Beneficiation of Iraqi Akash at Phosphate Ore Using Organic Acids for the Production of Wet Process Phosphoric Acid

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Abstract

In the present work, leaching process studied using organic acids (acetic acid and lactic acid) to extract phosphate from the Iraqi Akashat phosphate ore by separation of calcareous materials (mainly calcite). This approach characterized by energy conservation, environmental enhancement by recovery of calcite as calcium sulfate (gypsum), keeping the physical and chemical properties of apatite. Samples were analyzed using X-ray diffraction and FTIR spectrophotometer. From the obtained experimental data it was found that using the two organic acids yields closed purity values of the produced apatite at the optimum conditions, while at different acid concentrations, it was found that the efficiency of acetic acid is higher at the low acid concentration (2 wt%), and that lactic acid gives the higher efficiency at high acid concentration (10 wt%). Concerning the ratio of acid volume to ore weight ratio, it was found that reducing this ratio to 5 ml/gm cause an increase in the purity of apatite at the optimum concentrations of the two acids. In addition, it was found that the reaction of the two organic acids with the calcareous material are fast and that the optimum reaction time, in which high purity apatite produced is 10 minutes.

Keywords: Iraqi Akashat phosphate ore, selective leaching, beneficiation, calcareous phosphate ore, organic acids

1. Introduction

To meet the food needs of the increasing world population, there is a steadily growing demand for phosphate fertilizers. The phosphoric acid production is directly linked to the phosphate fertilizer consumption, which is continuously rising. This represents an increase of the phosphoric acid production.

Phosphate rocks are vital non-renewable resources and essential components in fertilizers and phosphorus-based chemicals. It is neither substitutable nor recyclable, therefore, the total demand must be provided through the mining, beneficiation and chemical processing of natural resources of this ore. Phosphate deposits may be divided in three major groups, according to their origin:

1. Deposits from sea sediments.
2. Igneous and metamorphic deposits.

It should be mentioned that most of world's phosphate resources are of sedimentary deposits origin [1,2].

Apatite (the desired component in phosphate rock) has the general formula, $Ca_{10}(PO_4)_{6}X_2$ where $X$ is typically $F$ (fluorapatite, FAp), $OH$ (hydroxyapatite, OHAp), or $Cl$ (chlorapatite, ClAp). The apatite lattice is very tolerant of substitutions, vacancies and solid solutions, for example, $X$ can be replaced by $\frac{1}{2}CO_3$ or $\frac{1}{2}O$; $Ca$ by $Sr$, $Ba$, $Pb$, $Na$ or vacancies; and $PO_4$ by $HPO_4$, $AsO_4$, $VO_4$, $SiO_4$ or $CO_3$ [3].

In sedimentary deposits of marine origin, the phosphate material occurs in admixtures with detritus materials such as quartz, mica and clay,
often with limestone and occasionally with dolomite. Igneousapatitementcontain other impurities, not commonly found in sedimentary deposits, originating from other constituents of the magma from which the apatite crystallized [4].

Phosphate deposits in Iraq are part of a wide Arab phosphate which stretches from Mauritania in the west to Iraq and Saudi Arabia in the east through North Africa and Eastern Mediterranean Sea.

The most important of these formations is Akashat phosphate layer, thickness of up to ten meters in which the proportion of phosphorus pent-oxide between 21-22% which can be increased to more than 25% by simple physical methods. Phosphatedeposits in sedimentary layers appears freely with limestone and clay stone [5].

The phosphoric acid production is directly linked to the phosphate fertilizer consumption, which is expected to rise. It can be produced from phosphate ore via two major process routes, the so-called wet processes, using strong mineral acids for digestion of the ore and the dry processes, producing elemental phosphorus as an intermediate by burning of the ore in an electric furnace or in a rotary kiln. Since phosphoric acid produced through dry routes contains less impurities its application lies mainly in the "high added value" areas such as detergents, silicates, feldspar, mica, calcite, dolomite and clays to meet the requirements of the phosphate industry [8].

The marketable sedimentary and igneous phosphate ore usually has 28–36% and 35–39% \( P_2O_5 \) respectively. Phosphate ores should not contain more than 8% carbonates in order to be economical [9]. It is necessary in the fertilizer industry for the phosphate ores to have:

- \( P_2O_5 \) content larger than 30%.
- \( CaO/P_2O_5 \) ratio smaller than 1.6,
- \( MgO \) content less than 1% and \( Fe_2O_3 \) and \( Al_2O_3 \) content: maximum 2.5% [10].

Effective beneficiation can be achieved by various processes, depending upon the liberation size of phosphate and gangue minerals and other ore specifications. Different processes like screening, scrubbing, heavy media separation, washing, roasting, calcinations, leaching and flotation may be used.

The presence of free carbonates in the phosphate rocks usually requires additional acid (sulfuric acid) during the manufacture of phosphoric acid and superphosphates by the "wet process". In addition, the carbon dioxide produced during the acid addition causes more foaming and results in the production of smaller size gypsum crystals that may blind the downstream phospho-gypsum filters. Hence, a low quality phosphoric acid is produced [11].

The beneficiation of sedimentary phosphate ores containing carbonate gangue is a worldwide problem and adequate technology for processing such ores on an industrial scale does not exist at present.

Calcination is used in areas having low cost energy and limited water resources like the Al-Jalamid phosphate ore in Saudi Arabia which contain 40–50% carbonate, 8–10% organic matter and 16–25% \( P_2O_5 \). It is processed by calcination at 850 °C for about 1 h, followed by leaching with water to remove lime and quenching by 5% \( NH_4NO_3 \) to remove magnesium [12]. Calcinationis
a thermal decomposition of calcareous material. Depending on the process conditions, calcination may lead to almost complete elimination of the calcareous materials that existed in the phosphate ore.

Flotation of calcareous phosphate ores may be effective only if the phosphate particles are highly liberated from the gangue materials and exhibit a relatively coarse size. The flotation process seems to work best on ores containing well-crystallized carbonates. When the ore contains soft or chalky carbonates, the results are less satisfactory [13].

With regard to the problems with sedimentary phosphate ores, acid leaching is a promising method that can be applied to treat the calcareous phosphate ores and more attention is being given to leaching methods. Since nearly 80% of the world’s phosphate resources are calcareous ores, including Akashat Iraqi ore, an experimental work is to be adapted to specify the suitable operating conditions of beneficiation.

The selected leaching agents should not attack the phosphate minerals, but unfortunately, strong acids also attack the apatite while leaching the carbonates. However, weak organic acids show an appreciable degree of selective leaching of calcareous material in low grade phosphate rocks and ores [14].

Organic acids are selective leaching agents for the beneficiation of low grade phosphate rock, depending on the reaction conditions, nature and size of the particles. Although organic acids are promising leaching agents, there are some restrictions in the selection of the organic acids and this beneficiation method has some drawbacks that should be taken into consideration.

Using this leaching method, many of the problems encountered during the manufacture of phosphoric acid and superphosphates are resolved. At the same time, both calcium and magnesium carbonates are removed in the form of highly soluble salts. The reaction time needed for leaching is small, thus the destructive action of dilute organic acids on the phosphate minerals is minimum. Typically, organic acid extractions are carried out under moderately acidic conditions and their degradation is biologically easy. Furthermore, in industrial processes, organic acids cause a little corrosion [13].

Due to the previous mentioned information, an experimental compartment study is to be conducted on Iraqi Akashat phosphate ore to separate the calcareous gangue materials (mainly calcite) using organic acids leaching (acetic and lactic) to specify the optimum conditions that give a marketable phosphate ore with the necessary $(P_2O_5)$ content as a raw material of wet process phosphoric acid required for fertilizers industry.

2. Chemistry of Leaching

In the case of acetic acid, the reaction between acetic acid and calcareous materials can be written as follows [9]:

$$CaCO_3(s) + 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2(aq) + CO_2(g) + H_2O(l) \quad \ldots(3)$$

The acid ratio (used/stoichiometric) is the ratio of the used amount of acetic acid and the required amount for reaction (3). The stoichiometry is determined by using the following equation [20]:

$$\text{Acid stoichiometry} = \frac{\text{mol. of } CH_3COOH}{\text{mol. of } CO_2} = 2:1$$

Completion of this reaction depends on the product solubility, acetic acid concentration, process temperature, reaction time, and other process conditions. However, the dissolution kinetics could also control the overall rate of selective leaching of calcareous minerals in the phosphate rocks and ores.

The mechanism of carbonate dissolution in acetic acid solution involves the initial formation of $Ca(CH_3COO)_2$ and carbonic acid which decomposes into $CO_2$ and $H_2O$. If the acetic acid expresses no selectivity, then the following reaction may occur:

$$Ca_{(s)}(PO_4)_{10}F_2 + 20CH_3COOH \rightarrow 10Ca^{2+} + 20CH_3COO^- + 2HF + (6-x)H_3PO_4 + xH_2PO_4^- + xH^+ \quad \ldots(4)$$

However, acetic acid should not attack the phosphate minerals and thus reaction (4) does not take place while reaction (3) proceeds to completion.

Similarly, in the dissolution of carbonate minerals using lactic acid, the reaction between lactic acid and calcareous material is as follows:

$$CaCO_3(s) + CH_3CH(OH)COOH(aq) \rightarrow Ca(CH_3CH(OH)COO)_2(aq) + CO_2(aq) + H_2O(l) \quad \ldots(5)$$

Under normal conditions, reaction (5) may be considered as an irreversible reaction due to the removal of $CO_2$ produced during the process by stirring the reaction mixture. The reactions for the other impurities depend on the nature and composition of the raw phosphate ore. The simplest mechanism for the rational understanding of these selective leaching processes can be expressed as follows [15]:
where: $M=Ca^{2+}$ and/or $Mg^{2+}$, and $X=CH_{2}CH(OH)COO^{-}$ (lactate) or $CH_{2}COO^{-}$ (acetate).

Again, the acid should not attack the phosphate minerals and thus reaction (7) does not take place while reaction (6) proceeds to completion or equilibrium depending on the solubility products ($K_{sp}=8.35, 7.46$ for $CaCO_{3}$ and $MgCO_{3}$, respectively) and acidity constants for lactic acid ($pK_{a}=3.86$ at 25 °C) and $CO_{2}$ ($pK_{a}=6.35$, $pK_{a}=10.33$ for $H_{2}CO_{3}$).

The main factors investigated by researchers were: leaching reagent, acid concentration, reaction time, liquid/solid ratio (pulpsolid percent); temperature, particle size distribution, stirring speed and type and nature of the ore.

The organic acids most commonly used in carbonate leaching are: acetic acid, lactic acid, formic acid and succinic acid which are all fully miscible with water, although succinic acid has a lower solubility (67 g/L at 22 °C) and is limited by its solubility at low temperatures. The fully miscible acid salts are soluble in water and can be easily separated from the beneficiated solid phosphate product by filtration.

In the weak organic acids, the increasing concentrations of organic acids cause little increase in the solution acidity because they are only partially dissociated in aqueous solution. For example, 1.0 M acetic acid has a pH of 2.4, indicating that merely 0.4% acetic acid molecules are dissociated.

According to the literature, all the organic acids give good results for the selective leaching of calcareous material. Acetic and formic acids may cause corrosion effects on the equipment, along with a tendency to attack the phosphate minerals, whilst lactic acid causes less corrosion on the equipment with minimal risk of phosphate mineral dissolution. It is reported that by dilution of the acid with water, the surface area of contact between the acid and the carbonates will increase [16].

Highly concentrated organic acid solution does not react with calcium carbonate because of the large polarity of the O–H bond of the acid molecules and it is necessary to use dilute solution for an effective reaction. In dilute solutions, water molecules tend to decrease the effect of polarity of the organic acids O–H bond [15].

Organic acids are also less destructive if some of the produced solution is added or recycled to the process [16].

Acid concentration is one of the key factors in achieving good results in the selective dissolution of calcareous mineral in phosphate ores. In general, the $P_{2}O_{5}$ content increases with increasing acid concentration to reach a certain level, and then remains almost constant.

Under optimum concentrations, there are no physical or chemical changes in the phosphate rock, or losses of its tri calcium phosphate (TCP) content. There are differences in the optimum organic acid concentrations reported in previous studies which could be attributed to the differences in origin of the various sedimentary resources. The acid concentration that gives the best leaching result has been found to depend on the acid type, carbonates mineral content and the liquid/solid ratio [13].

The effect of reaction time on the dissolution of carbonate minerals in the leaching process was studied by many investigators. It is clear that with increasing reaction times up to an optimum value, the $P_{2}O_{5}$ percentage increases along with the corresponding reduction in calcareous materials content. At the optimum time, the reaction either reaches equilibrium or is prevented from further leaching because of the formation of a solid product.

Investigators mentioned the value ranges from 45 to 60 min for effective dissolution; it appears that the optimum leaching time varies from 30 to 60 min. It is concluded that the time required to minimize the carbonate content depends on the size of the phosphate particles, the nature of the adherent materials in the phosphate rock, or losses of its calcium phosphate content [15].

The leaching rate of carbonate minerals and its efficiency also associated with the increase in surface area and the liberation of more calcareous material from the phosphateminerals matrix.

3. Mathematical Model

Box–Wilson statistical experimental design was employed to determine the effects of operating variables on phosphate recovery and to find the combination of variables resulting in maximum recovery. The Box–Wilson design is a response surfacemethodology which is an empirical modeling technique devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three
major steps; performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response with checking the adequacy of the model [17].

This design consists of \((2^P)\) factorial points (coded to the \(\mp 1\) notation), augmented by \(2P\) axial points \((\mp \alpha, 0, 0), (0, \mp \alpha, 0), (0, 0, \mp \alpha)\) and center points \((0,0,0)\). A central composite design is made rotatable by the choice of \(\alpha\). The value for rotatability depends on the number of variables \(P\) (i.e. for \(P=2, \alpha=\sqrt{P} = 1.414\) and for \(P=3, \alpha=\sqrt{3} = 1.732\)). The relation between the coded levels and the corresponding real variables is shown as follows in equation (8):

\[
X_{\text{cod}} = \frac{(X_{\text{real}} - X_{\text{center}})}{(X_{\text{center}} - X_{\text{min}})} ... (8)
\]

where:

\(P=\) No. of variables

The number of experiments \((N)\), needed is estimated using eq. 2:

\[
N = 2^P + 2P + 1 \quad ... (9)
\]

Thus for three variables design, the number of experiments needed according to eq. (9) is \((15)\) plus 3 experiments around the center point to certify the relation.

Acid concentration \((C)\) in weight percent, Liquid volume to solid weight ratio \((L/S)\) in ml/gm and leaching time \((t)\) in min., were considered as independent variables and designated as \(X_1, X_2\) and \(X_3\) respectively. Phosphate recovery was considered as dependent variables in the Box–Wilson statistical design method. The acid concentration \((X_1)\) was varied between 2 and 10 weight percent, the ratio \((X_2)\) of acid liquid volume (ml) to ore weight (gm) between 5 to 15 (ml/gm) and the time \((X_3)\) between 10 and 90 min. according to eq.(8) the relation between the coded levels and the corresponding real variables shown as follows:

\[
X_{1\text{Coded}} = \frac{X_{1\text{Real}}}{(2.31)} ... (10)
\]

\[
X_{2\text{Coded}} = \frac{X_{2\text{Real}}}{(2.89)} ... (11)
\]

\[
X_{3\text{Coded}} = \frac{X_{3\text{Real}}}{(23.1)} ... (12)
\]

Experimental conditions determined by the Box–Wilson statistical design are presented in Table 1. The experiments consist of six axial (A), eight factorial (F) and center point. The centerpoint (experiment no. 15) was repeated four times and the mean is taken.

<table>
<thead>
<tr>
<th>No</th>
<th>Coded Values</th>
<th>Real Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X_1)</td>
<td>(X_2)</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>3</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>6</td>
<td>-1</td>
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<tr>
<td>8</td>
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<td>-1</td>
</tr>
<tr>
<td>9</td>
<td>+(\alpha)</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>+(\alpha)</td>
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<td>-(\alpha)</td>
</tr>
<tr>
<td>14</td>
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<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Computation was carried out using multiple regression analysis using the least squares method. The resulting equation (13) represents response function, was used in correlating the phosphate recovery \((PR)\) and calcite removal efficiency \((CR)\) with independent parameters \((X_1, X_2, X_3)\).

\[
Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (13)
\]

The STATISTICA 5.5 Release computer program was employed for the determination of the coefficients of (Eq.1) by regression analysis of the experimental data for each variable using Rosenbrock and Quasi-Newton method; where \(Y\) is predicted Recovery, \(b_0\) is constant, \(b_1, b_2, b_3\) are linear coefficients, \(b_{12}, b_{13}, b_{23}\) are cross product coefficients and \(b_{11}, b_{22}, b_{33}\) are quadratic coefficients.
4. Sample Preparation and Analysis

In order to identify the behavior of the phosphate bearing minerals and the associated impurities with respect to particle size, representative samples of the phosphate (crushed to -10mm particle size) was subjected to dry sieving. All of the samples were dried in an electric oven at about 105 °C for 2 hrs, cooled to room temperature and stored in closed desiccators. Each size fraction obtained was weighed and analyzed in terms of apatite and calcite. The distribution percentages were calculated accordingly. The results obtained are tabulated as shown in Table 2. These sample fractions were characterized by X-ray powder diffraction (Model Lab-X, XRD 6000, Shimadzu, Japan) in the National Center for Construction Laboratories and Research, Ministry of Construction and Housing. Then analyzed using FTIR Spectrophotometer (Model IRAffinity-1, Shimadzu, Japan) in the Environmental Central Laboratory, College of Science, University of Baghdad.

<table>
<thead>
<tr>
<th>Fraction (mm)</th>
<th>Weight %</th>
<th>CUMULATIVE DISTRIBUTION</th>
<th>Particle size distribution of the studied phosphate.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cumulative Distribution</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calcite RIR %</td>
</tr>
<tr>
<td>+0.6</td>
<td>29.13</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>+0.3</td>
<td>13.01</td>
<td>61.31</td>
<td>38.69</td>
</tr>
<tr>
<td>+0.15</td>
<td>20.05</td>
<td>62.67</td>
<td>37.33</td>
</tr>
<tr>
<td>+0.125</td>
<td>11.99</td>
<td>65.79</td>
<td>34.21</td>
</tr>
<tr>
<td>+0.075</td>
<td>13.05</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>-0.075 (base)</td>
<td>12.77</td>
<td>81.65</td>
<td>18.35</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) spectrometry is one of the most powerful analytical tools available for identifying unknown crystalline substances. All crystals are composed of regular, repeating planes of atoms that form a lattice. When coherent X-rays are directed at a crystal, the X-rays interact with each atom in the crystal, exciting their electrons and causing them to vibrate with the frequency of the incoming radiation. The electrons become secondary sources of X-rays, re-radiating this energy in all directions at the same wavelength as the incident beam, a phenomenon called coherent scattering. These secondary or diffracted X-rays, which can be thought of as waves traveling in all directions, form interference patterns, much like interference patterns formed by dropping two rocks into water. This interference may be constructive, forming larger waves, or destructive, canceling out the waves entirely. The pattern of interference created depends on the distance between atomic layers, chemical composition, and the angle that the X-rays diffract away from the atoms, thus it indirectly reveals a crystal’s structure.

Using an XRD spectrometer, the diffraction pattern created by constructive interference is recorded by a beam detector as the X-ray tube and the detector are rotated around the sample. The relationship between angle at which diffraction peaks occur $2\theta$ and the inter-atomic spacing of a crystalline lattice (d-spacing) is expressed by Bragg’s law: $n\lambda = 2d \sin \theta$. For historical reasons, XRD diffractograms, are expressed in degrees two theta ($2\theta$).

Since each crystalline structure is unique, the angles of constructive interference form a unique pattern. By comparing the positions and intensities of the diffraction peaks against a library of known crystalline materials, samples of unknown composition can be identified. This works even with mixtures of materials, where each separate crystalline material can be identified and semiquantified.

Fourier transform infrared (FTIR) spectroscopy is a powerful analytical technique for the characterization of materials. Thus, to distinguish the presence of a specific group (bond) and also the degree of probable separation of a reacted component during acid treatment, FTIR analysis was performed in the present investigation.

The measurements were carried out in the transmission mode in the mid-infrared range with wave numbers 400 cm$^{-1}$ to 4000 cm$^{-1}$. FTIR samples were first ground in a mortar, in a manner similar to that used in the preparation of XRD samples, and then mixed with KBr powder in a ratio of 1:100, followed by forming a pellet by using a uniaxial cold press.

5. Experimental Procedure

For selective leaching studies, phosphate ore of (-0.15+0.30mm) size fraction was used in a well mixed three necked funnel glass batch reactor of (500 ml) size, equipped on a magnetic stirrer.
having a controller unit. A known amount of acetic acid with a specific concentration (in weight%) and liquid/solid (L/S) ratio was slowly pipetted into the reactor vessel containing 10.0g of the sample for a specific time each run according to the set of experiments shown in table (1). Temperature for all experiments fixed on 30°C to prevent crystallization of calcium acetate at higher temperatures. Mixing speed found to be efficient at 300 rpm to ensure steady dispersion of particles in the liquid phase. At the end of each reaction, the reaction vessel was immediately stopped mixing to end the reaction before the separation of the leach slurry by vacuum filtration.

The same procedure repeated using lactic acid to specify the best results. The resulting samples were then dried, weighed and analyzed by X-ray diffraction in order to show the difference in composition.

To confirm the results for the efficiency of beneficiation, the solid phase after the leaching process was also analyzed by FTIR spectroscopy.

6. X-Ray Diffraction

Apatite can be identified by a highest intensity peak located at approximately (2θ) 31.9°, closely followed by three more high intensity peaks located between (2θ) 32° and 34°. Apatite also has weaker intensity diagnostic peaks located at approximately (2θ) 26°as shown in Figs. 1 and 2. The locations and intensities of these peaks clearly differentiate apatite from the vast majority of the study materials that are for the most part composed of calcium carbonates, silicates, or sulfates. For example, plaster of Paris (Gypsum), charcoal ash, wood ash and both kinds of sheetrock all lack peaks near (2θ) 11°, calcite lack peak near (2θ) 29.4°. If a sample lacks any of the diagnostic peaks listed and/or the relative peak heights are significantly different, then the sample is not apatite, or the sample is contaminated [18].

To give more details on the characterization runs, samples for XRD analyses were first ground in an agatemortar using an agate pestle and then sprinkled onto ethanol-damped single-crystal quartz sample holders to form a thin layer, followed by tapping to remove excess powder. The XRD was operated at 40 kV and 30mA with monochromated CuKα radiation. XRD data over the range of angle (2θ=20–50°) were collected with a step size of 0.05 degree and a preset time of 0.75 sec at each step.

Table 4 shows the relative intensity ratio (RIR) of each main component of the ore [19]:

\[ RIR\% = \frac{I_i}{\sum I_i} \times 100\% \]  …(14)

Where:
\( I_i \) = main peak intensity of component (i)

![Fig. 1. X-Ray Diffraction of the Mixed Size Sample phosphate ore (before Acid Leaching).](image1)

![Fig. 2. X-Ray Diffraction of (0.15-0.30 mm) Fraction Phosphate Ore (before Acid Leaching).](image2)

7. FTIR Analysis

Fig.3 shows the FTIR spectra of the mixed size phosphate ore. In all the obtained spectra, PO_4 absorption bands were observed at 1,000–1,100 cm\(^{-1}\) and 550–600cm\(^{-1}\), which were assigned to PO_4\(^{3-}\) ion in the apatite lattice. Absorption band at 1,400–1,500 cm\(^{-1}\) was assigned to CO_3\(^{2-}\) ion in the apatite lattice. Appearance of CO_3\(^{2-}\) peak indicated that the apatite phase was CAp (Calcite-Apatite).
Two types of CAP exist with respect to the substitution site of $CO_3^{2-}$ ion in the apatite lattice. One is A-type CAP, in which $CO_3^{2-}$ groups substituted $OH$. For B-type CAP, $CO_3^{2-}$ groups substituted the $PO_4$. In the present study, the obtained spectra were typically those of B-type CAP, in which the absorption band of $CO_3$ had two maxima at 1,455 cm$^{-1}$ and 1,410 cm$^{-1}$ [20]. $CO_3$ content was calculated from the absorbance ratio of $CO_3$ band at 1,410 cm$^{-1}$ to $PO_4$ band at 575 cm$^{-1}$ based on a method described by Featherstone et al. [20].

![Fig. 3. FTIR Spectra of Mixed Size Sample of Phosphate Ore (before Acid Leaching).]

All bands observed in the FTIR of Fig. 4 are associated with the inorganic components of apatite which were present in the phosphate ore. These bands can be divided into three main categories associated with phosphate, carbonate and hydroxyl groups.

One strong and relatively broad band at 1033 cm$^{-1}$, two relatively strong and sharp bands at 569 cm$^{-1}$ and 603 cm$^{-1}$ and another band at 966 cm$^{-1}$ which appear on the FTIR spectrum of are due to the phosphate group. The bands which appear at 873 cm$^{-1}$, 1417 cm$^{-1}$ and 1456 cm$^{-1}$ are associated with the carbonate group.

8. Results and Discussion

8.1. Sieving

From the sieving results of the apatite ore shown in table 2, it was found that phosphate ($P_2O_5$) content is commonly concentrated in the fractions range (150-300 nm), while decrease out of this range, i.e. in the particle size larger than 300 nm and smaller than 150 nm as shown in Figure 4. This behavior can be explained due to the difference in hardness between apatite and calcite (main constituent), leading the powder to contain coarse apatite particles and fine calcite particles during crushing of ore.

![Fig. 4. Effect of Particle Size on Phosphate Content in the Phosphate Ore.]

8.2. Acid Leaching

Leaching of apatite using acetic acid achieved according to the conditions summarized in table (1). After each run the extracted ore filtered by Buchner funnel, and dried at 105 °C for two hours and then analyzed using X-ray diffraction. Figures 5, 6 show the XRD of the best run using acetic acid leaching and the best run using lactic acid leaching respectively.

![Fig. 5. X-Ray Diffraction of the Best Run using Acetic Acid Leaching.]

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The calcite and apatite relative intensity ratios (RIR%) obtained from the experiments are fixed in Table (3) columns (5,6) respectively.

A regression analysis applied to get the polynomial of equation (15) using STATISTICA ® kernel release 6.0. This equation represents the best mathematical form that relates apatite content as a relative intensity ratio (RIR %), with the three studied variables, acid concentration (wt.%), liquid to solid ratio (ml/gm) and reaction time (min.). Value of correlation coefficient was 0.9041.

\[
\text{Ap.RIR%} = 91.01890 - 0.538442 \times C + 0.313744 \times R - 0.087618 \times t - 0.015311 \times C \times R + 0.010784 \times C \times t + 0.008245 \times C^2 + 0.019954 \times R^2
\]

(15)

Where:
Ap. RIR%: percentage of relative intensity ratio of apatite content
C = acid concentration (wt. %)
R = acid volume to ore weight ratio (ml/gm)
t = reaction time (min.)

The same procedure repeated using lactic acid leaching and the results shown in Table (4). Again a regression analysis applied using the same procedure to get a mathematical polynomial as shown in equation (16) express the variables affecting leaching using lactic acid with correlation coefficient was 0.9372.

\[
\text{Ap.RIR%} = -10.9799 + 15.86836 \times C + 6.364276 \times R + 1.012614 \times t - 0.807941 \times C \times R - 0.120940 \times C \times t - 0.082444 \times R \times t + 0.009692 \times C \times R \times t - 0.447970 \times C^2
\]

(16)

Parameters of equation (16) are the same as in equation (15).

These mathematical forms are used to plot graphical figures relating apatite content versus each corresponding variable (acid concentration, acid to ore ratio and reaction time), to evaluate the optimum operating conditions which give the best phosphate concentration resulting from the leaching process.

Table 3,
Intensities of Ore Main Components Obtained by X-Ray Diffraction of the Acetic Acid Leaching.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Calcite Intensity</th>
<th>Apatite Intensity</th>
<th>Total Intensity</th>
<th>Calcite RIR%</th>
<th>Apatite RIR%</th>
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<tbody>
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<td>614</td>
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<td>15.19</td>
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<td>948</td>
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<tr>
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<td>15.01</td>
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Table 4,
Intensities of Ore Main Components Obtained by X-Ray Diffraction of the Lactic Acid Leaching.

<table>
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<th>Exp. No.</th>
<th>Calcite Intensity</th>
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<th>Total Intensity</th>
<th>Calcite RIR%</th>
<th>Apatite RIR%</th>
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</tbody>
</table>

8.3. Effect of Acid Concentration

The effect of acid concentration (wt.%) on the apatite content in the ore, using acetic acid leaching is shown in Fig. 7.

This figure shows the relation between acetic acid concentration (in weight percent), and apatite content expressed as relative intensity ratio based on X-ray diffraction of the beneficiated samples at different ratios of acid volume to ore weight in a range of (5-13 ml/gm) at a constant reaction time of 10 min.

It is clearly found that increasing the acid concentration leads to a decrease in the apatite content. The explanation of this case is, at low concentrations of acetic acid, there is a desirable reaction with calcite (reaction 3, page 3). Increasing the acid concentration decreases the selectivity of acetic acid reaction leading to an undesirable reaction with the required material (apatite) in the ore as shown in the reaction 4 (page 4) [10].

Malash[12], showed that at lower acetic acid concentrations, there is a greater probability of the reaction between calcium carbonate and the acetic acid with a result of an increase of the P₂O₅ grade in the treated rock. Then as the concentration of the acetic acid increase there is a corresponding increase in the polarity of the OH group, the acid will react with the calcium carbonate to a lesser extent and hence more calcium carbonate will remain with the solid residue remaining after the experiment, and therefore the P₂O₅ grade in the treated rock will decrease again.

The effect of ratio of acid volume to ore weight is less than that of acid concentration. Generally at low concentration the high ratio (L/S=13) gives more efficient beneficiation than that of low ratio (L/S=5).

When lactic acid used as a leaching agent to concentrate phosphate it gives a different behavior compared with acetic acid as shown in Fig. (8).
This figure shows the relation between lactic acid concentration and apatite content expressed as relative intensity ratio as in Figure 10, at different ratios of acid volume to ore weight in a range of (5-15 ml/gm) and a constant reaction time of 10 min.

This figure shows that at low ratios of acid volume to ore weight, increasing the acid concentration leads to a distinct increase in the apatite content. It means that apatite content is related to the stoichiometry amount of acid necessary to react with calcium carbonate. When this amount exceeds the stoichiometry limits, reaction selectivity decreased as the acid start the undesired reaction with apatite.

Gharabaghi et al [14], stated that the acid concentration that gives the best leaching result has been found to depend on acid type, carbonates mineral content and the liquid/solid ratio.

8.4. Effect of Acid Volume to Ore Weight

Figure (9) shows the effect of ratio of acid volume to ore weight at different concentrations of acetic acid and a fixed leaching time of 10 minutes.

It was found that increasing the ratio at high acid concentrations decreases the apatite content.

Malash [12], explained that at high acid concentrations when the quantity of acid increases, it leads to more phosphate loses because a greater chance of the reaction of the acid with tricalcium phosphate found in the phosphate rock. This happens because the reaction of acetic acid with phosphate rock begins at the surface particles, and as the quantity of the acid increases it begins to penetrate to the inner layers leading to increased attack and hence more P₂O₅ loses.

Leaching with lactic acid shows different behavior from that of acetic acid in the case of acid to ore ratio as shown in figure (10).

Increasing that ratio at low acid concentration leads to an increase in the apatite content. While at high lactic acid concentrations it gives undesired result by reducing the apatite content.

This explains the selective reaction of lactic acid with calcium carbonate at low concentrations of acid, related to the stoichiometry amount of acid sufficient to digest the calcite, while this selectivity decreased when acid concentrations increased above 8 weight percent (i.e. at higher concentration the acid begin an undesired reaction with apatite).
From the mentioned figures it can be noticed that the optimum conditions of acid concentration and volume of acid to ore weight ratio for acetic acid are (2wt%) and (13ml/gm) respectively. For lactic acid these conditions are (10wt%) and (5ml/gm) respectively.

8.5. Effect of Reaction Time

In all of the experiments, pH data was recorded versus reaction time. Because the reaction is taken place between the acid and ore, hydrogen ion concentration must be decrease with time and this decrease considered as an indication to the reaction continuity.

Figure 11 shows pH data vs. time for acetic acid leaching. It was noted that the reaction is fast through the first 3 minutes, and then its speed decreased until reach 10 minutes. After this limit, the reactants pH be stable in most of the experiments (3-15) and in experiments 1 and 2 it be constant when reach time of 20 minutes.

Variation of pH data with time using lactic acid is similar to that of acetic acid as shown in figure 12. This means that the optimum reaction time can be taken 10 minutes. Figures 13 and 14 demonstrate variation of apatite content with reaction time at different acid concentrations.
It can be deduced from Fig. 13 that more than 90 percent of the apatite recovery occurs in the first ten minutes, and the change in acid concentration leads to a small effect on the behavior of the acid.

The recovery of apatite using lactic acid is more influenced by acid concentration as shown in Fig. 14. At low acid concentrations, apatite content increased slowly and more time was required reaching the desired recovery. While at high acid concentrations most of the apatite recovered in the first 20 minutes.

8.6. FTIR Analysis

Figure 15 explains the FTIR spectra of the treated sample of apatite ore using lactic acid at the optimum conditions of (10wt%), (5ml/gm) and (10min.).

In the obtained spectra, $PO_4^{3-}$ absorption bands were observed at 1,000–1,100 cm$^{-1}$ and 550–600 cm$^{-1}$, which were assigned to $PO_4^{3-}$ ion in the apatite lattice as noticed in Fig. 3. Absorption band at 1,400–1,500 cm$^{-1}$ was assigned to $CO_3^{2-}$ ion in the apatite lattice. It is deduced that after acid leaching, the absorbancy of carbonate band $CO_3$ at 1400–1500 cm$^{-1}$ was decreased to values smaller than the absorbency bands of apatite at 575 and 1100 cm$^{-1}$, this ensures that a selective reaction occurred by the acid with calcite and enhance the apatite concentration in the extracted ore.

9. Conclusions

1- From the established work, it is concluded that beneficiation of Akashat phosphate ore to improve apatite content using leaching with organic acids (acetic acid and lactic acid) was characterized by high efficiency, low cost, simple operating conditions (room temperature and atmospheric pressure), possibility to recover the organic acid, keeping the surface properties of the produced phosphate. In addition, it does not cause particular environmental hazards through the ability to produce pure calcium sulfate (Gypsum).

2- Using the two acids (acetic acid and lactic acid) yields closed purity values of apatite at the optimum conditions. When comparing the produced apatite purity at different acid concentrations, it was found that the efficiency of acetic acid is higher at the low concentration (2wt.%), while lactic acid gives the higher efficiency at high concentration (10wt.%).
3- With respect to the ratio of acid volume to ore weight ratio it was found that increasing this ratio to (13ml/gm) cause an increase in the purity of apatite at the optimum concentration for acetic acid. While for lactic acid this ratio found to be optimum at (5ml/gm) when the acid concentration be (10wt%).

4- It was found that the reaction of organic acids with the calcareous material is fast and that the apatite purity increased to the best result reaction time of 10 minutes.

10. References


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الخلاصة

البحث الحالي يتضمن دراسة لعملية الاستخلاص باستخدام الحوامض العضوية (حامض الخليك وحامض اللاكتيك) لغرض استخلاص مادة الايبتايت من خام الفوسفات العراقي المستخرجة من منطقة عكاشات. تتميز هذه الطريقة بعدة مزايا، منها التقليل من كمية الطاقة المصروفة، التقليل من التلوث البيئي، التقليل من محتوى الكربون في المنتج، وتخزين المادة الكلسية في شكل قابل للبضائع. FTIR المستخدمة لتحليل العينات بالحالة الصلبة باستخدام طريقة الحوامل بالأشعة السينية، X-ray diffraction والطيف ضوئي للإيبتايت المفصولة تحت الحرارة. من خلال بيانات النتائج العملية، وجد أن استخدام الحموض العضوية عند الظروف المثلى ينتج مادة الأيبتايت بنقاوة عالية، بينما عند استخدام محتوى الحمض عن وزن الخام وجد بأن تقليل نسبة حموضة المستخدمة يؤدي إلى زيادة في نقاوة الأيبتايت المنتجة. بالإضافة إلى ذلك، وجد بأن تفاعل الحموض العضوية مع المواد الكاربونية سريع وان أفضل زمن للفصول

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