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LEACHING OF CALCINED PHOSPHATE ORE PARTICLES WITH PHOSPHORIC AND ACETIC ACID SOLUTIONS AT 25°C: KINETIC CURVES AND RELATED TEXTURAL CHANGES

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The reactivity of calcined Tunisian phosphate ore was studied in both phosphoric and acetic solutions. Phase analysis from X-ray diffraction and IR absorption data indicate that carbonate apatite, or francolite, and fluorapatite are the main phases. However, it was observed that the calcium oxide phase, evident at the most intense peak (d=2.401 Å; 2θ = 37.42°) and at the absorbant band around 700 cm⁻¹, disappeared or were weakly defined for the solid leached in acetic medium. Nitrogen adsorption-desorption analysis shows a rising of mesopores at the surface of the leached particles and then an increase of their specific surface area, S_BET. The scanning electron microscope micrographs of the particles and their size distribution show a constancy of their outer dimensions during attack.

KEY WORDS: phosphate ore, porosity, calcination, acid dissolution, kinetics

1. INTRODUCTION

With regard to the increasing demand of phosphate and fertilizers, certain producer countries have begun to exploit low-grade phosphate reserves such as calcareous, dolomitic, or siliceous ores. This requires some enrichment methods. The heat treatment or calcination, flotation, selective extraction, and leaching using acidulated solutions are the main methods.

There are some investigations of enrichment of sedimentary and calcareous phosphate ore using selective extraction of calcite with HCl and NH₄Cl (Tsaias et al., 1980), dilute H₃PO₄ (Economou, 1984; Sdoukos, 1985a, 1985b), and dilute acetic acid solutions (Sadeddin and Abu-Eishah, 1990; Abu-Eishah et al., 1991; Economou and Vaimakis, 1997). These selective extraction methods were based on the relatively higher rate of dissolution of the calcite compared with that of the carbonated apatite or francolite. These two minerals are mainly present in sedimentary phosphate ores such as the Tunisian ore from the Gafsa mining area (Mgaidi et al., 2004) or the phosphorite Greek deposits (Economou et al., 1998). It was reported by the latter authors that the francolite minerals have the empirical formula Ca₉.₅₁Na₀.₃₅Mg₀.₁₄(PO₄)₁.₄₇(CO₃)₁.₂₆F₂.₅₀, which is generally accompanied by the calcite (CaCO₃) and...
dolomite (MgCO₃) minerals. The same authors indicated that the selective dissolution of carbonates with dilute acetic acid was used as an enrichment method of low-grade phosphate ores from the Epirus area. Accordingly, this process leads to a phosphate concentration of about 31% P₂O₅ from only 13.92% for the starting material.

In the same way, we have previously studied the leaching process of Tunisian phosphate ore in diluted phosphoric acid solutions (Ben Brahim et al., 1997, 1999; Mgaidi et al., 2003). We have investigated the change in porosity of the raw material (Ben Brahim et al., 1997; Mgaidi et al., 2003), and we have particularly pointed out the effect of the mesoporous structure on the kinetic rates (Ben Brahim et al., 1999).

On the other hand, some previous contribution studies dealing the enrichment method of phosphate rocks by calcination have been published. Some of them have been applied at different scales (Abouzied et al., 1980; Kumar, 1980; Lehr and Hsieh, 1981; Fava et al., 1981; Becker, 1983; Kaljuvee et al., 1995; Zafar and Pritchard, 1995; Blazy and Jdid, 1995; Mgaidi et al., 2004). Dealing with Moroccan deposits, Arafan et al. (1998) applied a new calcination process that consists of two-stage thermal processing under a controlled atmosphere. This process leads to a calcined phosphate rock having high P₂O₅ content (>32.25%) and very low impurity levels (CO₂ < 1%, organic C < 250 ppm, sulfur compounds < 60 ppm).

In a more recent work, Özer et al. (2002) studied a flue gas desulfuration with phosphate rock in a fluidized bed. Raw and calcined phosphate ore samples were considered. They have pointed out that according to Lodha et al. (1984), the presence of carbonates in rocks is undesirable from a H₃PO₄ manufacturing point of view. First, carbonates consume additional H₂SO₄ during the manufacture of phosphoric acid and superphosphates. Second, carbon dioxide produced during the reaction causes foaming, and this leads to the formation of smaller gypsum crystals. These blind the downstream phosphogypsum filters, and a low-quality phosphoric acid may be produced.

In spite of all these studies dealing with the heat treatment of natural phosphate ores, neither the evolution of the textural parameters nor the kinetic behavior in acidic media of calcined phosphate ore samples have yet been investigated. As early as 1972, Levenspiel (1972) pointed out that heat and mass transfer may play important roles in determining the rates of the solid-liquid reactions. In that case, the problem is to find out which parameters, related to the solid, affect the rate of dissolution and to what degree. According to Becker (1989), the major factor that controls the reaction rates is the specific surface area of the phosphate rock. So if the rock was coarse and non-porous, the reaction rate would be low. Previous studies in our laboratory have shown the importance of mesoporosity in the dissolution of phosphate ore in dilute aqueous phosphoric acid solutions (Ben Brahim et al., 1997, 1999; Mgaidi et al., 2003).

The present work consists of a contribution to the investigation, at laboratory scale, of the behavior of heat-treated natural phosphate during an acid attack. It concerns the dissolution of a sample of one size fraction particles in two acidic media, phosphoric and acetic. In this study, both the structural and textural changes of the remaining solids as well as the evolution of the chemical compositions of the leach solutions were investigated.

2. EXPERIMENTAL SECTION

The material used was natural phosphate ore from the Gafsa mining area in southwest Tunisia. A certain quantity of phosphate was sieved, and the 63–250 µm fraction was collected. The heat treatment of the obtained sample was performed in an electric furnace at 780°C for 1 hour under air atmosphere. The rise of temperature was 10°C min⁻¹. We have noted that the sintering process did not induce any collage on the side of the crucible. The dissolution was carried out in 100 mL jacked glass maintained at constant temperature with circulating water kept at 25°C. For each experiment, 50 mL of a 1.4 M acid solution (phosphoric or acetic) was transferred into the reactor. Phosphoric and acetic acids used are reagent grade.

The reaction was initiated by adding 5 g of calcined phosphate at time t = 0; the particle residence time in the reactor was varied between 0 and 30 min. At the end of each experiment, the unreacted remaining solid was separated by filtration as quickly as possible and then was washed, dried, and weighed. In addition, the solid and the liquid phases were kept for further investigation and analysis. In a separate experiment, we have recorded in situ the pH variation versus time using a glass electrode.

X-ray powder diffractometry was used to identify the mineralogical constituents of the phosphate ore samples. The phases present were determined by comparing the patterns with JCPDS standards. Measurements were made on a PHILIPS diffractometer apparatus using CuKα radiation. Scans were performed over the 2θ range from 20° to 60°. The phosphate samples were further investigated by IR spectroscopy analysis on a PERKIN ELMER instrument using the KBr pastille technique.

The P₂O₅ and CaO contents of each filtrate were determined. P₂O₅ was analyzed using a colorometric method...
using a Unicam UV/Vis spectrophotometer, while the
liberated CaO was measured titrimetrically with DTA/E. To-
tal CO₂ content of the different solids was determined by
a coulometric method using a Coulmat 702 Ströhlein
Instruments apparatus. The dissolved CO₂ in the leach
solution was then deduced by the difference between the CO₂
content of the starting solid and that of the remaining one
at a considered reaction time.

The porosimetric parameters of the solids were ob-
tained from the analysis of the adsorption-desorption
isotherms of nitrogen at 77 K using an automatic appara-
tus (Micromeritics ASAP 2000 Norcross GA). The par-
ticle size distributions of the solids were measured by laser
diffraction using a MasterSizer Malvern 2000 apparatus,
and their morphologies were observed under a scanning
electron microscope (SEM) system (PHILIPS, XL SE-
RIES, XL 30).

3. CHARACTERIZATION OF THE STARTING
MATERIAL

The compositions of both raw and calcined particles are
presented in Table 1, and the X-ray powder diffractogram
of the calcined sample is depicted in Fig. 1. Results show
that the ore is sedimentary deposit with carbonate apatite
and fluorapatite as the main phases. Moreover, values of
Table 1 show that the calcination leads to a phosphate
with relatively higher P₂O₅ and CaO contents (15% in-
crease) and a low CO₂ content (70% decrease). So, as re-
ported by Arafa et al. (1998), calcination constitutes an

<table>
<thead>
<tr>
<th>TABLE 1: Characterization of the 63–250 μm phosphate fraction before and after calcination at 780°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Raw ore</td>
</tr>
<tr>
<td>Calcined at 780°C</td>
</tr>
</tbody>
</table>

FIG. 1: X-ray powder diffractograms of the 63–125 μm calcined phosphate fraction before and after leaching with both acetic and phosphoric acid solutions.
enrichment method notably for sedimentary apatite varieties. However, as also seen in Table 1, we note a defacement of the surface properties of the heat-treated sample such as specific surface area and volume of pores. In the next part of this work, we are going to elucidate the behavior of such particles toward an acid attack by following their chemical and structural changes during dissolution.

The IR spectrum of the initial sample was recorded, and bands have been assigned. Results are shown in Fig. 2 and Table 2. The bands at 468, 567, 604, 960, 1042, and 1092 cm\(^{-1}\) correspond to the phosphorus group (PO\(_4^{3-}\)). This assignment is in fair agreement with those reported by Nyquist and Kagel (1971) and Nakamoto (1978). The first band is due to the \(\nu_2\) mode of vibrations, whereas the second and third correspond to the asymmetrical \(\nu_4\) stretching, and the peak at 960 cm\(^{-1}\) corresponds to \(\nu_1\) vibrations of the phosphate group; those at 1042 and 1092 cm\(^{-1}\) were assigned to the \(\nu_3\) stretching vibrations. The doublet at 1425 and 1455 corresponds to \(\nu_3\) vibrations of the carbonate group (CO\(_3^{2-}\)) of the apatite lattice. Similar assignment was attributed by Nyquist and Kagel (1971) and Nakamoto (1978). Dealing with the lat-

<table>
<thead>
<tr>
<th>Mode</th>
<th>Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_2) (PO(_4^{3-}))</td>
<td>468</td>
</tr>
<tr>
<td>(\nu_4) (PO(_4^{3-}))</td>
<td>567</td>
</tr>
<tr>
<td>(\nu_4) (PO(_4^{3-}))</td>
<td>604</td>
</tr>
<tr>
<td>(\nu_4) (CO(_3^{2-}))</td>
<td>645</td>
</tr>
<tr>
<td>(\nu) (CO(_3^{2-})) calcite</td>
<td>686</td>
</tr>
<tr>
<td>(\nu_2) (CO(_3^{2-}))</td>
<td>864</td>
</tr>
<tr>
<td>(\nu) (CO(_3^{2-})) calcite</td>
<td>870</td>
</tr>
<tr>
<td>(\nu_1) (PO(_4^{3-}))</td>
<td>960</td>
</tr>
<tr>
<td>(\nu_3) (PO(_4^{3-}))</td>
<td>1042</td>
</tr>
<tr>
<td>(\nu_3) (PO(_4^{3-}))</td>
<td>1092</td>
</tr>
<tr>
<td>(\nu) (CO(_3^{2-})) calcite</td>
<td>1382</td>
</tr>
<tr>
<td>(\nu_3) (CO(_3^{2-}))</td>
<td>1425</td>
</tr>
<tr>
<td>(\nu_3) (CO(_3^{2-}))</td>
<td>1455</td>
</tr>
<tr>
<td>(\delta) (O–H)</td>
<td>1626</td>
</tr>
</tbody>
</table>

**FIG. 2:** IR spectra of calcined phosphate particles before and after leaching in acetic solution.

**TABLE 2:** Assignment of IR absorption bands.
ter group, the peaks at 864 and 645 cm$^{-1}$ correspond to $v_2$ and $v_4$ vibration modes, respectively. This assignment agrees with the results of Brassens (1975). However, 3-weekly defined bands were observed at 686, 870, and 1382 cm$^{-1}$. As early as Gerald and Thomas (1960), these bands have been related to the calcite mineral.

4. REACTIONS AND KINETIC CURVES

It is well known that the dissolution process of natural phosphate in acidic media is an acid-base-type reaction. So the pH of the aqueous solution will be considered as an indicator of species. In a preliminary test, we have determined in situ the variation of pH versus reaction time. As seen in Fig. 3, the pH varied between 0.73 and 1.88 ($<pK_{a1} = 2.12$) for the phosphoric acid dissolution, in which case only H$_2$PO$_4^-$ anions and molecular H$_3$PO$_4$ species are present.

When fluorapatite or carbonate apatite is added into the acid solution, the reactions taking place can be written as follows, respectively:

$$\text{CaF}_2 \cdot 3\text{Ca}_3\text{(PO}_4\text{)}_2(s) + 14\text{H}^+ = 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{HF}(1)$$

$$\text{CaCO}_3 \cdot 3\text{Ca}_3\text{(PO}_4\text{)}_2(s) + 14\text{H}^+ = 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + \text{CO}_2 + \text{H}_2\text{O}(2)$$

Besides, as early as 1940, the P$_2$O$_5$, H$_2$O-CaO phase diagram was studied by Elmore and Far (1940). They have noted that at 298 K, the Ca(H$_2$PO$_4$)$_2$ is very soluble in water and gives Ca$^{2+}$ and H$_3$PO$_4$ ions in solution. For the acetic attack, as seen in Fig. 3, the pH ranged between 2.26 and 3.58, values inferior to the $pK_a = 4.75$.

This range corresponds to the coexistence of both molecular and dissociated forms of the organic acid. The selective dissolution of calcite in such media can be described by the following equation:

$$\text{CaCO}_3(s) + 2\text{CH}_3\text{COOH} = \text{Ca}^{2+} + 2\text{CH}_3\text{COO}^- + \text{CO}_2 + \text{H}_2\text{O}$$ (3)

To explore the kinetic results, we have considered the extraction yield profiles expressed as P$_2$O$_5$, CaO, and CO$_2$ in the leach solutions. The conversion fractions were calculated as follows:

$$P_2O_5(\%) = \frac{m_{0}X_{0,P_2O_5} - m_{t}X_{t,P_2O_5}}{m_{0}X_{0,P_2O_5}}$$ (4)

where $m_{0}$, $X_{0,P_2O_5}$ and $m_{t}$, $X_{t,P_2O_5}$, are the mass and P$_2$O$_5$ contents of the initial (at $t = 0$) and remaining solids (at a time $t$), respectively.

Figure 4 shows that the conversion fraction of P$_2$O$_5$ is higher in H$_3$PO$_4$ solution, at about 40%. The corresponding one obtained in acetic acid does not exceed 2% after

![FIG. 3: In situ recorded pH of the leach solutions versus reaction time.](image-url)
FIG. 4: Profile of the extent of dissolution of $\text{P}_2\text{O}_5$, $\text{CaO}$, and total $\text{CO}_2$ against the reaction time.

30 min of reaction time. It can be also seen in the same figure that the $\text{CaO}$ yield follows a similar variation. So it is slightly inferior to 60% in phosphoric medium, and it remains less than 10% in the other one. From the same figure, it appears that the dissolved $\text{CO}_2$ in phosphoric acid is twice the corresponding one obtained with acetic leaching, at about 40% and 20%, respectively.

According to Eqs. (1) and (2), the dissolved $\text{CaO}$ from the francolite network should be related to the release of $\text{P}_2\text{O}_5$. Thus we have determined the $\text{CaO}$-to-$\text{P}_2\text{O}_5$ ratio in the leach solutions. Curves plotted in Fig. 5 show that for the acetic dissolution, the ratio reaches a relatively high value of about 5.5 in the few first minutes of reaction time. The selective and fast dissolution of the calcite phase, de-

FIG. 5: $\text{CaO}$ to $\text{P}_2\text{O}_5$ mass ratio in the leach solutions versus reaction time.
scribed by Eq. (3), and the low value of the denominator are responsible for this fact. In the case of phosphoric attack, this ratio is less inferior, and it does not exceed 1.6. This latter value corresponds to the effective ratio deduced from the empirical formula of the francolite. That is an additional argument that the destruction of the apatite network occurs only in the phosphoric medium, described somehow by Eqs. (1) and (2).

5. CHARACTERIZATION OF THE REMAINING SOLIDS

As revealed by Fig. 1, the phase analysis from X-ray diffraction data indicated that all compositions of the material before and after leaching consisted of francolite and fluorapatite phases. However, as illustrated in diffractogram (a), it can be seen that a calcium oxide phase, evident at the most intense peaks ($d = 2.401$ Å at $2\theta = 37.42^\circ$ and $d = 3.327$ Å at $2\theta = 26.78^\circ$), is present in the starting material. These two peaks are weakly defined for the (b) diffractogram of the solid obtained after leaching in acetic medium. This is in agreement with the selective dissolution of this mineral. On the other hand, IR analyses were performed on the remaining solids. Results are shown in Table 2 and Fig. 2. We note that the 3-week characteristic bands of calcite mineral at 686, 870, and 1382 cm$^{-1}$ disappear after leaching in acetic medium.

Investigations of the textural parameters of the raw and calcined ore are shown in Table 1. The calcined phosphate presents a very low specific surface area, $S_{BET}$, determined by the Brunauer, Emmet and Teller (BET) method (Brunauer et al., 1938). We have reported in a previous paper (Mgaidi et al., 2004) that above $500^\circ$C of calcination temperature, the drastic decline of $S_{BET}$ was attributed to the diffusion of matter between bounded grains and then to the reduction of porosity.

The evolution of the texture during acid dissolution was also performed. Figure 6 shows the adsorption-desorption isotherms of the remaining solids after 20 min of reaction time in two acidic media. Each one of the curves shows the appearance of an hysteresis loop during the leach procedure. It is well noted that the isotherm of the calcined sample at $780^\circ$C, which is not represented here, was badly defined and so the hysteresis phenomenon was absent.

According to the IUPAC classification (IUPAC, 1985), the observed loops from Fig. 6 correspond to the H3 type. This latter may indicate the apparition of the ink-bottle-shaped mesopores (20–500 Å diameter). Similar loop types were independently observed for different ores: a

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**FIG. 6**: Nitrogen adsorption-desorption isotherms of calcined phosphate particles after leaching (dashed lines for desorption).
raw Tunisian phosphate (Ben Brahim et al., 1997) and a manganiferous ore leached with sulfuric acid and lactose (Vegliò et al., 2001).

Additionally, the desorption branches of the isotherms were considered to obtain the cumulative pore volumes \( (V_p) \) and the cumulative surface areas \( (S_{cum}) \). These two porosimetric parameters as well as the \( S_{BET} \) are reported in Table 3. It may be seen that all these textural parameters increase with increasing dissolution time. This fact is assigned to the gradual appearance of mesopores that are so narrow as to allow the capillary condensation of the adsorbed gas. As a consequence, the hysteresis phenomenon was observed between the adsorption and desorption branches (see Fig. 6). As revealed by the experimental results, the textural changes are more pronounced for the phosphoric dissolution; in this medium, the apatite lattice was more affected.

The particle size distribution of the solid samples was determined using laser diffraction with water as a dispersant. In this medium, the material used is insoluble. Plots of Fig. 7 show monomodal curves of volume averages. The initial sample as well as the leached sample in acetic medium had the same mean particle diameter of about 150 \( \mu m \). This latter is practically close to the calculated mean value of 156.5 \( \mu m \) for the 63–250 \( \mu m \) used fraction. However, the plot of the remaining solid in phosphoric acid presents a little displacement to the low size values. This fact can be related to the disintegration of some grains due to the frailness of the more reactive sites of the apatite lattice in phosphoric medium. Figure 8 confirms the morphological changes of the ore particles observed by SEM analyses. It can be seen in Fig. 8a that apart from some cracked particles by the previous heat treatment, the initial solid presents a perfect smooth surface, while the remaining solid micrographs (Figs. 8b and 8c) show that the particles became porous and that they preserve their outer dimension during dissolution. In a previous work, dealing with the dissolution of raw phosphate (Mgaidi et al., 2003), we also observed that all particles were submitted to the same sequences of states without disintegration.

### 6. CONCLUSION

The dissolution of a calcined Tunisian phosphate ore in two acid solutions, phosphoric and acetic, at the same concentration of 1.4 M was studied. Results show the following.

<table>
<thead>
<tr>
<th></th>
<th>Before dissolution</th>
<th>Acetic acid (1.4 M)</th>
<th>Phosphoric acid (1.4 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{BET} ) (m(^2) g(^{-1}))</td>
<td>0.66</td>
<td>3.26</td>
<td>22.01</td>
</tr>
<tr>
<td>( S_{cum} ) (m(^2) g(^{-1}))</td>
<td>0.25</td>
<td>10.87</td>
<td>29.48</td>
</tr>
<tr>
<td>( V_p ) (10(^{-3}) cm(^3) g(^{-1}))</td>
<td>32.8</td>
<td>700.5</td>
<td>1212.4</td>
</tr>
</tbody>
</table>

**TABLE 3**: Porosimetric analysis of the calcined phosphate ore before and after acid dissolutions.

**FIG. 7**: Size distribution of the calcined phosphate particles before and after dissolution.
FIG. 8: Scanning electron microscope micrographs of calcined phosphate particles: (a) unleached; (b) leached in acetic solution; (c) leached in phosphoric solution

1. The ore is sedimentary deposit with francolite and fluorapatite as the main phases accompanied by the calcite mineral. X-ray diffraction and IR absorption analysis showed the selective dissolution of the calcite phase in acetic medium.

2. The extraction yield profiles expressed as $\text{P}_2\text{O}_5$, CaO, and $\text{CO}_2$ show that the release of the latter element is higher in phosphoric solution. This is linked to the carbonate released from the calcite and francolite network in the phosphoric medium and from only the first cited mineral when the acetic dissolution was performed.

3. The specific surface area and volume of pores of the calcined phosphate sample increase during leaching in the two acidic media. A gradual appearance of the hysteresis phenomenon occurs consequently, showing the appearance of mesopores during leaching.

4. The particle size distribution curves of the samples show a mononodal distribution.

Investigations in this area constitute a database for further calculation and modeling of the kinetics of dissolution of calcined phosphate ore in acidic media. More investigations are required at a greater scale, but nevertheless for industrial modeling.

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