiments were carried out for studying the pH effect on iron solubilisation (5 h long). To maintain the pH in acidic domain (2.0 to 5.0) droplets of standard HCl/NaOH solutions (0.01N) were used. The initial pH values were measured with a Corning Pinnacle 555 device.

At different moments (0.5, 1, 2, 3, 4, 5 hours for the first experiments series and after 5 h for the second series) small volumes of solution (5 mL) were taken to analyze the solubilisation yield. The concentration of residual iron contents was determined photometrically with *o*-phenanthroline as complexing agent, at 508 nm, using a MPM 1500 microprocessor photometer. Another 5 ml of water were added to Erlenmeyer flasks to have similar volumes of solutions (additional dilution was considered). All the chemicals were reagents grade.

Results and discussions

Oxalic acid

The experiments with oxalic acid were performed at 0.1M and 0.01M concentrations, respectively. Some previously experiments realized with sodium dithionite solution, at 40^0C, for 1 h, showed that around 40–50% of total iron can be removed from the samples used in experiments, which mean the remaining iron is associated with the crystalline structure of the minerals from the ores (Veglio et al., 1996). The experiments with oxalic acid show that the diluted solution of extracting agent (0.01M) is most efficient in iron solubilisation, comparable with the other solution (0.1M) especially for the first interval of the determinations (fig. 1).

As can be seen, a decrease in oxalic acid concentration favors the iron dissolution, for all intervals of time: the diluted solution of oxalic acid solubilizes 29.85 $mg \cdot L^{-1}$ iron from the mineral structure, during the first hour of experiment, while the other solution

solubilizes around 18 mg·L^{-1} in the first 3 hours of experiment. After that, for both solutions, the amount of iron solubilized is decreasing in the next hours of experiments. A higher oxalic acid concentration caused adverse effect on the iron dissolution reaction: the level of solubilized iron for 0.01M oxalic acid was higher comparable with the level obtained with 0.1M oxalic acid.

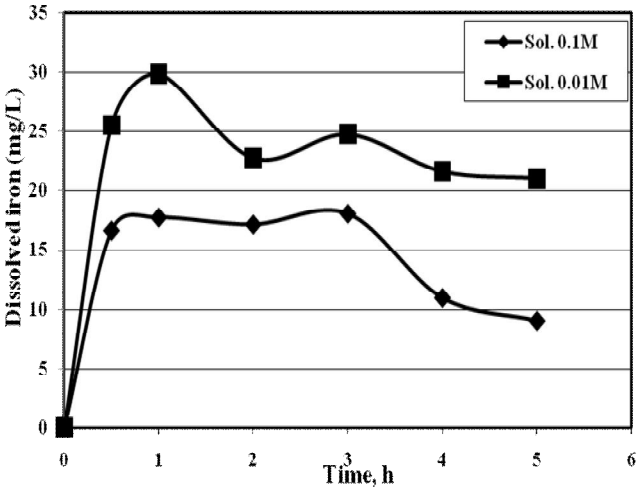

Fig. 1 Effect of oxalic acid (0.1M and 0.01M concentrations, respectively) on iron solubilisation from kaolin (for 5h treatment time)

Experiments with oxalic acid of 0.1M and 0.01M, respectively and pH between 2 and 5 were performed and the results for 5 h treatment time are shown in figure 2. As can be seen, an increase in acidity favors the iron solubilisation for both solutions, in acidic domain (pH ≤ 3.1). Above this pH value the amount of iron solubilized is reduced, for both working solutions. So, the dissolution effect reaches a maximum value for pH between 2.0–3.1.

The use of different organic/inorganic acids for iron dissolution has been utilized in several studies, like alternative to classical clorination technique. Numerous studies reported that the dissolution of magnetite and goethite with oxalic acid reaches a maximum value at pH = 2.7–3.0, while outside of this interval, the dissolution rate decreased very much.

Veglio et al. (1996) show that the effect of oxalic and ascorbic acids decrease at lower pH values, during 5 h of experiments. This decrease indicate that the presence of organic acid is less important when H_2SO_4 is used to adjust the pH value. When organic acid are used for iron dissolution, the maximum extraction yields are achieved after 3 or 4 h of experiments.

Studies with the iron removal process from a yellow kaolin of industrial interest by oxalic and sulphuric acids were performed later by Veglio et al. (1998). For a given oxalic acid concentration, they found that an increase in pH value decreases the yield of the

dissolution. The authors explain this effect by the lower stability of the complexes that are formed and by lower protonation of the mineral surface at higher pH. Good results are obtained even for pH ≤ 1, in the first 30 min. of experiement.

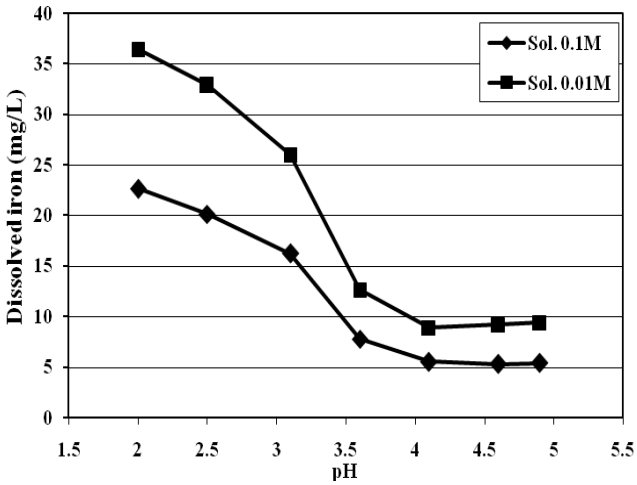

Fig. 2 Effect of pH on iron solubilisation from kaolin with oxalic acid (for 5h treatment time)

Ambikadevi and Latithambika (2000) tested several organic acids in solubization and the results showed that oxalic acid is the most efficient agent that can be used to dissolve iron oxide from ceramic minerals. For 0.15 M oxalic acid the yield of the process was around 70% (or 1.86 $g \cdot L^{-1}$ Fe_2O_3).

Cornell and Schindler (1987) used oxalic acid and they found that the dissolution of hematite (Fe_2O_3) was slower than for some iron oxy-hydroxides like magnetite, goethite and lepidocrocite.

Similar experiments with different oxalic acid solutions show a great leaching capacity for this acid, comparable with the other organic acids and also with the amount of HCl added to adjust the pH value (Cameselle et al., 1997); its intrinsic acidity implies that is necessary to add less HCl to reach low pH values. Oxalic acid is capable of dissolving iron oxides from kaolin, but the yield of the process is strongly dependent by the pH value. Under pH = 2, oxalic acid solubilize a great quantity of iron, forming a soluble complex whose ratio oxalic acid/ferric iron varied between 1/1 to 3/1 (Hochella and White, 1990). Dissolution of iron from kaolinite structures in oxalate solution take place in two-stage reactions: (a) a slowly release of iron through complexation by adsorbed oxalate and (b) a faster reaction, reductive dissolution step involving ferrous oxalate, which accounts for the bulk of the dissolution. Oxalate adsorbs on kaolinite in the pH range used in the experiments. The first step in the slow dissolution process seems to be a step in the formation of a surface iron-oxalate complex. The oxalic acid speciation

in bulk solution as a function of pH shows that the predominant specie at pH 2.6 is $HC_2O_4^-$, suggesting that the proton concentration was equal to the oxalate concentration at this pH (Hochella and White, 1990). The pH value of the working solution govers the distribution of oxalic ions in the leaching system. Below pH = 1.2, oxalic acid exists as $H_2C_2O_4$, where as in pH = 2.5–3.0 domain, the most dominat species is $HC_2O_4^-$ (more than 92%). Above pH = 4, $C_2O_4^{2-}$ ion is the predominant species. Also, the speciation of iron-oxalate complex is pH dependent. For pH greater than 2.5 and more than 0.1 M oxalic acid concentration, the dominat Fe(III)-oxalate species is $Fe(C_2O_4)_3^{3-}$ and for Fe(II)-oxalate species is $Fe(C_2O_4)_2^{2-}$.

The reductive dissolution mechanism of iron oxide minerals by organic reagents has been investigated by Stone and Morgan (1984). Their model for reductive dissolution involves the following surface chemical reactions: diffusion of reductant molecules to the mineral surface; surface chemical reaction with formation of inner sphere complex (where the metal coordination center binds directly to the ligand which substitutes surface H_2O and OH^-) or outer sphere complex (where the inner coordination sphere of the metal centre remains intact); release of oxidized organic product; release of reduced metal ion. A good review on iron dissolution with oxalic acid from different minerals was realized by Lee et al. (2007). It seems that from all the possible complexing carboxyl ligands, oxalic acid (or oxalate ion) is most effective for iron dissolution from mineral substratum. The authors proposed a general reaction summarised below:

$$H^+ + Fe_2O_3 + 5HC_2O_4^- \rightarrow 2Fe(C_2O_4)_2^{2-} + 3H_2O + 2CO_2 \qquad (1)$$

The reaction indicates that species involved in dissolution would be hydrogen ions, oxalate and iron oxide particles. Under optimal conditions (pH = 2.5–3.0, temperature, oxalate concentration, iron oxide mineralogy and size of particle), a high rate of the dissolution will be attained. Once the surface complex has been formed, the dissolution mechanism differs depending on the type of iron mineral concerned (hematite, magnetite, goethite etc.).

Citric acid

The study was done in an analogous way to those presented above for oxalic acid. Figure 3 shows the results for iron solubilization with citric acid.

As we expected, a higher citric acid concentration caused adverse effect on the iron dissolution reaction. Like in the case of oxalic acid, the concentration of solubilized iron from kaolin is higher for the diluted extractable solution, comparable with the concentrated solution of citric acid. As can be seen, the results of the deferrization process with citric acid are lower than those obtained with oxalic acid: the diluted solution of citric acid solubilizes 10.32 $mg \cdot L^{-1}$ iron after 1 h of experiment, while the other solution solubilized 7.7 $mg \cdot L^{-1}$ iron from the mineral structure, in the same interval of time. After that, for both solutions, the amount of iron solubilized is decreasing in the next hours of experiments.

The dissolution of iron from kaolinit with citric acid seems to be also governed by pH which was found to reach a peak in acid domain. The study was realized in the same way for different pH values, meaning that the pH was adjusted with droplets of HCl/NaOH 0.01N (fig. 4).

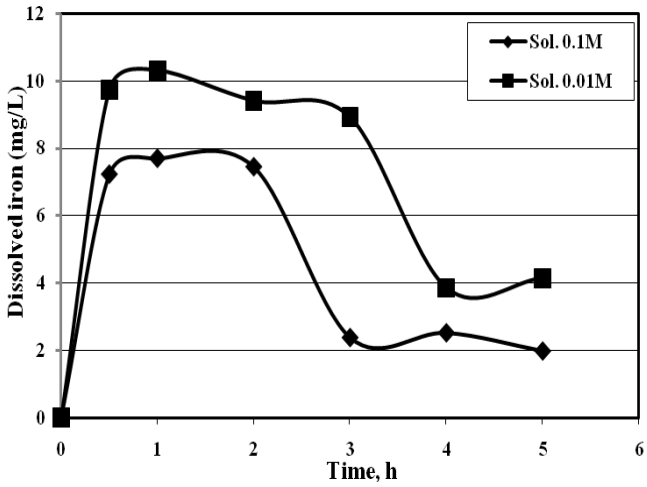

Fig. 3 Effect of citric acid (0.1M and 0.01M concentrations, respectively) on iron solubilisation from kaolin (for 5h treatment time)

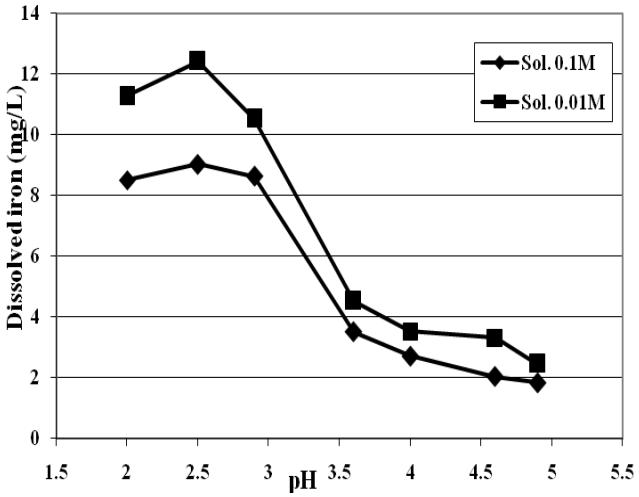

Fig. 4 Effect of pH on iron solubilisation from kaolin with citric acid (for 5h treatment time)

The solubilization of iron from kaolin appears to be better at pH = 2.0–3.0 and than the process is decreased for the pH between 3.0–5.0, for both solutions of citric acid. So,

the dissolution effect with citric acid reaches a maximum value for pH between 2.0–2.9. In the literature, it was clearly presented, that the solubilization of iron with citric acid for pH under 2, adjusted with HCl conc., is due to the added HCl and not to the critic solution of citric acid (Cameselle et al., 1997). That is why, the experiment starts with the pH = 2.

Like in the other case, this effect of decreasing of iron dissolution at higher pH values may be bound up with the lower stability of the complexes that are formed in solution and with the lower protonation of the surface of mineral. Concerning the dissolution with citric acid, the mechanism postulated in the literature for the release of Fe is the classic one of reductive dissolution (Stone and Morgan, 1984). The results show that the process proceeds at a slower rate than in the case of oxalic acid and, also, the yields of dissolution processes are smaller than in the case of oxalic acid.

Conclusions

Chemical methods (specialy leaching with organic acids) are more effective and convenient in iron dissolution from mineral structure. Among these acids (oxalic, gluconic, citric, ascorbic acids etc.), oxalic acid is capable of dissolving large amounts of iron from kaolin, thus making the kaolin suitable for industrial applications.

This paper presents a preliminary study of iron chemical dissolution from kaolin, using oxalic and citric acids (different concentrations) and also the influence of pH value on dissolution. A decrease in oxalic acid concentration favors the iron dissolution, for all intervals of time: the diluted solution of oxalic acid solubilizes almost 30 $mg \cdot L^{-1}$ iron from the mineral structure, during first hour of experiment, while the other solution solubilizes 17.74 $mg \cdot L^{-1}$ in the first 3 hours of experiment. For citric acid, the results are lower than those obtained with oxalic acid: the diluted solution of citric acid solubilizes 10.32 $mg \cdot L^{-1}$ iron after 1 h of experiment, while the other solution solibilized 7.7 $mg \cdot L^{-1}$ iron from the mineral structure, in the same interval of time. In all the cases, the amount of iron solubilized is decreasing in the next hours of experiments.

A higher concentration of oxalic and citric acids has an adverse effect on iron dissolution rate in our study; a precipitation efect of iron-oxalate complex, either on mineral surface or in the bulk solution also affects the concentration of dissolved iron from kaolinit. This means that the adverse effect of high acids concentrations is due to a passivation process and a higher acid concentration contributes to the precipitation of Fe(III) or Fe(II) oxalates. These results are in accordance with other studies on iron dissolution.

The critical effect of solution pH was confirmed with an optimal dissolution that take place at pH = 2.0–3.1 for oxalic acid and at pH = 2.0–2.9 for citric acid. Like in the other cases, this effect of decreasing of iron dissolution to higher pH values may be bound up with the lower stability of the complexes that are formed in solution and with the lower protonation of the mineral surface.

The use of the oxalic and citric acids was investigated because in the literature there are some informations regarding their application on the leaching of iron from kaolins. Moreover, their use could be an alternative for the use of other kind of reagents, such as sodium hypochlorite, sulfur dioxide or sodium dithionite.

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