KINETICS OF THE ACID LEACHING OF PALLYGORSKITE: INFLUENCE OF THE OCTAHEDRAL SHEET COMPOSITION

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ABSTRACT: A study has been carried out on the influence of acid concentration, time and temperature of reaction, liquid to solid ratio and chemical composition of the mineral on the extension and selectivity of the octahedral cations extracted during acid leaching of palygorskite. The mechanism of the extraction of Mg$^{2+}$, Al$^{3+}$, and Fe$^{3+}$ is discussed on the basis of kinetic models fitted for a reacting-shell model, taking into account particle shape and the rate controlling step. A model is given from which kinetics parameters and the activation energy of the process are calculated. The different behaviour observed for the two palygorskites could be explained on the basis of their differences in surface areas.

Palygorskite is a hydrated magnesium silicate with a fibrous morphology, whose structure was first reported by Bradley (1940). It is composed of talc-like units arranged alternately, generating channels of \(3.7 \times 6.4\) \(\text{Å}\) along the \(c\)-axis of the fibre. A significant amount of octahedral Mg$^{2+}$ is substituted by Al$^{3+}$ and Fe$^{3+}$. The presence of trivalent cations in octahedral positions creates an excess of positive charge which is compensated by vacancies thereby conferring dioctahedral characteristics to the mineral (Caillere & Hénin, 1961; Drits & Alexandrova, 1966; Drits & Sokolova, 1971; Serna et al., 1977; Mifsud et al., 1978). As for other silicates, the presence of Al$^{3+}$ in the octahedral sheet has an effect on the reactivity of the sample to acid leaching (Osthaus, 1956; Gastuche et al., 1960; Chaussidon & Vilain, 1962; Ross, 1967).

In a previous paper (Corma et al., 1987) we have studied the behaviour to acid leaching of two palygorskites with different chemical compositions by varying some experimental conditions such as temperature, time of reaction, liquid to solid ratio, and H$^+$ concentration. In the present work, the influence of these variables on the selectivity for the extraction of octahedral cations (Mg$^{2+}$, Fe$^{3+}$ and Al$^{3+}$) has been studied. Kinetics models have been developed that enable deductions to be made about the mechanisms of acid attack, and values to be calculated for the activation energy of the process.

EXPERIMENTAL

Two Spanish palygorskites, from Serradilla and Torrejón, were mechanically ground and particles <200 mesh used. The structural formulae of these minerals and experimental details of the techniques employed were described in the earlier paper (Corma et al., 1987).
RESULTS AND DISCUSSION

Selectivities for the leaching of different cations

The percentages of Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$ leached at different reaction times from the octahedral sheet of the Torrejón palygorskite in HCl solutions of different molarities were illustrated in Fig. 1 of our earlier paper (Corma et al., 1987). From these data, the selectivity plots for the extraction of the three cations at 20, 50 and 70°C in 1 M HCl solution have been obtained and are presented in Fig. 1. It is clear that, at the levels of extraction studied, the process is more selective for Mg$^{2+}$ than for Fe$^{3+}$ or Al$^{3+}$. This is particularly true in the initial stages of extraction, suggesting that Mg$^{2+}$ ions are more easily removed than Fe$^{3+}$ or Al$^{3+}$. The selectivity for Mg$^{2+}$ extraction is at a maximum at low levels of extraction, and decreases as extraction proceeds so that at 22% leaching, its selectivity is already equal to, or even lower than, that for Al$^{3+}$ and Fe$^{3+}$. This is one indication that the octahedral positions at the edges are occupied mainly by Mg$^{2+}$. Moreover, it also indicates that Mg$^{2+}$ is proportionally more difficult to leach than Al$^{3+}$ or Fe$^{3+}$. Indeed, at higher levels of leaching, when the internal part of the octahedral sheet is being extensively attacked, relatively higher amounts of Fe$^{3+}$ and Al$^{3+}$ are extracted. With the leaching model described above it is possible to consider that the extraction of the three cations takes place simultaneously but at different rates. In other words, the kinetics of the process can be formally treated as three reactions occurring in parallel.

Kinetic model

The leaching of the palygorskite could be included in the group of solid-liquid reactions in which the products of the reaction, i.e., cations and H$_2$O formed by reaction of H$^+$ with the (OH) groups of the octahedral sheet, are released from the solid and go into the liquid phase. On the other hand, the other reaction product which may be formed, i.e., SiO$_2$, remains on the surface of the untreated fibres. If this is so, then three steps have to be considered in the overall reaction: (a) diffusion of the protons from the solution to the surface of the silica generated during the reaction and covering the particles (ashes); (b) chemical reaction of the protons with the framework; (c) diffusion of the cations from the crystal to the solution.

In a process of this type there is always a nucleus which has not reacted and in which the radius of the unaltered core decreases as a function of time (Levenspiel, 1979). A shell-reaction model of this type can be kinetically represented (Carberry, 1976) by assuming that the diffusion of the hydrated protons is slower than the rate of reaction of the protons with the silicate, i.e., the concentration of HCl in the interior of the non-reacted nucleus is practically zero. Thus, the kinetic equations developed for different types of particles are given in Table 1 assuming that one of the three steps described above is the controlling step in the reaction. If the diffusion of the cations either through the ashes or from the ashes to the solution is the controlling step, the kinetic equation would be analogous to the case of proton diffusion, and therefore it is not possible kinetically to distinguish both types of diffusion.

We have also considered a potential kinetic equation in which the order with respect to the concentration of Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$ is equal to one, and the order with respect to the concentration of protons is equal to $a$. A model of this type has been used in the literature.
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Fig. 1. Dependence of percentage cation leached on total cation exchanged at different temperatures for Torrejón palygorskite (liquid to solid ratio = 4 and (H⁺) = 1).

(Osthaus, 1956; Abdul-Latif & Weaver, 1969) to study the kinetics of the acid attack of different silicates.

To find the kinetic model which fits our experimental results best, the reaction has been followed up to a certain time for which the change in the concentration of protons in the solution is <15% of the original. This allows us to consider that in any experiment the acid concentration remains constant and practically equal to the initial concentration. The
TABLE 1. Kinetics of the liquid-solid reaction for particles of constant size and different shapes

<table>
<thead>
<tr>
<th>Shape of the particle</th>
<th>Controlled by external diffusion</th>
<th>Controlled by diffusion through the ashes</th>
<th>Controlled by chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat plate</td>
<td>$K' t = (1 - X_{cation})$</td>
<td>$K' t = (1 - X_{cation})^2$</td>
<td>$K' t = (1 - X_{cation})$</td>
</tr>
<tr>
<td></td>
<td>$K' = \frac{bK_1}{\rho_{cation}L} H^+$</td>
<td>$K' = \frac{2bD_e}{\rho_{cation} L^2} H^+$</td>
<td>$K' = \frac{bK_1}{\rho_{cation}L} H^+$</td>
</tr>
<tr>
<td>Cylinder</td>
<td>$K' t = (1 - X_{cation})$</td>
<td>$K' t = (1 - X_{cation}) + X_{cation} \ln X_{cation}$</td>
<td>$K' t = (1 - X_{cation})$</td>
</tr>
<tr>
<td></td>
<td>$K' = \frac{2bK_1}{\rho_{cation}R} H^+$</td>
<td>$K' = \frac{4bD_e}{\rho_{cation} R^2} H^+$</td>
<td>$K' = \frac{bK_1}{\rho_{cation}R} H^+$</td>
</tr>
<tr>
<td>Sphere</td>
<td>$K' = \frac{3bK_1}{\rho_{cation}R} H^+$</td>
<td>$K' = \frac{6bD_e}{\rho_{cation} R^2} H^+$</td>
<td>$K' = \frac{bK_1}{\rho_{cation}R} H^+$</td>
</tr>
</tbody>
</table>

$D_e = \text{effective diffusion coefficient cm}^2/\text{seg.}$

$b = \text{constant.}$

$\rho = \text{molar density of the cation in the solid phase: (mol/cm}^3\text{).}$

$X_{cation} = \text{fraction of extracted cation.}$

$L = \text{length of plate.}$

$R = \text{radius of cylindrical particle.}$

results obtained have been fitted to the different models presented in Table 1, by means of the least squares criteria and the adequacy of the models has been compared by using the statistical tests, i.e., correlation coefficient (c.c.), Fisher's $F$ and Exner's $\psi$ parameters (Fisher, 1955; Exner, 1966). The higher $F$, the lower $\psi$, and the closer the correlation coefficient to 1, the better is the fit.

The kinetic constant, together with the statistical parameters for the leaching of Mg$^{2+}$, Fe$^{3+}$ and Al$^{3+}$ are listed in Tables 2, 3 and 4. It can be seen that a better fit is obtained for models in which the controlling step is diffusion through the ashes, than for models in which the chemical reaction of the proton with the framework of the palygorskite is the slowest step. Nevertheless, it is not possible, by statistical criteria, to distinguish between the two geometries, i.e., cylinder and flat plate. This is in agreement with Carberry (1976) who stated that for gas-solid reactions, and with models controlled by diffusion, the equation corresponding to different geometries yields similar results for degrees of conversion $<30\%$, which is greater than the degrees of leaching obtained in this work. In our case it appears that the process is not purely diffusion controlled throughout the range of experimental conditions. Indeed, a first-order equation with respect to the concentration of cations fits the results very well. Moreover, the selectivity for the extraction of the different cations changes with the experimental conditions used. Therefore, all these results would indicate that away from equilibrium, diffusion is the slowest step; but when the reaction proceeds, the chemical step becomes slower and can be the controlling one.
Acid leaching of palygorskite

Table 2. Kinetic constants obtained with different models for leaching of Mg^{2+} (liquid to solid ratio = 200)

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$H^+$ (mol$^{-1}$)</th>
<th>$K'$ ($\times 10^{-4}$) (min$^{-1}$)</th>
<th>Flat plate Parameters</th>
<th>Cylinder Parameters</th>
<th>Sphere Parameters</th>
<th>First order reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ext.* Diff.** Diff.* Diff.** Chem. Diff. Chem. reaction</td>
<td>ashes ashes ashes reaction reaction</td>
<td>ashes ashes reaction reaction</td>
<td>ashes ashes reaction reaction</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>2.5134 2.3407 0.8305 1.4825</td>
<td>0.5854 1.0435 8.9477</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c.c.$ 0.9961 0.8863 0.9948 0.9959</td>
<td>0.9947 0.9958 0.9970</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi$ 0.1249 0.6549 0.1445 0.1282</td>
<td>0.1449 0.1295 0.1092</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F$ 254 73272 189 241</td>
<td>188 236 333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.25</td>
<td>3.6999 2.0314 1.1878 2.1721</td>
<td>0.8361 1.5275 13.3513</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c.c.$ 0.9990 0.9991 0.9991 0.9990</td>
<td>0.9991 0.9990 0.9995</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi$ 0.0627 0.0570 0.0578 0.0606</td>
<td>0.0577 0.0607 0.0772</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F$ 1016 1227 1193 1085</td>
<td>1200 1084 669</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.05</td>
<td>1.4717 0.8146 0.2621 0.8534</td>
<td>0.6000 0.7231 11.077</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c.c.$ 0.9310 0.9325 0.9328 0.9314</td>
<td>0.9329 0.9315 0.9286</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi$ 0.5164 0.5107 0.5098 0.5150</td>
<td>0.5095 0.5145 0.5247</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F$ 13 13 13 13</td>
<td>13 13 12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.05</td>
<td>2.8772 1.4689 0.8502 1.6670</td>
<td>0.5939 1.1673 11.280</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$c.c.$ 0.9844 0.9843 0.9843 0.9844</td>
<td>0.9843 0.9844 0.9844</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi$ 0.2186 0.2492 0.2493 0.2486</td>
<td>0.2494 0.2486 0.2487</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F$ 62 62 62 62</td>
<td>62 62 62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.05</td>
<td>2.9444 1.5243 0.8822 1.7103</td>
<td>0.6185 1.1986 11.398</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c.c.$ 0.9976 0.9986 0.9988 0.9978</td>
<td>0.9988 0.9979 0.9963</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi$ 0.0974 0.0737 0.0698 0.0932</td>
<td>0.0683 0.0918 0.1211</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F$ 419 734 819 458</td>
<td>854 472 270</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Parameters found by fitting to a kinetic model in which control is by external diffusion.
** Parameters found by fitting to a kinetic model in which control is by diffusion through the ashes.

All kinetic constants ($K'$) of the different theoretical models include the concentration of the protons:

$$K' = K[H^+]^a$$

In order to find the apparent order of reaction with respect to the concentration of acid we have measured $K'$ for a model in which the controlling step is diffusion through the ashes, at different initial concentrations of acid (Tables 2–4), and fitted these data to the equation:

$$\ln K' = \ln K + a \ln [H^+]$$

The values of $K$ and $a$ obtained for each of the three leached cations were calculated and are given in Table 5. The order with respect to $[H^+]$ is different for the three cations and $<1$, indicating that the acid attack of palygorskite is more complex than a simple diffusion-reaction process which has been used to deduce the models given in Table 1.

Activation energy

From the kinetic rate constants for the extraction of the different cations obtained from the diffusion models at different temperatures of leaching (Tables 2–4) the activation
energies for extraction of Mg$^{2+}$, Fe$^{3+}$ and Al$^{3+}$ have been calculated by means of the Arrhenius equation and are listed in Table 6. The activation energies for the three cations are <10 kcal mol$^{-1}$, which is a good indication that diffusion is playing an important role in these processes. Moreover, the activation energies for the extraction of the three cations are different and follow the order Al$^{3+}$ > Fe$^{3+}$ > Mg$^{2+}$ which could be related to different accessibility to the reactant. The activation energy data show, as the kinetic results did, that the degree of accessibility should be Mg$^{2+}$ > Fe$^{3+}$ > Al$^{3+}$, and taking into account the selectivity curves in Fig. 1, most of the octahedral positions at the edges are occupied by Mg$^{2+}$, some by Fe$^{3+}$, and practically none by Al$^{3+}$. This conclusion is in agreement with the results of Singer (1977) and Heller-Kallai & Rozenson (1981) who found by Mössbauer spectroscopy that some Fe$^{3+}$ can be located in the octahedral edge positions, which are mainly occupied by Mg$^{2+}$.

**Influence of the type of palygorskite**

In Table 7 the kinetic rate constants for the acid leaching of the Serradilla palygorskite, calculated for a diffusion model, are listed and it can be seen that the rate constants for the extraction of Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$ are lower than for the Torrejón palygorskite (Table 5).
Acid leaching of palygorskite

TABLE 4. Kinetic constants obtained with different models for leaching of Al\(^{3+}\) (liquid to solid ratio = 200)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Flat plate</th>
<th>Cylinder</th>
<th>Sphere</th>
<th>First order reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ext.* diff.</td>
<td>10.931</td>
<td>11.415</td>
<td>8.0898</td>
<td>7.9025</td>
</tr>
<tr>
<td>Diff. ** ashes</td>
<td>6.1234</td>
<td>5.9683</td>
<td></td>
<td>22.139</td>
</tr>
<tr>
<td>c.c.</td>
<td>0.9954</td>
<td>0.9951</td>
<td>0.9949</td>
<td>0.9953</td>
</tr>
<tr>
<td>ψ</td>
<td>0.1353</td>
<td>0.1429</td>
<td>0.1370</td>
<td>0.1434</td>
</tr>
<tr>
<td>F</td>
<td>216</td>
<td>193</td>
<td>211</td>
<td>192</td>
</tr>
<tr>
<td>20</td>
<td>0.05 K'</td>
<td>1.3059</td>
<td>1.6048</td>
<td>1.8995</td>
</tr>
<tr>
<td>Diff. ** ashes</td>
<td>1.6422</td>
<td>1.3264</td>
<td>1.3639</td>
<td></td>
</tr>
<tr>
<td>c.c.</td>
<td>0.9555</td>
<td>0.9535</td>
<td>0.9532</td>
<td>0.9550</td>
</tr>
<tr>
<td>ψ</td>
<td>0.4174</td>
<td>0.4264</td>
<td>0.4277</td>
<td>0.4282</td>
</tr>
<tr>
<td>F</td>
<td>21</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>0.05 K'</td>
<td>2.6660</td>
<td>2.1714</td>
<td>1.3945</td>
</tr>
<tr>
<td>Diff. ** ashes</td>
<td>1.0157</td>
<td>1.2596</td>
<td>6.5486</td>
<td></td>
</tr>
<tr>
<td>c.c.</td>
<td>0.9545</td>
<td>0.9565</td>
<td>0.9552</td>
<td>0.9554</td>
</tr>
<tr>
<td>ψ</td>
<td>0.4219</td>
<td>0.4124</td>
<td>0.4186</td>
<td>0.4082</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>21</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>50</td>
<td>0.05 K'</td>
<td>5.5846</td>
<td>4.9739</td>
<td>3.2930</td>
</tr>
<tr>
<td>Diff. ** ashes</td>
<td>2.4265</td>
<td>2.7581</td>
<td>12.5560</td>
<td></td>
</tr>
<tr>
<td>c.c.</td>
<td>0.8982</td>
<td>0.8926</td>
<td>0.8906</td>
<td>0.8989</td>
</tr>
<tr>
<td>ψ</td>
<td>0.6216</td>
<td>0.6376</td>
<td>0.6431</td>
<td>0.6452</td>
</tr>
<tr>
<td>F</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>70</td>
<td>0.05 K'</td>
<td>5.5846</td>
<td>4.9739</td>
<td>3.2930</td>
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<tr>
<td>Diff. ** ashes</td>
<td>2.4265</td>
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<tr>
<td>c.c.</td>
<td>0.8982</td>
<td>0.8926</td>
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<tr>
<td>ψ</td>
<td>0.6216</td>
<td>0.6376</td>
<td>0.6431</td>
<td>0.6452</td>
</tr>
<tr>
<td>F</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

* Parameters found by fitting to a kinetic model in which control is by external diffusion.
** Parameters found by fitting to a kinetic model in which control is by diffusion through the ashes.

This could be explained by the fact that the process is diffusion controlled, and the surface area of the Torrejón palygorskite (60–200 m\(^2\).g\(^{-1}\)) is higher than that of the Serradilla mineral (43–60 m\(^2\).g\(^{-1}\)). Then the chemical composition of the octahedral sheet does not play a predominant role in cation extraction by acid leaching. Therefore, the different behaviour of the two palygorskites to acid leaching could be explained on the basis of the surface area differences.

CONCLUSIONS

Acid attack of palygorskite does not obey a purely diffusion controlled process. Diffusion is the controlling factor at low levels of leaching, while at high levels the chemical reaction can be the rate-determining step.

TABLE 5. Values of \(K\) and \(a\) obtained for each of the three cations leached from the Torrejón palygorskite for a model in which the controlling step is diffusion through the ashes.

<table>
<thead>
<tr>
<th>Cation</th>
<th>(K) (min(^{-1}).mol(^{-1}).l(^{-1}))</th>
<th>(a) (mol.l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>(2.46 \times 10^{-4})</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>(0.103 \times 10^{-4})</td>
<td>0.38</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>(0.96 \times 10^{-4})</td>
<td>0.71</td>
</tr>
</tbody>
</table>
The low values found for the activation energies of the three cations provide a good indication that diffusion plays an important role in these processes. The activation energies and the selectivities for cation extraction show that the degree of accessibility should be $\text{Mg}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$.

The rate constants for the extraction of cations in a palygorskite from Serradilla are lower than those for a palygorskite from Torrejón, and the different behaviour of the two minerals could be explained on the basis of their differences in surface area.

### REFERENCES


Acid leaching of palygorskite


