KINETICS STUDY OF IRON LEACHING FROM KAOLINITIC CLAY USING OXALIC ACID

Felipe Legorreta G., PhD
Academic Area of Earth Sciences and Materials / UAEH, México
Eleazar Salinas R., PhD
Technical University of Esmeraldas "Luis Vargas Torres" Engineering and
Technologies Faculty / Esmeraldas Ecuador (Research Stay)
Leticia E. Hernandez C., PhD
Roman A. Hernandez H., PhD
Eduardo Cerecedo S., PhD
Academic Area of Earth Sciences and Materials / UAEH, México

Abstract

The kinetics study of iron leaching from kaolin clay from the County of Agua Blanca (Mexico) was carried out using solutions of oxalic acid for iron dissolution. The effects of acid concentration and temperature were studied to determinate kinetics parameters during iron leaching in oxalic acid media. It was found that iron dissolution rate increased with increasing of concentration and temperature, respectively. Leaching results showed that iron dissolution from the kaolin clay could be due to a chemical reaction control. The energy of activation calculated in this work was of 50.32 kJ • mol^{-1}, for the interval of temperatures from 273 to 333 K; which is characteristic of a process controlled by chemical reaction. According to the results shown above, iron removal is possible, and this can improve the economic value for this kind of kaolin clay, being possible its use in the ceramic and paper industries as raw material of high quality.

Keywords: Iron leaching, Kaolin clay, Kinetics study, Chemical control

Introduction

The red to yellow pigmentation noticed in many kaolin clay deposits are mainly due to the associated oxides, hydroxides and hydrated oxides of ferric iron such as hematite (red), magnetite (reddish brown), goethite (brownish yellow), lepidocrocite (orange), ferrihydrite (brownish red), etc. These oxides and hydroxides occur either as coatings on individual grains or as discrete fine particles throughout the clay mass *(Yan, L.G. et al., 1978).*

12

Removal of these associated impurities becomes imperative to make the material value-added. The beneficiated clay finds use in paper coating, paper filling and as extenders in paints and polymers.

The use of some inorganic and organic acids or complexing reagents for iron dissolution has been reported to clean up these clays. Most of these are focused on mechanisms of dissolution of hematite and magnetite, using different chemical and experimental conditions *(Saikia, N.J. et al., 2003; Veglio, F. and Toro L., 1993; Veglio, F., Passariello, B., Toro, L. and Marabini, A.M., 1996; Veglio, F. and Toro, L., 1994).*

Reductive dissolution of iron oxide minerals by organic reagents has been investigated by several researchers, and many experimental studies on the basic mechanisms involved have been published *(Segal, M.G. and Sellers, R.M., 1984; Blesa, M.A. and Maroto, A.J., 1986; Borghi, E.B., Regazzoni, A.E., Maroto, A.J. and Blesa, M.A., 1989; Dos Santos, A.M. et at., 1990; Torres, R., Blesa, M.A. and Matijevic, E., 1990; Ambikedavi,V.R. and Lalithambika, M., 2000; Lee, S. et al., 2006; Lee, S. et al., 2007; Panias, D., Taxiarchou, M., Paspaliaris, I. and Kontopoulos, A., 1996).*

Panias et al., *(1996)* have reviewed existing research and initially suggested a reaction mechanism for the dissolution of Fe oxides in organic acids. The mechanism comprises three processes: (1) adsorption of organic ligands from the solution to the solid Fe oxide surface, (2) non-reductive dissolution, and (3) reductive dissolution consisting of an induction and an autocatalytic period. Suggested mechanism indicates the involvement of protons in the dissolution process. Although it may be valid description of the reactions taking place during dissolution of iron oxide, pH was discussed only as a parameter affecting dissolution and, in this case, no additional experimental work was conducted to further verify the validity of the suggested reaction mechanism. The authors concluded that non-reductive dissolution was not a viable reaction pathway at low temperatures.

Panias et al., (1996) have studied the kinetics of dissolution of hematite in oxalic acid too, and found that dissolution was best described by diffusion - controlled shrinking core model. The authors also concluded that dissolution of Fe oxides in oxalic acid was very slow at temperatures ranging from 298 to 333 K and that, is contrary to *Taxiarchou et al, (1997)*, who determinate that dissolution of hematite could be correlated with the oxalate concentration in the mother liqueur.

Lee et al., (2007), have also suggested that the formation of an iron oxalate product layer, at a pH range of 1.6 - 3.2, can inhibit dissolution of hematite in oxalic acid and that increase in the rate of dissolution can be observed with the addition of magnetite (Fe_3O_4) into the studied system. The addition of magnetite to the system was roughly the 10 wt.%.

Martinez et al., (2011), studied the leaching kinetics of low-grade kaolin in oxalic acid solutions; the study variables were temperature, acid concentration and particle size and were found higher dissolution rates with increasing temperature and acid concentration, but decreases with particle size increasing. The authors also concluded that the controlling step is diffusion through the product layer, with energy of activation of 46 kJ•mol^{-1}.

The contribution of kinetics data for minerals of industrial interest such as kaolin clay is important because these are quite different from their geological origin and in contents of iron minerals of complex interactions. Therefore, kinetics data for remove iron from the kaolin clay by using oxalic acid, are considered of great interest to find more industrial applications to these kind of clays such as in the paper coating, advanced ceramics, paints, medicine, etc. The objective of this work is to evaluate the kinetics of leaching of iron from kaolin clay coming from the county of *"Agua Blanca Iturbide, Hgo. (México)"*, using oxalic acid solutions.

Experimental Procedure

Materials: The kaolin mineral sample was obtained from the county of *"Agua Blanca de Iturbide, Hidalgo (México)"*, which was previously reduced in size and was classified by sieving using an ASTM mesh. Mineral particles were used in an average size of 35 microns (µm) in the leaching experiments. In order to know the mineralogy and chemical composition of kaolin clay, three analytic techniques were used: X-ray diffraction with Cu K$_\alpha$ radiation at 40 kV and 40 mA, optical microscopy and atomic absorption spectrophotometry (AAS).

Methodology: The experimental procedure was quite similar to that used in some previous works *(Lee et al., 2007; Martínez, L.A. et al., 2011)*. The present work is based on that done by *Martínez L. A. et al (2011)*, but with a different type of Kaolin clay from mineralogical and geochemical point of view. However, we decided to do a kinetic study for this kind of material taking in account only the study of the effect of acid concentration and temperature, without the evaluation of the effect of particle size, because as was mentioned this material is quite different to that studied for the authors above cited. All the experiments were done using a liter glass kettle put over a hot plate (a thermocouple was used to control the temperature) coupled to a mechanical stirrer (Caframo motor). In order to evaluate the effect of the concentration, were used 0.005 kg kaolin ($\pm$ 35 µm) at an initial volume of 5 x 10^{-4} m^3, a stirring rate of 7200 seconds^{-1} (s^{-1}), and concentrations of 10, 100 and 500 moles of oxalic acid • m^{-3}, and a temperature of 373 K (100 °C); except for experiments in which the effect of temperature was determined, and then 298, 313, 333, 353 and 373 were studied. For experiments where the temperature was evaluated, oxalic acid

concentration was 500 mol • m^{-3}. The pH was kept constant at 1.5 for all experiments by addition of small amounts of saturated NH_4OH and H_2SO_4 solutions. In this work, the effect of particle size was not evaluated, because it was so difficult to get the different particle sizes due to physical mineral characteristics. Then, only was studied acid concentration and temperature effect to determine order of the reaction and energy of activation of global process.

The progress of reaction was followed by taking samples of the solution throughout the experiment at prefixed times, filtering to stop reaction and ensure the real iron content at the prefixed time t, and measuring the dissolved Fe during kinetics study by way of atomic absorption spectrophotometry (AAS). Variations in the mass balance due to the sampling and reagent addition were corrected.

Results and Discussion

Mineralogical Analysis: The results found for the mineralogical and chemical analyses of the kaolin clay are shown in figure 1, figure 2 and table 1. Figure 1 shows the image of the kaolin clay sample with an average particle size of 35 µm, observed at an optical microscope. This image shows a heterogeneous particle size, of reddish color, with some amounts of iron oxides presenting the punctual particulate form; which could contribute in certain manner to the color of the mineral kaolin sample.

Figure 1 General image of sample of kaolin mineral (100x, Optical Microscopy)

On the other hand, figure 2 shows the X-ray diffraction spectrum where can be observed the nature of the crystalline phases present in the mineral. In this spectrum can be appreciated that sample is composed by a greater proportion of kaolinite specie (PDF 089 – 6538), with minor contents of silica in the form of quartz and tridymite. For these kind of kaolinitic minerals, the iron is always considered as an impurity when is present as magnetite (Fe_3O_4), hematite (Fe_2O_3), oxide ferrous titaniferous (Fe_2TiO_4) and

15

greigite (Fe_3S_4). The figure also shows the decreasing of the peaks that corresponds to magnetite and hematite for; (a) natural kaolin mineral and (b) leached kaolin clay; so according with this, we can conclude that during leaching process, it reached a 96% of iron dissolution.
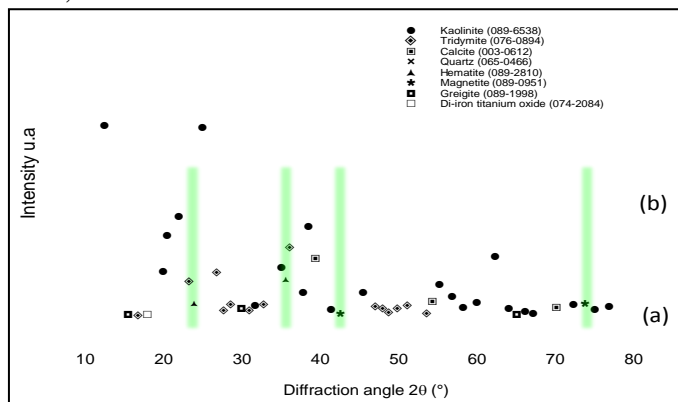

Figure 2 X-ray diffractogram of: a) kaolin mineral (PDF 089 – 6538) and (b) leached kaolin (average particle size of 35 µm)
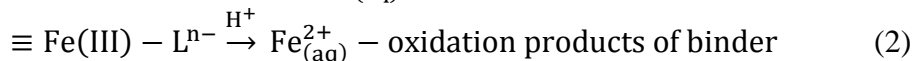
Table 1 Results of Chemical Analysis of the kaolin sample

Components	Wt %
SiO_2	65.00
Al_2O_3	27.00
Fe_3O_4	0.70
CaO	0.04
MgO	0.57
Na_2O	2.65
K_2O	2.42
TiO_2	0.67
LIO*	0.95

LIO* = Loss of ingnition

The table shows the chemical composition of the kaolin clay with adequate values of SiO_2, Al_2O_3 and low contents of Fe_3O_4, which indicates that this material has an ideal composition to the kinetics study of leaching with oxalic acid.

It is important to point that this identification is a general scheme for iron oxides dissolution using carboxylic acids, and includes two types of direct leaching: non-reductive dissolution (equation 1) and reductive dissolution (equation 2). In a critical point, reductive dissolution by Fe (III) - L, eventually becomes dominant *(Panias, D., Taxiarchou, M., Paspaliaris, I. and Kontopoulos, A., 1996)*. Therefore, this point could be the mechanism

that can explain these two steps. When iron is dissolved in oxalic acid solutions, a free oxalate complex is adsorbed on iron surface and detachment of iron from the iron ore surface occurs through a redox reaction *(Blesa, M.A. and Maroto, A.J., 1986).*

$$\equiv Fe(III)\text{-}L^{n-} \xrightarrow{H^+} Fe(III)\text{-}L_{(aq)} \tag{1}$$

$$\equiv Fe(III) - L^{n-} \xrightarrow{H^+} Fe^{2+}_{(aq)} - \text{oxidation products of binder} \tag{2}$$

Where:

L^{n-} : any kind of organic binder with oxidation number n, such as oxalate (L^{n-} = $C_2O_{4\,2-}$ o HC_2O_{4-}), citrate (L^{n-} = $C_6H_5O_{7\,3-}$ o $C_6H_6O_7^{2-}$ o $C_6H_7O_{7-}$).

$\equiv$: Particle surface.

$\equiv$ Fe (III): Lattice of trivalent iron on the particle surface.

$\equiv$ Fe (II): Lattice of bivalent iron on the particle surface

The fast dissolution of magnetite by oxalic acid could be auto-accelerated by Fe^{2+} in magnetite; however reduction of Fe^{3+} to Fe^{2+} in oxalic acid solution was the rate-determining stage of reaction. When ions of Fe (II) were present in the reaction system, reaction rate was increased owing to the high electrons activity on the surface of iron oxide due to the activity of ferrous oxalate complex. The specie involved in the auto-acceleration of the dissolution reaction, is the Fe (II) ion, which is transferred from the solid to solution. In the absence of Fe (II) ions, the generation of ions in solution can be described by equations (1) and (2). When sufficient ferrous oxalate was formed in the dissolution system, the secondary reductive dissolution step became dominant and the whole process was described by equation (3).

$$Fe_3O_4 + 8HC_2O_4^- \rightarrow 2Fe(C_2O_4)_3^{3-} + Fe(C_2O_4)_2^{2-} + 4H_2O \tag{3}$$
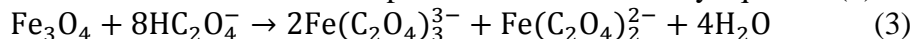
Thus, magnetite which has a structure Fe (II, III)-O can be quickly dissolved, in comparison with hematite (structure Fe (III)-O) in oxalic acid solutions.

Oxalic acid was used as leaching reagent due to the fact that it has been reported as the best for extracting iron from kaolin, in comparison with other organic acids such as citric, malonic, and acetic acid. This is attributed to the fact that oxalic acid has higher acidity, complexing power, and possibly a better reduction ability. This was studied for some authors that tried to find the factors that could influence the iron dissolution process from kaolin with relatively low iron concentrations, using oxalic acid (Saikia N.J. et al., 2003; Veglio, F., Passariello, B., Toro, L. and Marabini, A.M., 1996; Ambikadevi, V.R. and Lalithambika, M., 2000).

Kinetic study: The results obtained during kinetics study of iron extraction, evaluating the effect of oxalic acid concentration and temperature in the range 298 to 373 K were treated with the decreasing core model for heterogeneous reactions both for diffusive and chemical control.

Iron extraction from kaolin clay can be explained with the decreasing core model for spherical particles of constant size *(Levenspiel, O.,1972)*, in which:

$$aA_{fluid} + bB_{particle} \rightarrow Product \qquad (4)$$
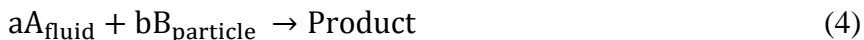
If the reaction rate is controlled by diffusion through an inert product layer, the integrated rate equation is as follows *(Levenspiel, O., 1972)*:

$$1 - \left(\frac{2}{3}\right)X - (1 - X)^{\frac{2}{3}} = K_d t \qquad (5)$$

The above equation represents the shrinking core model for diffusive control. If reaction is controlled by a chemical reaction, equation (5) is transformed to equation (6) and this is called the shrinking core model for chemical control *(Shon, H.Y. and Wadsworth, M.E., 1986)*.

$$1 - (1 - X)^{\frac{1}{3}} = K_T t \qquad (6)$$

Where X is the fraction that have reacted, t is the reaction time and K_d (for diffusive control) and K_T (for chemical control) are the rate constants which are calculated from equations (5) and (6), respectively.

Effect of acid concentration: In order to observe the effect of oxalic acid concentration in the range of 10, 100 & 500 mol • m^{-3}, experiments were done at 298, 313, 333, 353 and 373 K, respectively. The results showed that increasing oxalic acid concentration also increases the iron dissolution rate from the kaolin clay. It was also observed that the iron leaching rate at 500 mol • m^{-3} is higher than for 10 mol • m^{-3}; where the iron extractions were of 96% and 19%, respectively.

The results found in this study are also in accordance with other studies *(Lee, S. et al., 2007; Suter, D., Banwart, S. and Stumm, W., 1991)* where it was determined the dissolution of synthetic hematite and goethite particles by ascorbate, malonate, oxalate, and iron (II). In both cases, the dissolution rate was proportional to the concentration of the reducing species on the surface of the dissolved solid.

The apparent rate constants, K_d and K_T, obtained from equations (5) and (6), and the regression coefficients were calculated from the graph at each concentration. The graph for equation (5) yield straight lines with regression coefficients (R^2) lower than 0.97, showing a slight deviation from linearity. The graph of $1 - (1 - X)^{1/3}$ vs. time (figure 3) yield straight lines with regression coefficients R^2 around to 0.98 for oxalic acid concentrations of 500 mol • m^{-3}. These regression coefficient values show that iron dissolution from kaolin clay is controlled by chemical reaction. Also it can be seen that increasing acid concentration iron dissolution increases too.
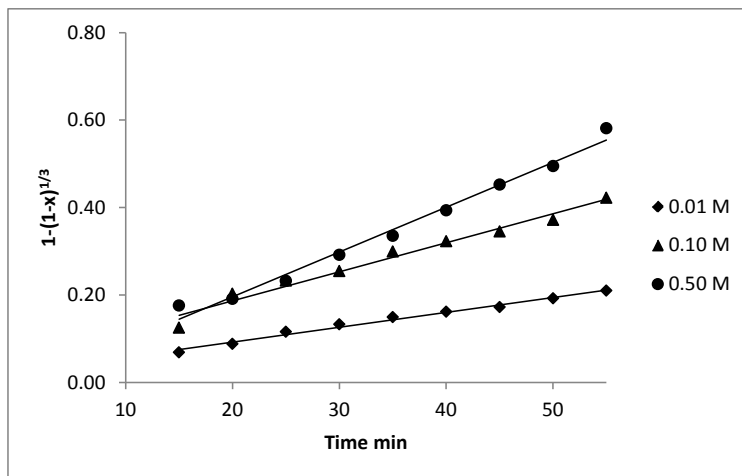
Figure 3 Graph of 1 - (1 - X)$^{1/3}$ vs. time. Effect of acid concentration

The lines for the graph were calculated according to the model 1 - (1 - X)$^{1/3}$, from which was obtained a graph of log K_T vs. log [Ox]. A straight line from this graph gave a slope from where was calculated a reaction order of n=0.29 according to the equation (6), that is shown in figure 4.
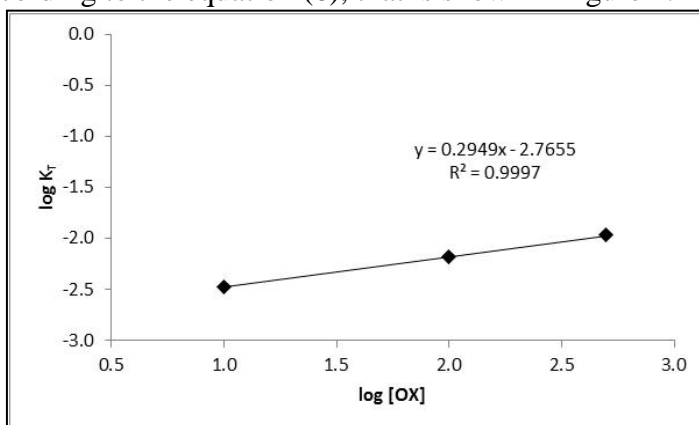

Figure 4 Graph of logK_T vs. log [Ox] (reaction order n = 0.29)

Effect of Temperature: In order to study the effect of temperature during kinetics of iron extraction, several experiments were carried out in the range of temperatures of 298 – 373 K in 500 mol•m^{-3} oxalic acid solutions. It were found the common curves of reaction rate and it was noted that the dissolution rate is quite sensitive to temperature. Also it can be observed that iron dissolution was very slow at temperatures in the range of 273 – 333 K, but its reaction rate increased greatly above 333 K. However, it has been reported that a reasonable reaction rate can only be achieved at temperatures above 353 K *(Lee, S. et al., 2006)*. That means that iron dissolution using oxalic acid could be thermally activated to improve its efficiency. The results

in table 2 shows that iron dissolution from kaolin clay in the temperature range of 298 – 373 K fit well with the chemical control model shown in equation (6).

Table 2 The K_d and K_T values and regression coefficients for each temperature.

Temperature (K)	K_d ($x10^{-3}$ min^{-1})	R^2	K_T ($x10^{-3}$ min^{-1})	R^2
298	0.50	0.986	1.20	0.988
313	1.40	0.984	3.50	0.994
333	4.80	0.985	10.20	0.979
353	5.80	0.970	12.60	0.985
373	7.00	0.970	15.50	0.981

The apparent rate constants, K_d and K_T, obtained from equations (5) and (6) and the regression coefficients were calculated from the graph at each temperature tested. These values were treated with equation 6, and the resulting data are shown in figure 5. The analysis of these graph revealed straight lines for 298, 313, 333, 353 and 373 K with regression coefficients (R^2) of 0.99, 0.99, 0.98, 0.98 and 0.98, respectively. It is important to mention that the results obtained from the graph of the temperature effect, also were analyzed with the diffusion model through an inert product layer (equation 5) and the data did not fit well with this model. Therefore, it can be dismissed that the controlling stage is diffusion through an inert product layer.
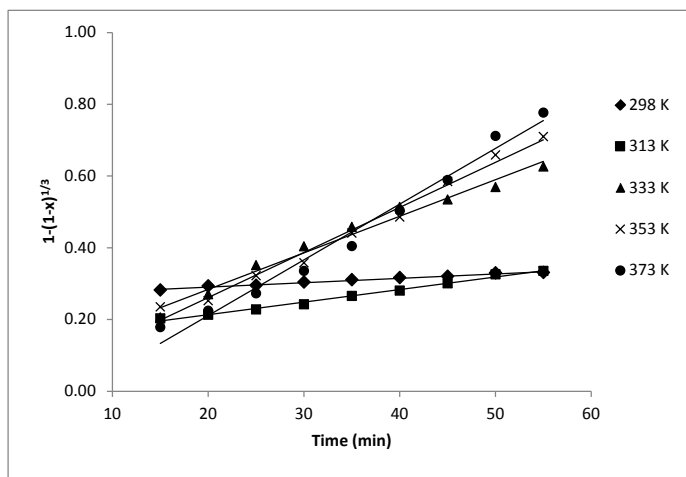

Figure 5 Graph of 1 - (1 - X)$^{1/3}$ vs. time. Effect of temperature

The apparent rate constant, K_T, for iron dissolution was calculated from the slopes in the graph of figure 5. It was made a graph showing the variation of 298–373 K and gave a straight line that is shown in figure 6. According the above, there seems to be a change in the slope of the graph corresponding to a decreasing in the activation energy of the leaching

process. The linearity seems to fit best for the temperature range 298 – 333 K. The activation energy for the dissolution of the magnetite by the oxalate was 50.32 kJ•mol^{-1} in this temperature range. This result confirmed that iron dissolution from kaolin clay is controlled by chemical reaction. At the same way, these results are in concordance with that reported by Lee et al (2006) where he pointed that iron dissolution is slow at temperatures ranging from 298 to 333 K, besides it was found that we can conclude that for higher temperatures (333 to 373 K), the iron dissolution increases notoriously.

The result can be explained as follows; the reaction is controlled by non-reductive dissolution at high temperature, which removes only the more reactive sites of the oxide surface, by hydrogen ion in solution *(Blesa, M.A. and Maroto, A.J., 1986)*. It showed that the dissociation of oxalic acid depends strongly on the reaction temperature and its increase enhanced the activity of oxalate species in oxalic acid solution. This is due to fact that oxalic acid was not completely dissociated at low temperatures.

Above this temperatures range, the activation energy seems to decrease dramatically such is shown by the change of slope in the graph. Taking the last 3 points of the line (333, 353 and 373 K) for the calculation of activation energy; it was obtained a value of 10.79 kJ•mol^{-1}, with a regression coefficient (R^2) of 0.99.

This could be caused by the gradual formation of a passivation layer of iron oxalate $Fe(C_2O_4)_2^{2-}$ with respect to time; which is favored by the presence of Fe (II) soluble produced by the process of dissolution, that can be accumulated near the interface of reaction *(Lee, S. et al., 2006)*.
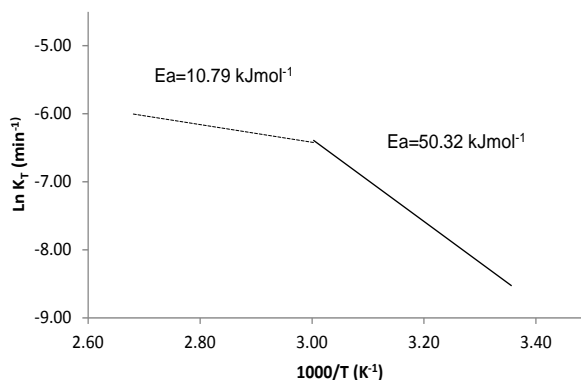

Figure 6 Graph of iron dissolution from kaolin clay. Energy of activation

Conclusion

It was found that increasing oxalic acid concentration increases the iron dissolution rate from kaolinitic clay. It was also seen that the reaction rate of iron leaching for 500 mol•m^{-3} is higher than that for 10 mol•m^{-3}; where the iron extractions were of 96% and 19%, respectively. In the same

way, it was observed that iron dissolution was very slow at temperatures in the range of 273 – 333 K, but its reaction rate increased greatly above 333 K. This could be due to the fact that oxalic acid was not completely dissociated at low temperatures, confirming that the oxalic acid can be activated to be thermally efficient, such it was pointed by several authors.

For the kinetics of iron leaching from kaolinitic clay using oxalic acid, the process showed an order of reaction of 0.29. The energy of activation calculated for the magnetite dissolution by the oxalate was of 50.32 kJ•mol^{-1} in the temperatures range of 273 to 333 K, with a regression coefficient (R^2) of 0.99. This result confirmed that iron dissolution from kaolin clay is controlled by chemical reaction. Above this temperatures range, the activation energy seems to decrease dramatically showing a change of slope in the graph. For this change, was obtained a value of 10.79 kJ•mol^{-1} for the energy of activation, with a regression coefficient (R^2) of 0.99. This change in linearity indicates that the controlling step of the process in this temperatures range could be due to the diffusion through inert products layer.

Acknowledgments

References:
Ambijadevi, V. R.; Lalithambika, M.; Appl. Clay Sci., 2000, 16, 133.
Blesa, M. A.; Marosto, A. J.; Dissolution of metal oxides, 1986, 83, 757.
Borghi, E. B.; Regazzoni, A. E.; Maroto, A. J.; Blesa, M. A.; J. Colloid Interface Sci., 1989, 130, 2.
Dos Santos, A. M.; Morando, P.; Blesa, M. A.; Banwart, S.; Stumm, W.; J. Colloid Interface Sci., 1990, 1, 138.
Lee, S.; Tran, T.; Jung, B.; Kim, S.; Kim, M.; Hydrometallurgy, 2007, 87, 91.
Lee, S.; Tran, T.; Park, Y.; Kim, S.; Kim, M.; Int. J. Miner. Process., 2006, 80, 144.
Levenspiel O. In Chemical reaction engineering, 2nd ed.; Wiley:New York, 1972.
Martínez L. A.; Rodríguez D. M. G.; Uribe S. A.; Carrillo P. F. R.; Osuna A. J. G.; Applied Clay Science, 2011, 51, 473.
Panias, D.; Taxiarchou, M.; Paspaliaris, I.; Kontopoulos, A.; Hydrometallurgy, 1996, 42, 257.

Saikia, N. J.; Bharali, D. J.; Sengupta, P.; Bordoloi, D.; Goswamee, R. L.; Saikia, P. C.; Borthakur, P. C.; Applied Clay Science, 2003, 24, 93.

Segal, M. G.; Sellers, R. M. In Advances Inorganic Bioinorganic Mechanisms; Sykes, A. G. Ed.; London. Academic Press, 1984, 3, 97.

Shon, H. Y.; Wadsworth, M. E. In Rate processes of extractive metallurgy, Plenum Press:New York, 1986.

Suter, D.; Banwart, S.; Stumm, W.; Langmuir, 1991, 7, 809.

Taxiarchou, M.; Panais, D.; Douni, I.; Paspaliaris, I.; Kontopoulos, A.; Hydrometallurgy, 1997, 44, 287.

Torres, R.; Blesa, M.; Matijevic, E.; J. Colloid Interface Sci., 1990, 2, 134.

Veglio, F.; Passariello, B.; Toro, L.; Marabini, A. M.; Ind. Eng. Chem., 1996, 35, 1680.

Veglio, F.; Toro, L.; Int. J. Miner. Process., 1993, 39, 87.

Veglio, F.; Toro, L.; Int. J. Miner. Process., 1994, 41, 239.

Yan, L. G.; Song, S. S.; Nan, H. L.; Cheng, Y. L.; Li, X. M.; Kong, Q. W.; Dai, Y. M. In Proceendings of the Second World Congress on Non-Metallic Minerals, Beijing, China, 1978, 17.