

THE LEACHING OF ALUMINIUM IN SPANISH CLAYS, COAL MINING WASTES  
AND COAL FLY ASHES BY SULPHURIC ACID.

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Abstract

The acid leaching of aluminium from several non traditional ores, bayerite, kaolinite, different clays, coal mining wastes and coal fly ashes, and the kinetic of their dissolution are described. The effects of time, temperature, acid concentration, sample calcination, particle size were examined. The leaching of aluminium is dependent on acid concentration and strongly on temperature. Generally, the time to reach a fixed percentage of dissolution decreases with increasing acid concentration in the range 6% to 40% acid by weight. On clays and coal mining wastes a good relation between Al removal and ratio kaolinite/illite was also observed at all temperatures and acid concentration tested. Coal fly ashes are particles that were heated at very high temperatures in the power station and Al compounds were transformed into mullite and so Al recovery was minor. Several rate equations describing the kinetics of the leach reaction were discussed and Kinetic parameters and activation energy values of samples are presented.

Introduction

Voluminous and recent literature on the use of low grade ores and extraction of metals from them is available (1, 2, 3, 4, 5, 6). Spain has important sources of non-traditional aluminium raw materials, as clay minerals, coal mining wastes, coal fly ashes and red muds (7, 8, 9).

Red mud is a chemical waste produces by the alkaline extraction of alumina from bauxite in the Bayer process. The chemical composition of the red mud varies depending on the mineralogical composition of the bauxite used in the extraction, but contains generally around 25%  $Al_2O_3$ ; Coal fly ashes have about 32%  $Al_2O_3$ , and coal mining wastes between 20-30%  $Al_2O_3$ . Many clays contain as much as 30-40% alumina. Kaolinite is a good candidate as a bauxite replacement for aluminium ore.

One of possible alternatives to removal aluminium from these raw materials, is the dissolution in caustic liquors (10, 11, 12, 13). Another one is by acid leaching at atmospheric pressure (14 15). In leaching to achieve the best aluminium recoveries, samples must first be calcined (14).

In this paper the acid leaching of aluminium from bayerite, kaolinite, different clays, coal mining wastes and coal fly ashes, and the kinetic of their dissolution are described. The effects of time, temperature, acid concentration, sample calcination, particle size were examined. Several rate equations describing the kinetics of the leach reaction were discussed and Kinetic parameters and activation energy values of samples are presented.

### Experimental

Bayerite, kaolinite, illite, different clays, coal mining wastes and coal fly ashes were used for the experimental extraction of alumina. The acid leaching process takes the alumina into solution by attack with mineral acids.

#### Reactor

A leach volume of 1400 ml was maintained by a water reflux condenser, with mechanical stirrer and thermostatically controlled heating jacket. After the acid solution of required concentration reached to temperature, sample was added to start the leach test. Samples of the leach were taken at various time intervals, the slurry was filtered and then was analysed by X-ray diffraction and the solution by atomic absorption spectrophotometry.

Samples were dried at 110°C and then calcined in a furnace at 700°C for 1 h. Tests were conducted at 50°C, 70°C, 80°C, 95°C y 105°C, pulp density was varied between 30 and 200 g sample/1000 ml, and leaching with 0.5M (stoichiometrically calculated quantity to dissolve all the soluble components of the sample), 2M, 4M, 5M, 7M and 9M acid.

#### Acid baking

In another tests, samples were mixed with 98% sulphuric acid and the mixture was baked at temperatures selected: 200°C, 300°C, 350°C and 400°C. After the desired reaction time, 30 min, the sample was leached with water and the liquor was analysed by A.A.S.

#### Dissolution in mineral acids

##### Reactor

##### Bayerite.

Bayerite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , with the chemical composition of 65.4 %  $\text{Al}_2\text{O}_3$  and 34.6 %  $\text{H}_2\text{O}$ , was used for the leaching with sulphuric acid. The concentration of acid used in leach tests were 0.53 M, 0.96 M, 2.37 M, 3.61 M and 5.2 M (5, 9, 20, 30 and 40% by weight) at 55°C, 70°C, 85°C and 95°C leaching temperatures. The influence of temperature on alumina dissolution (stoichiometrical conditions) is shown in Figure 1. An increase in Al dissolution with increasing temperature is observed from 55°C to 95°C. In a period of 30 min, the recovery of alumina was 35% at 55°C and 75% at 85°C.

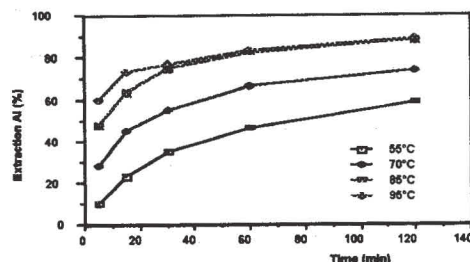


Figure 1 The influence of temperature on degree of reaction for bayerite with 0.53 M sulphuric acid (stoichiometrical conditions).

The dissolution curves at five acid concentrations show that a strong acid effect exists. Only 35% aluminium dissolution resulted using 0.53 M sulphuric acid at 55°C after 30 min, whereas 90% aluminium dissolution was reached using 2.37 M sulphuric acid at the same leach time and temperature as illustrated by Figure 2.

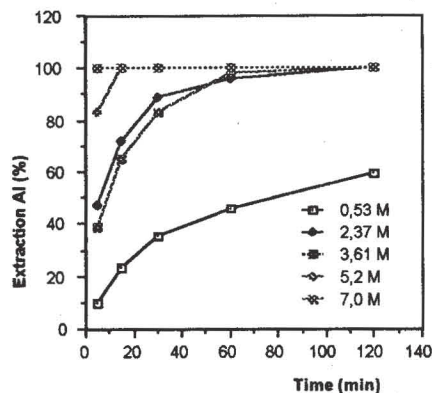


Figure 2 Effect of acid concentration on leaching bayerite, at 55°C.

##### Kaolinite.

Kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , having a chemical composition of 39.5 %  $\text{Al}_2\text{O}_3$ , 46.5 %  $\text{SiO}_2$  and 14 %  $\text{H}_2\text{O}$ , was leached with sulphuric acid. Samples were allowed to react with 2.37 M (20% by weight) sulphuric acid at 55°C and 70°C leaching temperatures. Only 1% aluminium dissolution resulted at 70°C after 120 min.

To achieve better aluminium recoveries, kaolinite must first be calcined at 500-600°C. New experiments have been conducted with calcined kaolinite at sulphuric acid concentrations of 0.26 M and 2.4 M (2.5 and 20% by weight) at 70°C, 85°C and 105°C leaching temperatures. The percentage extractions of alumina from calcined kaolinite with 0.26 M sulphuric acid (stoichiometrical conditions) at different temperatures are given in Figure 3. As temperature was increased from 70°C to 105°C the extraction increased from 25% to values above 80% in a period of 120 min.

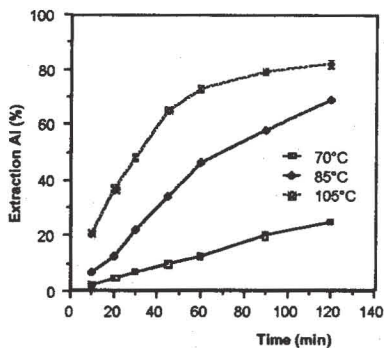


Figure 3 Effect of temperature on degree of reaction for calcined kaolinite with 0.26 M sulphuric acid (stoichiometrical conditions).

Figure 4 shows the acid concentration effect in leach tests conducted at 70°C, 85°C and 105°C.

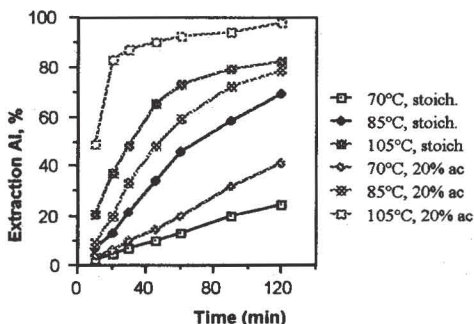


Figure 4 Effect of acid concentration on leaching calcined kaolinite at 70°C, 80°C and 105°C.

Clay 1

X-ray diffraction analysis of clay 1 showed that the major aluminium mineral present in the clay 1 is kaolinite (44%) and illite (11%), ratio K/I = 4 with a chemical composition (calcined sample) of 37.3% Al<sub>2</sub>O<sub>3</sub>, 54.6% SiO<sub>2</sub>, 3.6% Fe<sub>2</sub>O<sub>3</sub> and 0.9% K<sub>2</sub>O.

Tests were carried out at sulphuric acid concentrations of 0.7 M, 2.4 M, 5.3 M, and 9.0 M (6, 20, 40 and 60% by weight) at 55°C, 70°C, 85°C and 95°C leaching temperatures. In all experiments an increase in Al dissolution with increasing temperature is observed from 55°C to 95°C. In Figure 5 the leach results of calcined clay 1 with 0.7 M sulphuric acid (stoichiometrical conditions) at different temperatures are presented. In a period of 120 min, 71% of the aluminium was dissolved at 95°C, while only 23% were dissolved at 55°C.

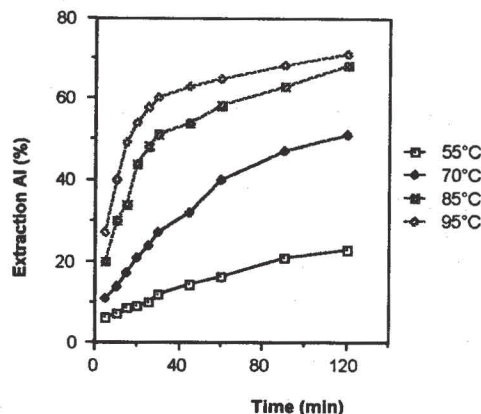


Figure 5 Effect of temperature on degree of reaction for calcined clay 1 versus time with 0.7 M sulphuric acid (stoichiometrical conditions).

The time to reach a fixed percentage of dissolution decreases with increasing acid concentration in the range 6% to 20% acid. But it should be pointed out that, if sulphuric acid 5.3 M (40% by weight) is used, the Al removal is not subject to this rule at 55°C; at 70°C the aluminium extraction follows the general law. When sulphuric acid 9.0 M (60% by weight) is used at low temperatures (55°C, 70, 85°C), the Al removal from calcined clay 1 is not subject to this rule (Figure 6). Aluminium and sulphate concentration are greatly high and a precipitate of aluminium sulphate is observed by X-ray diffraction analysis of the residues obtained from the acid attack. However, at 95°C the aluminium extraction follows the general law (Figure 7).

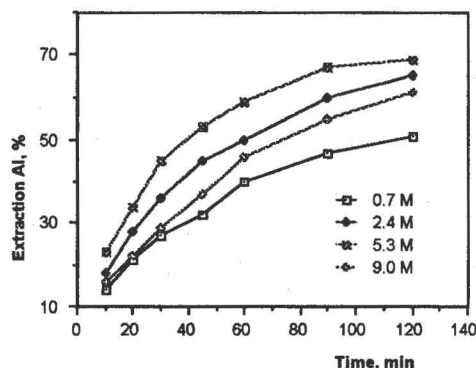


Figure 6 Effect of acid concentration on leaching calcined clay 1 at 70°C.



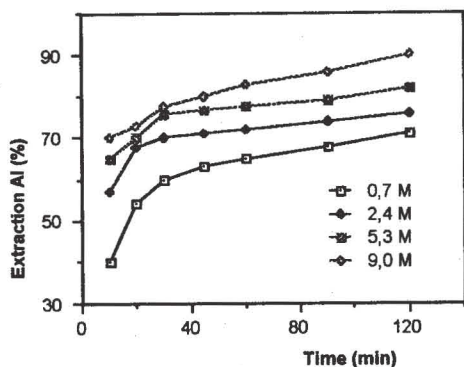


Figure 7 Effect of acid concentration on leaching calcined clay 1 at 95°C.

Clay 2

X-ray diffraction analysis of clay 2 showed that the major aluminium mineral present in the clay 2 is kaolinite (24%) and illite (31%), ratio K/I = 0.77 with a chemical composition (calcined sample) of 22.1% Al<sub>2</sub>O<sub>3</sub>, 64.4% SiO<sub>2</sub>, 6.2% Fe<sub>2</sub>O<sub>3</sub> and 2.2% K<sub>2</sub>O. Clay 2 was leached at sulphuric acid concentrations of 2.5 M, (20% by weight) at 55°C, 70°C, 85°C and 105°C leaching temperatures. In all experiments an increase in Al dissolution with increasing temperature is observed from 55°C to 105°C. Figure 8 illustrates the leaching rate of calcined clay 2 with 2.5 M sulphuric acid at different temperatures. In a period of 120 min, the Al removal achieved was 25% at 55°C and 64% at 105°C.

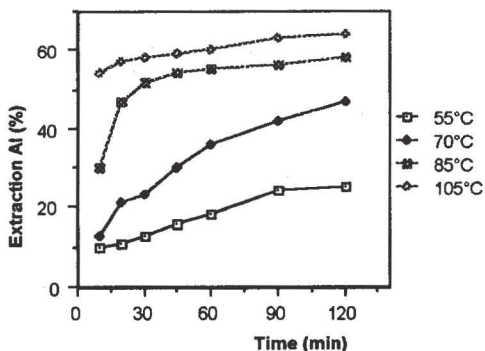


Figure 8 Effect of temperature on degree of reaction for calcined clay 2 versus time with 2.5 M sulphuric acid.

Clay 3

X-ray diffraction analysis of clay 3 showed that the major aluminium mineral present in the clay 3 is kaolinite (21%) and illite (42%), ratio K/I = 0.5 with a chemical composition (calcined sample) of 19.2% Al<sub>2</sub>O<sub>3</sub>, 66.9% SiO<sub>2</sub>, 3.8% Fe<sub>2</sub>O<sub>3</sub> and 5.3% K<sub>2</sub>O. Experiments have been conducted at sulphuric acid concentrations of 0.64 M, 2.5 M, 5.5 M, and 9.2 M (6, 20, 40 and 60% by weight) at 55°C, 70°C, 85°C and 95°C leaching temperatures. In all experiments an increase in Al dissolution with increasing temperature is observed from 55°C to 95°C. The

effect of temperature on degree of reaction for calcined clay 3 with 0.64 M sulphuric acid (stoichiometrical conditions) can be seen in Figure 9. In a period of 120 min, the leaching achieved for Al was 7.6% at 55°C and 40% at 95°C.

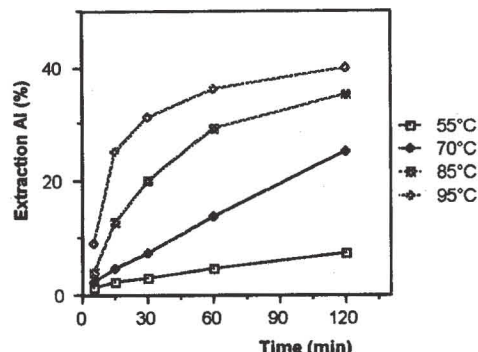


Figure 9 Effect of temperature on degree of reaction for calcined clay 3 with 0.64 M sulphuric acid (stoichiometrical conditions).

The time to reach a fixed percentage of dissolution decreases with increasing acid concentration in the range 6% to 20% acid. But if sulphuric acid 5.5 M (40% by weight) is used, the Al removal is not subject to this rule at low temperatures (55°C, 70°C, 85°C), as presented in Figure 10. Aluminium and sulphate concentration are greatly high and a precipitate of aluminium sulphate is observed by X-ray diffraction. However, at 95°C the aluminium extraction follows the general law, as was also observed in clay 1 with 9.0M (60% by weight) acid concentration. Increases in acid concentration to 5.5 and 9M led to a decrease in extraction rate from clay 3, at temperatures tested. Similar observations were made in the acid leaching of a manganese ore (16, 17).

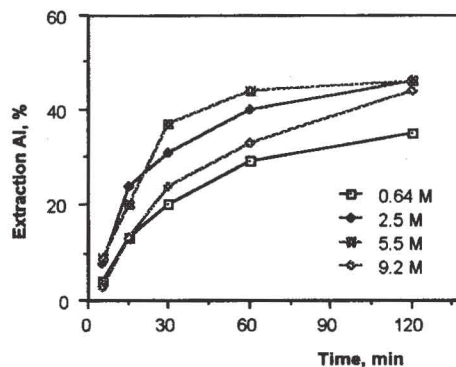


Figure 10 Effect of acid concentration on leaching calcined clay 3 at 85°C.

Illite

X-ray diffraction analysis of illite showed that the major aluminium mineral present is very little crystalline illite with a chemical composition (calcined sample) of 25.7% Al<sub>2</sub>O<sub>3</sub>, 7.8% Fe<sub>2</sub>O<sub>3</sub> and 7.1% K<sub>2</sub>O. Samples were allowed to react with 2.4 M (20% by weight) sulphuric acid at 55°C, 70°C, 85°C and

105°C leaching temperatures. In all experiments an increase in Al dissolution with increasing temperature is observed from 55°C to 105°C. The results of leaching of calcined illite with 2.4 M sulphuric acid at different temperatures are plotted in Figure 11. In a period of 120 min, the leaching achieved for Al was 21% at 55°C and 61% at 105°C.

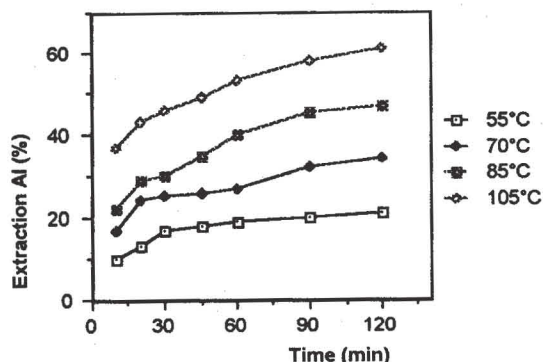


Figure 11 Effect of temperature on degree of reaction for calcined illite versus time with 2.4 M sulphuric acid.

Coal mining wastes.

X-ray diffraction analysis of coal mining wastes showed that the major aluminium mineral present is kaolinite (11%) and very crystalline illite (46%), ratio K/I = 0.24 with a chemical composition (calcined sample) of 25,3% Al<sub>2</sub>O<sub>3</sub>, 61,6% SiO<sub>2</sub>, 6,8% Fe<sub>2</sub>O<sub>3</sub>, 4,0% K<sub>2</sub>O and 1,10% TiO<sub>2</sub>. Laboratory study was done at nitric acid concentration of 50% by weight (200% of the stoichiometrically required) at 113°C leaching temperature (boiling temperature). Figure 12 illustrates the dissolution curve of calcined coal mining waste with 50% nitric acid at 113°C. In a period of 120 min, the leaching achieved for Al was only 36%, from what nitric acid was nevermore used.

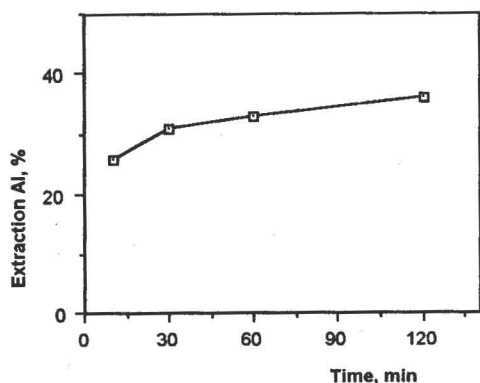


Figure 12 Dissolution curve of calcined coal mining waste with 50% by weight nitric acid at boiling temperature (113°C).

Experiments were carried out at hydrochloric acid concentration of 18% by weight (200% of the stoichiometrically required) at 110°C leaching temperature (boiling temperature). The

dissolution curve of calcined coal mining waste with 18% hydrochloric acid at 113°C is given in Figure 13. In a period of 120 min, the leaching achieved for Al was only 48%, from what hydrochloric acid was nevermore used.

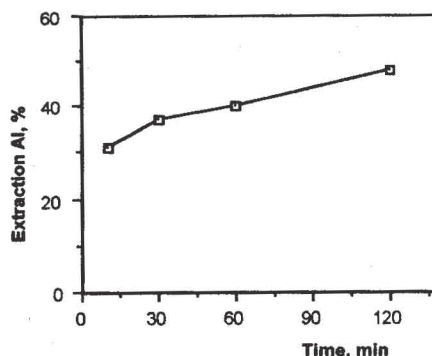


Figure 13 Dissolution curve of calcined coal mining waste with 18% by weight hydrochloric acid at boiling temperature (110°C).

Experiments were performed at sulphuric acid concentrations of 22, 34, 45 and 60% by weight (23, 84, 146 and 228% of the stoichiometrically required) at boiling leaching temperatures. In Figure 14 the effect of acid concentration on leaching of uncalcined coal mining waste with sulphuric acid is presented. The time to reach a fixed percentage of dissolution decreases with increasing acid concentration. In a period of 120 min, the leaching achieved for Al was 9% at sulphuric acid concentration of 22% and 61% at sulphuric acid concentration of 60%.

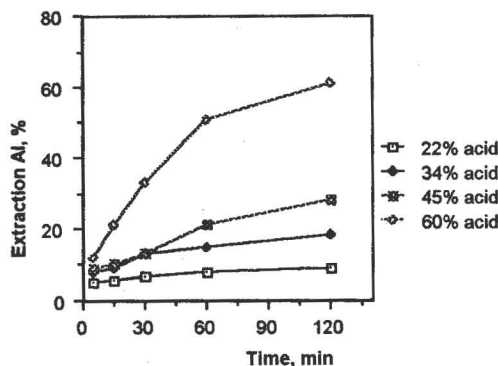


Figure 14 Effect of acid concentration on leaching uncalcined coal mining waste, at boiling temperature.

The influence of acid concentration on leaching calcined coal mining waste with sulphuric acid is shown in Figure 15. In a period of 120 min, the leaching achieved for Al was 34% at sulphuric acid concentration of 22% and 89% at sulphuric acid concentration of 60%.



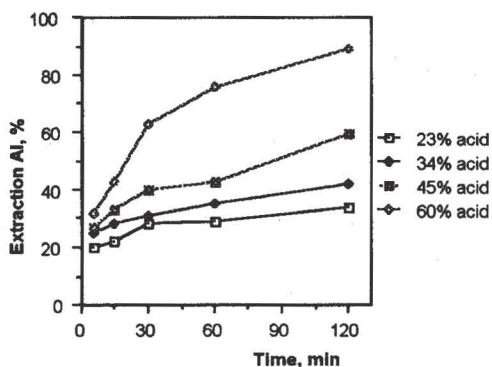


Figure 15 Effect of acid concentration on leaching calcined coal mining waste, at boiling temperature.

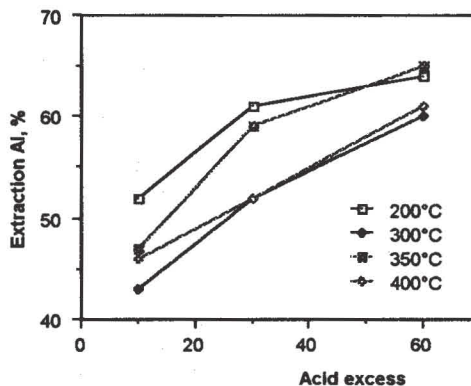


Figure 16 Effect of acid excess and temperature on baking uncalcined coal mining waste.

Acid baking

Coal mining waste.

The optimum bake conditions were determined for coal mining waste classified by particle size into four sets: 1-0.8 mm, 0.8-0.4 mm, 0.4-0.1 mm and < 0.1 mm. The results are given in Table 1. The results show that smaller particle size results in more aluminium being extracted of coal mining waste.

Samples were allowed to react with an amount of sulphuric acid that represent 110, 130, and 160% of the stoichiometrically required quantities needed for the removal of alumina, iron and potassium at 200°C, 300°C, 350°C and 400°C baking temperatures. The extent of baking of uncalcined coal mining waste with sulphuric acid are plotted in Figure 16. The time to reach a fixed percentage of dissolution decreases with increasing acid concentration whereas the higher temperature for baking cannot be considered an advantage, due to acid decomposition.

Table 1. Effect of particle size on baking efficiently.

Particle size mm	Al <sub>2</sub> O <sub>3</sub> (%) extracted
0,8 - 1	20
0,4 - 0,8	21
0,1 - 0,4	53
< 0,1	59

Conditions: coal mining waste uncalcined, amount of sulphuric acid represent 130%, of the stoichiometrically required, baking temperature of 350°C.

Tests were also conducted on calcined coal mining waste at sulphuric acid excess over stoichiometric of 10, 30, and 60% by weight at 200°C, 300°C, 350°C and 400°C baking temperatures. Similar results to Figure 16 were obtained, but the aluminium removal from calcined samples was greater (80%).

Coal fly ashes.

X-ray diffraction analysis of coal fly ashes showed that the major aluminium mineral present is mullite, 3Al<sub>2</sub>O<sub>3</sub> 2.SiO<sub>2</sub>, with a chemical composition of 32% Al<sub>2</sub>O<sub>3</sub>, 46% SiO<sub>2</sub>, 10% Fe<sub>2</sub>O<sub>3</sub>, 1,2% K<sub>2</sub>O and 1,1 % TiO<sub>2</sub>. Experiments were carried out on uncalcined and calcined coal fly ashes with stoichiometric sulphuric acid at 200°C baking temperature. Aluminium removal in both experiments was 45%, because coal fly ashes were heated up in the power station more than in the calcination furnace. Aluminium extraction from fine particles was 64%.

Analysis of Results

When a reactor have been used the best aluminium recovery was from bayerite. The leaching achieved for aluminium was 100% at sulphuric acid concentration of 20%.

Sulphuric acid leaching of spanish clays and coal mining wastes was investigated at different temperatures and using various acid concentrations. Results showed that extractions were affected by ratio kaolinite/illite. As Figures 17, 18, 19 and 20 illustrate, an increase in aluminium dissolution with increasing ratio kaolinite/illite is observed. Ratio kaolinite/illite is 4 for clay 1, 0.77 for clay 2 and 0.5 for clay 3. For coal mining waste ratio kaolinite/illite is 0.24 and aluminium recovery was low.

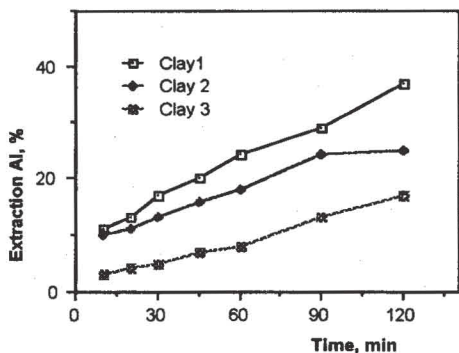


Figure 17 The effect of ratio kaolinite/illite on degree of reaction for various clays at 55°C with 2.4 M sulphuric acid.

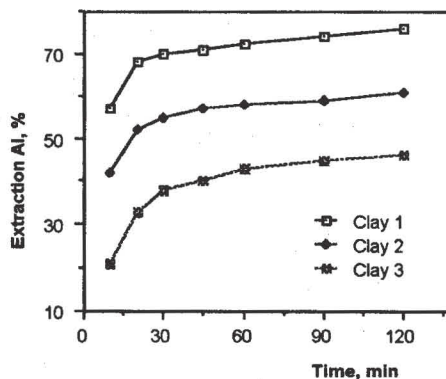


Figure 20 The effect of ratio kaolinite/illite on degree of reaction for various clays at 95°C with 2.4 M sulphuric acid.

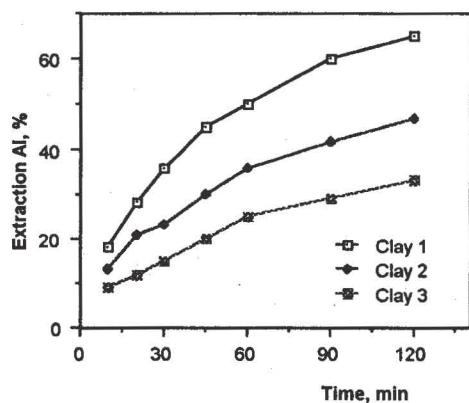


Figure 18 The effect of ratio kaolinite/illite on degree of reaction for various clays at 70°C with 2.4 M sulphuric acid.

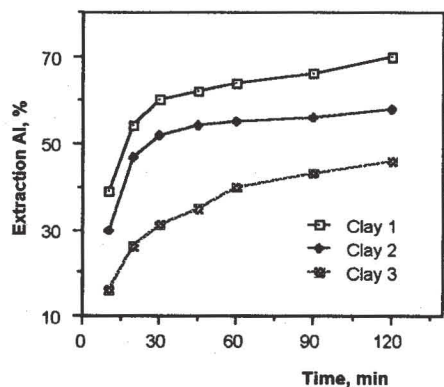


Figure 19 The effect of ratio kaolinite/illite on degree of reaction for various clays at 85°C with 2.4 M sulphuric acid.

Acid baking of spanish coal mining wastes and coal fly ashes was investigated at different temperatures and using various acid concentrations. Ratio kaolinite/illite is 0.24 for coal mining waste and aluminium recovery was 80%. Coal fly ashes contain mullite, difficult to dissolve and aluminium recovery was low (45%).

Published kinetic models

Leaching is a central unit operation in the hydrometallurgical treatment of ores and for this reason much attention is focused on the study of the kinetics of leaching reactions (17, 18, 19). Several models have been published to describe the rate of leaching of metals from its ores.

Patermarakis (20) studied the leaching of iron oxides in boehmitic bauxite by hydrochloric acid and proposed the following kinetic equation:

$$y = k' t^n \tag{1}$$

where y is the thickness of reacted layer, k' is a constant depending on the leaching temperature and hydrochloric acid concentration, t is leaching time interval, and n have the value of 0,68. The constant k' is a linear function of acid concentration:

$$k' = k C \tag{2}$$

where C is the concentration of HCl and k is the rate constant.

Zivkovic (21) developed the following kinetic model for the leaching of kaolinite:

$$[1 - (1 - a)^{1/3}]^2 = k t \tag{3}$$

where a is the fraction reacted, k the constant for the reaction rate, and t the duration of the reaction.

Dimitrijevic (22) investigated the leaching of pyrite by hydrogen peroxide in perchloric acid, and selected the rate equation:

$$[1 - (1 - X)^{1/3}] = k_s t \tag{4}$$

where X is the fraction of pyrite reacted, k<sub>s</sub> is the apparent rate constant, and t is time.

Hulbert (23) compared leaching rates of calcined kaolin in various acids and tested their date on a nucleation type model of the form:

$$\ln [1/(1 - X)] = (k t)^m \quad (5)$$

where X is the fraction of aluminium leached at time t, k is a first order rate constant and m is a parameter describing reaction mechanism, particle geometry, nucleation rate and hydration and complexing of products.

Ford (14) proposed the following leach model for the aluminium removal from kaolin using sulphuric acid:

$$X = 1 - \exp (k [H^+]^n t) \quad (6)$$

where  $[H^+]$  is the concentration of the sulphuric acid, n the acid term order, k the first order reaction rate constant and t the time.

The rate equations of Zivkovic and Dimitri (the surface reaction control shrinking core) and Patermarakis (diffusion controlled reaction) was inappropriate for mathematically expressing the data. The model of Hulbert was fitted to experimental data and Kinetic parameters were calculated. The values of m which range from 1.0 to 1.1 for the kaolinite kinetics are in accordance with the reported by Hulbert; for clays 1, 2 and 3 are in the range 0.5-0.7 and for illite are 0.3. Table 2 gives the values of acid concentration, temperature and m for several samples. It was observed from Table 2 that the value of m decreased with decreased kaolinite/illite ratio.

Table 2 Values of m at various leach temperatures and acid concentrations for kaolinite, clays and illite.

Sample	Acid conc. (M)	Temp. (°C)	m
Kaolinite	0.26	70	1.0
	0.26	85	1.1
	2.4	70	1.1
Clay 3	2.4	85	1,1
	0.64	70	0.7
	0.64	85	0.7
Illite	2.4	70	0.6
	2.4	85	0.6
	2.4	70	0.3

The dependence of k on temperature was modelled using the Arrhenius law of the form:

$$k = k_0 \exp (-E_a/RT) \quad (7)$$

where  $k_0$  is the Arrhenius frequency factor,  $E_a$  the activation energy, R the gas constant, and T the temperature of reaction.

Figures 21 and 22 present a plot of  $\ln k$  versus  $1000/T$  for clays 1 and 3, whose slopes yielded activation energies of approximately 100 KJ/mol

The experimental data were fitted still better to the rate equation proposed by Ford, which includes an acid term in the model. Kinetic parameters were obtained for each temperature and activation energies were calculated using the Arrhenius law. Figures 23 and 24 present a plot of  $\ln k$  versus  $1000/T$  for clays 1 and 3. From them, the following values were determined: for kaolinite leaching  $E = 65.8$  KJ/mol, according to values described elsewhere (14, 24), for clay 1 (kaolinite/illite ratio = 4)  $E = 92$  KJ/mol an for clay 3 (kaolinite/illite ratio = 0.5)  $E = 107$  KJ/mol. Once more, it was observed that kaolinite/illite ratio is

important.

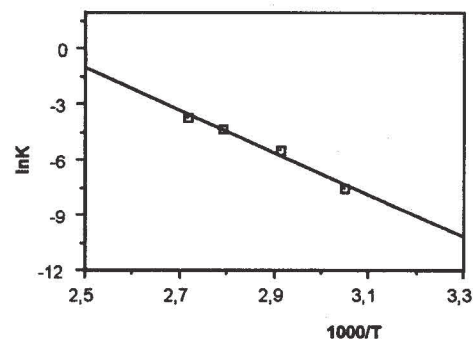


Figure 21 Arrhenius diagram for the leaching of clay 1 (Hulbert model).

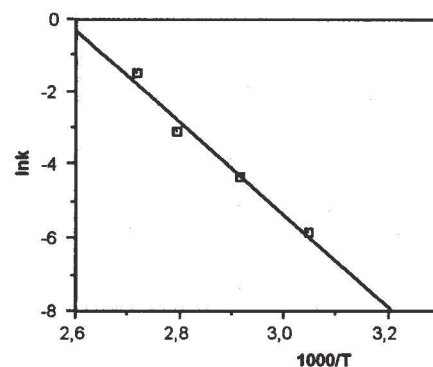


Figure 22 Arrhenius diagram for the leaching of clay 3 (Hulbert model).

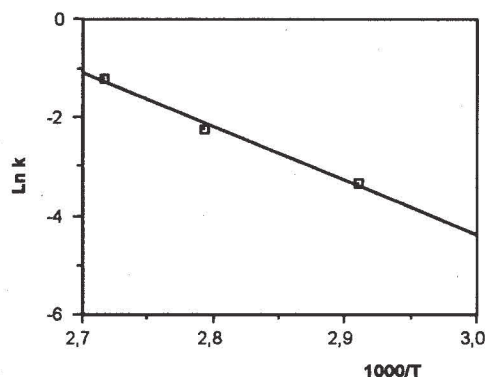


Figure 23 Arrhenius diagram for the leaching of clay 1 (Ford model).

The leach process is first order respect to aluminium and n order respect to acid. An acid concentration effect on clays was found with an order dependence of 0.3 for clay 1, and 0.45 for clay 3, lightly higher to the 0.23-0.30 reported by Ford for kaolinite. This acid concentration effect is in accordance with the data obtained. It is not easy to say what is the controlling step, but the high activation energy value  $E_a$  tends to indicate that the intrinsic leach process is chemically rate controlled.



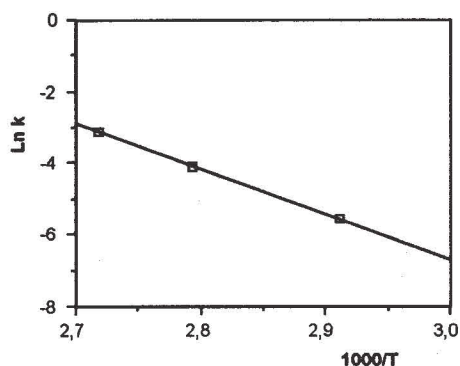


Figure 24 Arrhenius diagram for the leaching of clay 3 (Ford model).

#### Concluding Remarks

In all experiments an increase in Al dissolution with increasing temperature is observed from 55°C to 95°C. The time to reach a fixed percentage of dissolution from clays decreases with increasing acid concentration in the range 6% to 20% acid. But if sulphuric acid 5.5 M and 9.0 M is used, the Al removal is not subject to this rule at low temperatures. However, at 95°C the aluminium extraction follows the general law. The higher temperature for baking cannot be considered an advantage, due to acid decomposition. Results showed that extractions were affected by ratio kaolinite/illite. An increase in aluminium dissolution with increasing ratio kaolinite/illite is observed.

Several models have been published to describe the rate of leaching of metals from its ores. The model of Hulbert was fitted to experimental data and Kinetic parameters were calculated. It was observed that the value of  $m$  decreased with decreased kaolinite/illite ratio. The experimental data were fitted still better to the rate equation proposed by Ford, which includes an acid term in the model. Kinetic parameters were obtained for each temperature and activation energies were calculated using the Arrhenius law. Once more, it was observed that kaolinite/illite ratio is important. The leach process is first order respect to aluminium and  $n$  order respect to acid. The high activation energy value  $E_a$  tends to indicate that the intrinsic leach process is chemically rate controlled.

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