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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 studiedusing 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 ofthe 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 Akashatphosphate 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 acidproduction 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 phosphorous-based chemicals. It is neither substitutable nor recyclable, therefore, the total demand mustbe 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.
3. Biogeneticdeposits.

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

Apatite (the desired component in phosphate rock) has the general formula, $Ca_{10}(PO_4)_6X_2$ 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 ½CO_3 or ½O; 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. Igneous apatitemay contain 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 fromMauritania in the west to Iraq and Saudi Arabia in the east through North Africaand Eastern Mediterranean Sea.

The most important of these formations is Akashat phosphate layer, thickness of upto 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 *dryprocesses*, 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 and food additives, while phosphoric acid from wet processes is mainly further processed into fertilizers.

In the *dry processes*, the phosphate ore is reduced, by addition of silica and carbon, to phosphorus and slag at about 1500°C in a furnace:

$$Ca_{10}(PO_4)_6F_2 + 20SiO_2 + 28C \rightarrow 20CaSiO_3 + 28CO + 3P_4 + 2F_2 \quad \ldots(1)$$

ΔH = 27.9 MJ/kg of P_4produced [6]

Although the heat of combustion of the phosphorus and the carbon monoxideis recovered in the dry process, these processes are still too expensive for usein the fertilizer industry.

In the wet processes, Phosphoric acid can be released from phosphate ore by the action of strong mineral acids, such as nitric acid, hydrochloric acid and sulfuric acid.

Sulfuric acid is the only acid, which forms an insoluble precipitate with thecalcium from the phosphate ore, thus allowing the phosphoric acid to beseparated directly by filtration according to the reaction:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 \rightarrow 6H_3PO_4 + 10CaSO_4 + 2HF \quad \ldots(2)$$

The chlorides and nitrates of calcium are bothsoluble, so special techniques, like solvent extraction, ion exchange or cooling crystallization are required to recover the phosphoric acid [7].

In spite of this, phosphoric acid is being commercially produced using nitricacid as well as hydrochloric acid. The economical feasibility of these processesis mainly determined by the availability, price of the mineral acid,local production facilities and by the desired products.

Phosphate ore requires processing to reduce the content of gangue minerals such as carbonates, 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 notcontain 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_5content 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 mineralsand 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 usuallyrequires additional acid (sulfuric acid) during the manufacture ofphosphoric acid and superphosphates by the “wet process”. Inaddition, the carbon dioxide produced during the acid addition causesmore foaming and results the production of smaller size gypsumcrystals that may blind the downstream phospho-gypsum filters.Hence, a low quality phosphoric acid is produced [11].

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

Calcination is used in areas having low cost energy and limitedwater resources like the Al-Jalamid phosphate ore in Saudi Arabiawhich 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 byleaching with water to remove lime and quenching by 5% NH_4NO_3 toremove magnesium [12]. Calcinationis a thermal decomposition of calcareous material. Depending onthe process conditions, calcination may lead to almost complete eliminationof the carbonate gangue 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 thecalcareous phosphate ores and more attention 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 apatitewhile 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 encounteredduring the manufacture of phosphoric acid and superphosphates areresolved. At the same time, both calcium and magnesium carbonatesare removed in the form of highly soluble salts. The reaction timeneeded for leaching is small, thus the destructive action of dilute organicacid on the phosphate minerals is minimum. Typically, organic acidextractions are carried out undermoderately acidic conditionsand their degradation is biologically easy.Furthermore, in industrial processes, organic acids cause a littlecorrosion [13].

Due to the previous mentioned information, an experimental comportment 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 amountof acetic acid and the required amount for reaction (3). The stoichiometryis determined by using the following equation [20]:

Acidstoichiometry = (mol. of CH_3COOH*) / (mol. of* CO_2*)= 2:1*

Completion of this reaction depends on the product solubility, aceticacid concentration, process temperature, reaction time and otherprocess conditions. However, the dissolution kinetics could alsocontrol the overall rate of selective leaching of calcareous minerals inthe phosphate rocks and ores.

The mechanism of carbonate dissolution in acetic acid solutioninvolves the initial formation of $Ca(CH_3COO)_2$ and carbonic acidwhich decomposes into CO_2 and H_2O. If the acetic acid expresses noselectivity, then the following reaction may occur:

$$Ca_{10}(PO_4)_6F_2+20CH_3COOH= 10Ca^{+2}+20CH_3COO^{-}+2HF+(6-x)H_3PO_4+xH_2PO_4^{-}+xH^{+} \quad \ldots(4)$$

However, acetic acid should not attack the phosphate minerals andthus reaction (4) does not take place while reaction (3) proceeds tocompletion.

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 anirreversible reaction due to the removal of CO_2 produced during theprocess by stirring the reaction mixture. The reactions for the otherimpurities depend on the nature and composition of the raw phosphateore. The simplest mechanism for the rational understanding oftheselective leaching process can be expressed as follows [15]:

$$MCO_{3(s)} + 2HX_{(aq)} \rightarrow MX_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad \ldots(6)$$

$$M_3(PO_4)_{2(s)} + 6HX_{(aq)} \rightarrow 3MX_{2(aq)} + 2H_3PO_{4(aq)} \quad \ldots(7)$$

where: $M=Ca^{+2}$ and/or Mg^{+2}, and $X=CH_3CH(OH)COO^{-}$ (lactate) or CH_3COO^{-} (acetate).

Again, the acid should not attack the phosphate minerals andthus reaction (7) does not take place while reaction (6) proceeds tocompletion or equilibrium depending on the solubility products (K_{sp}=8.35, 7.46 for $CaCO_3$ and $MgCO_3$, (respectively) and acidity constants forlactic acid (pKa=3.86 at 25 °C) and CO_2 (pK_1=6.35, pK_2=10.33 for H_2CO_3).

The main factors investigated by researchers were: leachingreagent, acid concentration, reaction time, liquid/solid ratio (pulpsolid percent); temperature, particle size distribution, stirring speedand 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 fullymiscible 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 easilyseparated from the beneficiated solid phosphate product by filtration.

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

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

Highly concentratedorganic acid solution does not react with calcium carbonate because ofthe large polarity of the O–H bond of the acid molecules and it isnecessary to use dilute solution for an effective reaction. In dilutesolutions, water molecules tend to decrease the effect of polarity ofthe organic acids O–H bond [15]. The dilute organic acids are also less destructive if someof the produced solution is added or recycled to the process [16].

Acid concentration is one of the key factors in achieving good resultsin the selective dissolution of calcareous mineral in phosphate ores. Ingeneral, the P_2O_5 content increases with increasing acid concentrationto reach a certain level, and then remains almost constant.

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

The effect of reaction time on the dissolution of carbonate mineralsin the leaching process was studied by many investigators. It is clear thatwith increasing reaction times up to an optimum value, the P_2O_5percentage increases along with the corresponding reduction in calcareousmaterials content. At the optimum time, the reaction eitherreaches equilibrium or is prevented from further leaching because ofthe formation of a solid product.

Investigatorsmentioned the value ranges from 45 to 60 min for effectivedissolution;it appears that the optimum leaching time varies from 30to 60 min. It is concluded that the time required to minimize the carbonate content depends on the size of the phosphate particles, thenature of the adherent materials in the phosphate rock and otherprocess conditions [13].

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 responsewith checking the adequacy of the model [17].

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

$$X_{cod} = \frac{(X_{real} - X_{center})}{\left[\frac{(X_{center} - X_{min.})}{\sqrt{p}}\right]} \qquad \ldots(8)$$

where:
P=No. of variables
The number of experiments (N), needed is estimated using eq. 2:

$$N = 2^P + 2P + 1 \qquad \ldots(9)$$

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:

$$X_{1Coded} = \frac{X_{1\,Real} - 6}{(2.31)} \qquad \ldots(10)$$

$$X_{2Coded} = \frac{X_{2\,Real} - 10}{(2.89)} \qquad \ldots(11)$$

$$X_{3Coded} = \frac{X_{3\,Real} - 50}{(23.1)} \qquad \ldots(12)$$

Experimental conditions determined by the Box–Wilson statistical design are presented inTable 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.

Table1,
Experimental conditions according to a Box-Wilson Experimental Design.

No	Coded Values			Real Values		
	X_1	X_2	X_3	Wt %	(L/S)	Time (min)
1	+1	+1	+1	8.3	12.9	73
2	-1	+1	+1	3.7	12.9	73
3	+1	-1	+1	8.3	7.1	73
4	-1	-1	+1	3.7	7.1	73
5	+1	+1	-1	8.3	12.9	27
6	-1	+1	-1	3.7	12.9	27
7	+1	-1	-1	8.3	7.1	27
8	-1	-1	-1	3.7	7.1	27
9	+α	0	0	10	10	50
10	0	+α	0	6	15	50
11	0	0	+α	6	10	90
12	-α	0	0	2	10	50
13	0	-α	0	6	5	50
14	0	0	-α	6	10	10
15	0	0	0	6	10	50

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).

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

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 andb_{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 theassociated impurities with respect to particle size, representative samples of thephosphate (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 ofapatite and calcite. The distribution percentages were calculatedaccordingly. 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 2,
Particle size distribution of the studied phosphate.

Fraction (mm)	Weight %	Cumulative Distribution	
		Calcite RIR %	Apatite RIR %
+0.6	29.13	76	24
+0.3	13.01	61.31	38.69
+0.15	20.05	62.67	37.33
+0.125	11.99	65.79	34.21
+0.075	13.05	76	24
-0.075 (base)	12.77	81.65	18.35

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 sourcesof 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 crystals 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 2θ 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, XRDdiffractograms, are expressed in degrees two theta (2θ).

Since each crystalline structure is unique, the angles of constructiveinterference 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 apowerful analytical technique for the characterization ofmaterials. 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 analysiswas performed in the present investigation.

The measurements were carried out in the transmissionmode 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 mannersimilar to that used in the preparation of XRDsamples, and then mixed with KBr powder in a ratio of1:100, followed by forming a pellet by using a uniaxialcold 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 dispersionof 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 acidto 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 and2. 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 ontoethanol-damped single-crystal quartz sample holders toform a thin layer, followed by tapping to remove excess powder. The XRD was operated at 40 kV and 30mA with monochromated CuKaradiation. 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]:

$$RIR\% = \frac{I_i}{\sum I_i} \times 100\% \qquad \ldots(14)$$

Where:

I_i= main peak intensity of component (i)

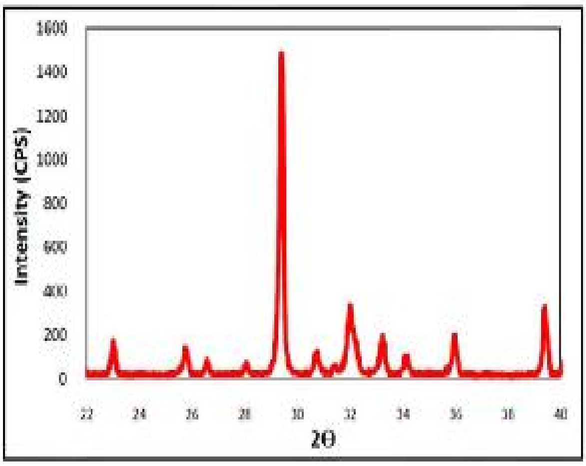

Fig. 1. X-Ray Diffraction of the Mixed Size Samplephosphate ore (before Acid Leaching).

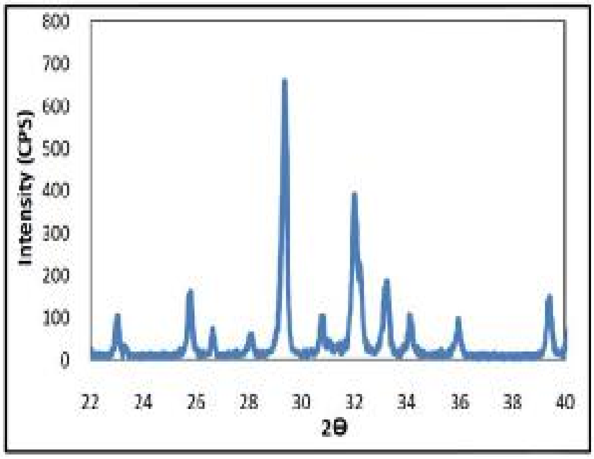

Fig. 2. X-Ray Diffraction of (0.15-0.30 mm) Fraction Phosphate Ore (before Acid Leaching).

7. FTIR Analysis

Fig.3 shows the FTIR spectra of the mixed size phosphate ore. In all the obtained spectra, PO_4 absorptionbands were observed at 1,000–1,100 cm^{-1} and 550–600cm^{-1}, which were assigned to PO_4^{3-} ion in the apatitelattice. Absorption band at 1,400–1,500 cm^{-1} wasassigned to CO_3^{2-} ion in the apatite lattice.Appearance of CO_3^{2-} peak indicated that the apatitephase was CAp (Calcite-Apatite).

Two types of CAp exist with respect tothe substitution site of CO_3^{2-} ion in the apatite lattice. One is A-type CAp, in which CO_3^{2-} groups substitutedOH. For B-type CAp, CO_3^{2-} groups substitutedthe PO_4. In the present study, the obtainedspectra were typically those of B-type CAp, in which theabsorption 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 absorbanceratio 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].

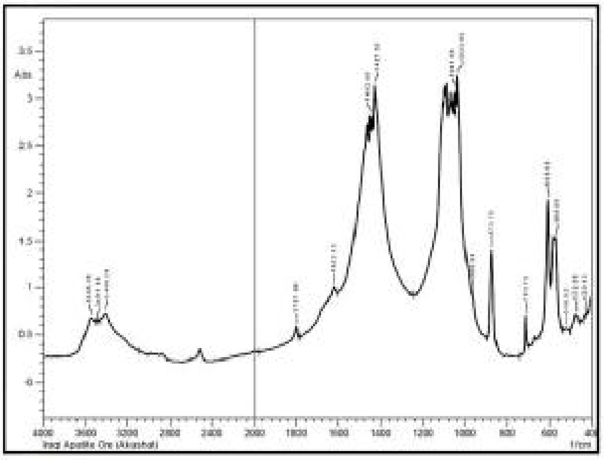

Fig. 3. FTIR Spectra of Mixed Size Sample of Phosphate Ore(before Acid Leaching).

All bandsobserved in the FTIR of Fig. 4 are associated with theinorganic components of apatite which were present in thephosphate ore. These bands can be divided into three maincategories associated with phosphate, carbonate and hydroxyl groups.

One strong and relatively broad bandat 1033 cm^{-1}, two relatively strong and sharp bands at569 cm^{-1} and 603 cm^{-1} and another band at 966 cm^{-1}which appear on the FTIR spectrum of are dueto the phosphate group. The bands whichappear at 873 cm^{-1}, 1417 cm^{-1} and 1456 cm^{-1} are associatedwith 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 iscommonly concentrate 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 Figure4.This behaviorcan 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.

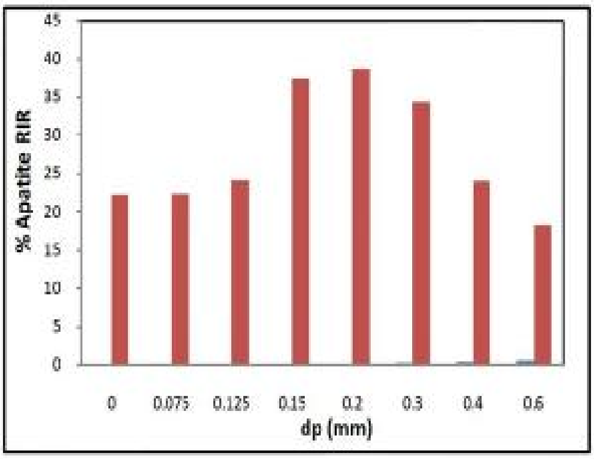

Fig. 4. Effect of Particle Size on Phosphate Contentin the Phosphate Ore.

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.

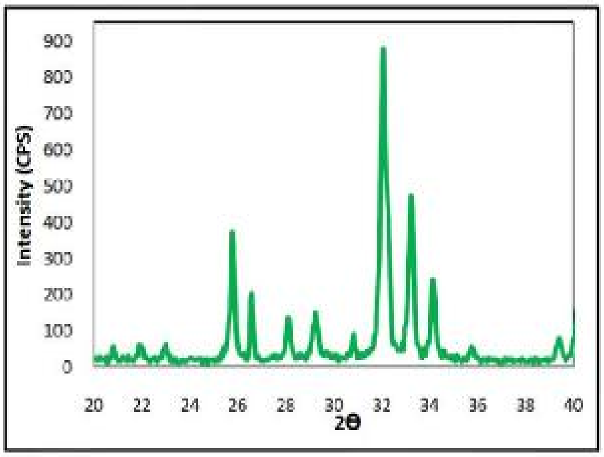

Fig. 5. X-Ray Diffraction of the Best Run using Acetic Acid Leaching.

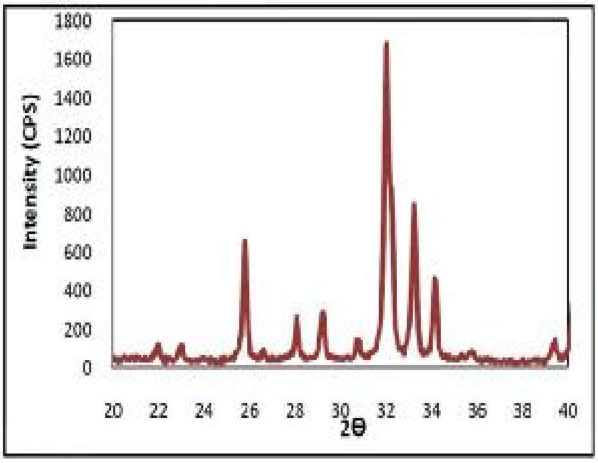

Fig. 5. X-Ray Diffraction of the Best Run using Lcetic Acid Leaching.

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.

$$\mathrm{Ap.RIR\%} = 91.01890 - 0.538442 * C0.313744 * R - 0.087618 * t - 0.015311 * C * R0.010784 * C * t + 0.008245 * C^2 + 0.019954 * R^2 \qquad \ldots(15)$$

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.

$$\mathrm{Ap.RIR\%} = -10.9799 + 15.86836 * C + 6.364276 * R + 1.012614 * t - 0.807941 * C * R - 0.120940 * C * t - 0.082444 * R * t + 0.009692 * C * R * t - 0.447970 * C\text{^}2 \qquad \ldots(16)$$

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.

Exp. No.	Calcite Intensity	Apatite Intensity	Total Intensity	Calcite RIR%	Apatite RIR%
1	110	614	724	15.19	84.80
2	148	828	976	15.16	84.83
3	142	806	948	14.97	85.02
4	156	782	938	16.63	83.36
5	108	604	712	15.16	84.83
6	104	632	736	14.13	85.86
7	144	802	946	15.22	84.77
8	126	820	946	13.31	86.68
9	152	860	1012	15.01	84.98
10	108	624	732	14.75	85.23
11	150	792	942	15.92	84.07
12	110	634	744	14.78	85.21
13	146	874	1020	14.31	85.68
14	130	796	926	14.03	85.96
15	148	824	972	15.22	84.77

Table 4,
Intensities of Ore Main Components Obtained by X-Ray Diffraction of the Lactic Acid Leaching.

Exp. No.	Calcite Intensity	Apatite Intensity	Total Intensity	Calcite RIR%	Apatite RIR%
1	276	1490	1766	15.62	84.37
2	272	1550	1822	14.92	85.07
3	246	1576	1822	13.50	86.49
4	270	1474	1744	15.48	84.51
5	300	1550	1850	16.21	83.78
6	274	1596	1870	14.65	85.34
7	272	1588	1860	14.62	85.37
8	556	1456	2012	27.63	72.36
9	276	1626	1902	14.51	85.48
10	264	1594	1858	14.20	85.79
11	268	1630	1898	14.12	85.87
12	646	1528	2174	29.71	70.28
13	292	1580	1872	15.59	84.40
14	284	1676	1960	14.4	85.5
15	310	1638	1948	15.91	84.08

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.

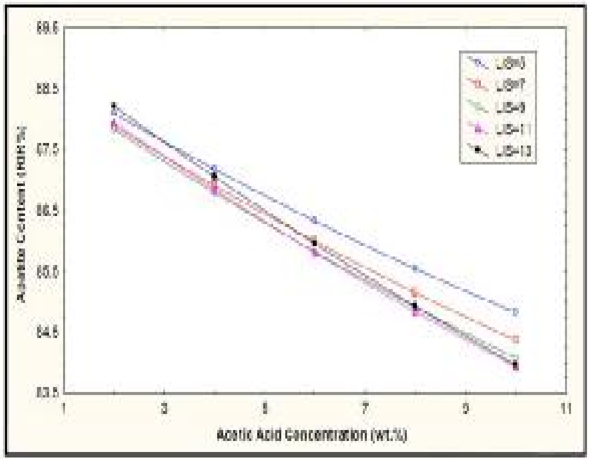

Fig. 7. Effect of Acetic Acid Concentration on Apatite Content at Various Ratios of Acid Volume to Ore Weight.

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 (reaction3, 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 (page4) [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 P_2O_5 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 P_2O_5 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).

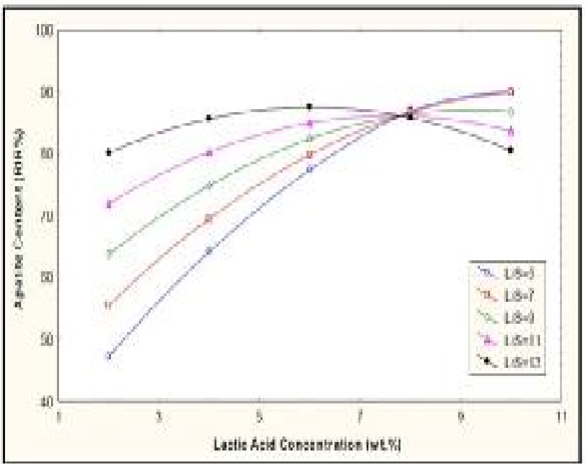

Fig. 8. Effect of Lactic Acid Concentration on Apatite Content at Various Ratios of Acid Volume to Ore Weight.

This figure shows the relation between lactic acid concentration and apatite content expressed as relative intensity ratio as in Figure 10, at differentratios 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 concentrationthat gives the best leaching result has been found to depend on acidtype, 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.

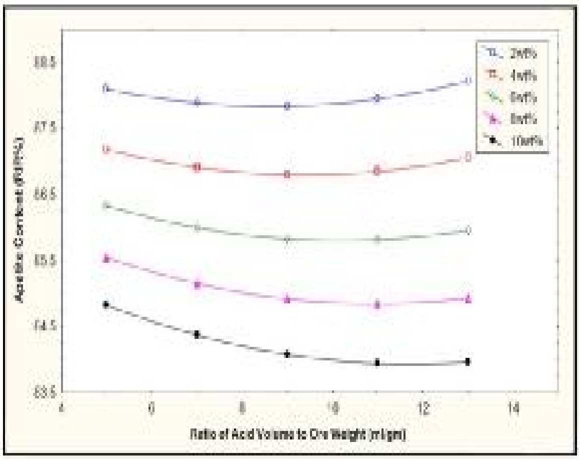

Fig. 9. Effect of Ratio of Acetic Acid Volume to Ore Weight on Apatite Content at Various Acid Concentrations.

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 P_2O_5 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 highlactic 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).

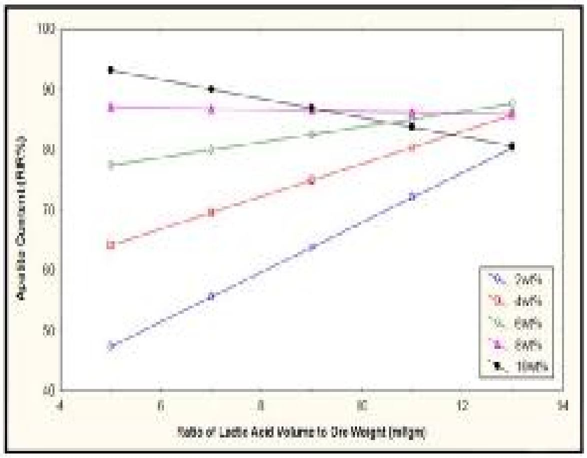

Fig. 10. Effect of Ratio of Lactic Acid Volume to ore Weight on Apatite Content at Various Acid Concentrations.

From the mentioned figures it can be noticed that the optimum conditions of acid concentration and volume of acidto 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.

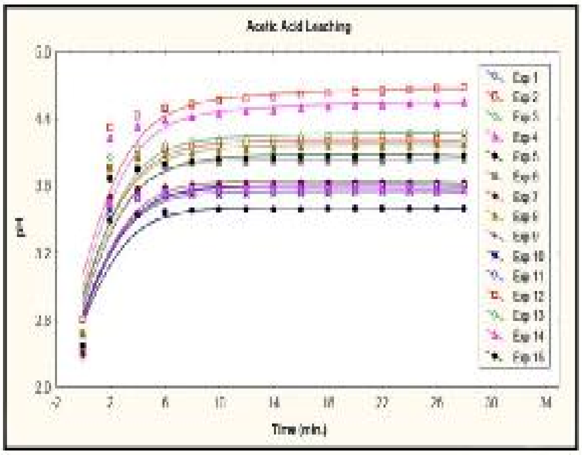

Fig. 11. pH Values vs. Reaction Time with Acetic Acid of all Experiments According to Conditions in Table (1).

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.

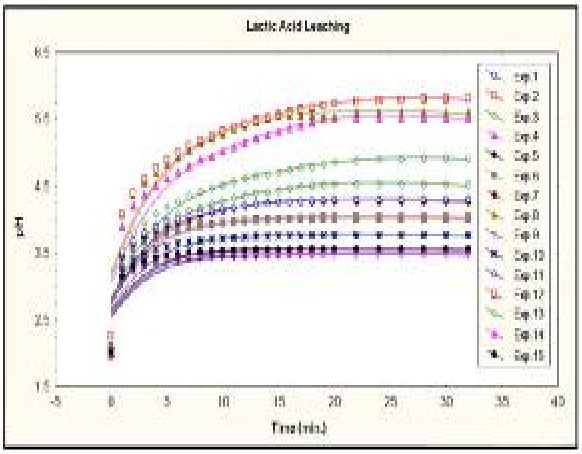

Fig. 12. pH Values vs. Reaction Time with Lactic Acid of all Experiments According to Conditions in Table (1).

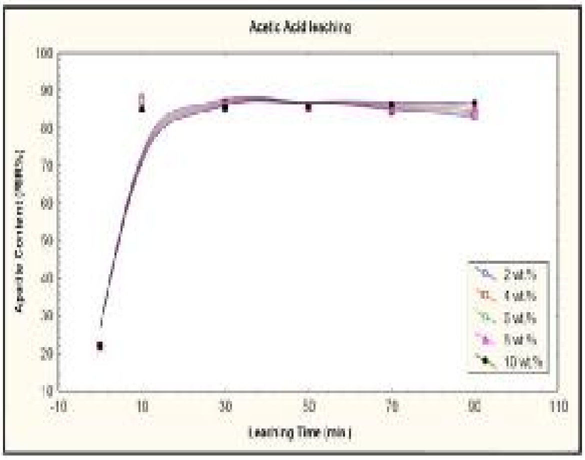

Fig. 13. Change in Apatite Content with Reaction Time using Acetic Acid.

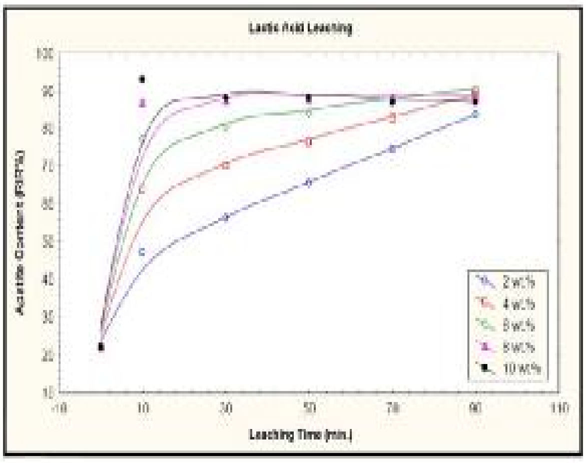

Fig. 14. Change in Apatite Content with Reaction Time using Lactic Acid.

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 toa 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 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 spectraof 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 absorptionbands were observed at 1,000–1,100 cm^{-1} and 550–600cm^{-1}, which were assigned to PO_4^{3-} ion in the apatitelattice as noticed in fig. 3. Absorption band at 1,400–1,500 cm^{-1} wasassigned to CO_3^{2-} ion in the apatite lattice. It is deduced that after acid leaching, the absorbency 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 ensure that a selective reaction occurred by the acid with calcite and enhance the apatite concentration in the extracted ore.

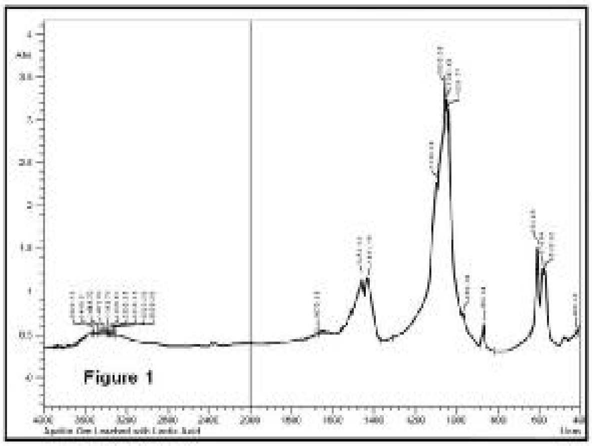

Fig. 15. FTIR Spectra of the Treated Phosphate Ore using Lactic Acid at the Optimum Conditions.

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 environmentalhazardsthrough 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 resultat reaction time of 10minutes.

10. References

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تنقية خام فوسفات عكاشات العراقية باستخدام الحوامض العضوية لغرض انتاج حامض الفسفوريك بالطريقة الرطبة

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الخلاصة

البحث الحالي يتضمن دراسة لعملية الاستخلاص باستخدام الحوامض العضوية (حامض الخليك وحامض اللاكتيك) لغرض استخلاص مادة الابتايت من خام الفوسفات العراقية المستخرجة من منطقة عكاشات وذلك بفصل المركبات الكلسية (بشكل رئيسي مادة الكلس).

تتميز هذه الطريقة بعدة مزايا، منها التقليل من كمية الطاقة المصروفة، التقليل من الملوثات البيئية من خلال استرجاع مادة الكلس على شكل كبريتات الكالسيوم (الجبس) بدلا عن طرحها الى التربة كناتج عرضي، الحفاظ على الخواص الفيزيائية والكيميائية لمادة الابتايت المفصولة والتقليل من كمية الماء المستهلك.تم تحليل العينات بالحالة الصلبة باستخدام طريقة الحيود بالاشعة السينية X-ray diffraction، والمطيافية الضوئية للاشعة تحت الحمراء FTIR.

من خلال بيانات النتائج العملية وجد بأن استخدام الحامضين العضويين عند الظروف المثلى ينتج مادة الابتايت بنقاوة متقاربة، بينما عند استخدام الحامضين بتراكيز مختلفة وجد بان كفاءة عملية الفصل بحامض الخليك هي الاعلى عند التراكيز المنخفضة وان كفاءة الفصل بحامض اللاكتيك هي الاعلى عند التراكيز العالية. بخصوص نسبة حجم الحامض المستخدم الى وزن الخام وجد بأن تقليل هذه النسبة الى ٥ مل/غم يؤدي الى زيادة في نقاوة مادة الابتايت المنتجة وذلك عند التراكيز المثلى للحامضين. بالاضافة الى ذلك، وجد بأن تفاعل الحامضين العضويين مع المواد الكاربونية سريع وان افضل زمن للتفاعل لانتاج الابتايت بنقاوة عالية هو عند ١٠ دقيقة.
