Upgrading of Abu-Tartur calcareous phosphate via selective leaching by organic acids

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Abstract - Abu-Tartur PR contains about 49.20% apatite mineral equivalent to 21.8% P_2O_5 and more than 50% of undesirable components including about 26% carbonate minerals. In this study acetic acid was used to eliminate the carbonate content of Abu-Tartur PR which would save acid consumption besides increasing the tenor of P_2O_5, U and Ln. The relevant acetic acid leaching factors involved the grain size, the acid concentration, the S/L ratio and the reaction time. Upgrading of Abu-Tartur PR has resulted in a marketable and industrially acceptable phosphate grades (about 30% P_2O_5) besides improving the assay of both U and Ln.

Index Terms – Abu-Tartur upgrading, calcareous phosohate, selective leaching, organic acids

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1 INTRODUCTION

Apart from being the principal source of phosphoric acid and phosphatic fertilizers, the phosphate ores are indeed a potential source of both uranium and lanthanides. This is actually based on their assay in these deposits where the Ln assay 0.4 and 0.5% while U attains 155 and 180 ppm in the Um Safi phosphate (El Maghreb) and the Florida phosphate (USA) respectively. Therefore, recovery of these metal values during processing of the phosphate ores is quite beneficial in many respects considering the total reserves of phosphate ores in the world which attain about 100 billion tons. The potential for recovery of U and the Ln from the phosphate ores is indeed substantial given the fact that both metal values would be available as by-product of a well-established and stable industry. In addition, U and the Ln from the phosphate ores are amenable for rapid exploitation through eco-friendly procedures. On the other hand, such a recovery could actually be considered economical since the treated ore would be equivalent to an ore

which has been mined, crushed, ground, digested and filtered i.e. would be ready for direct concentration and purification operations. In the meantime, it has to be mentioned that recovery of these two metal values as by-products during phosphate industry would represent an added value to this industry. According to **Gupta and Singh (2001) [1]**, based on the fact that 150 million tons of phosphate ores are annually processed, 10,000 tons of U and 150,000 tons of Ln can annually be produced therefrom.

Recovery of U and the Ln from the phosphate rocks can indeed be recovered whether from the bulk acid solubilization products or else through their selective leaching. Thus, U can be recovered from the phosphoric acid product using the two main recovery techniques; namely solvent extraction and ion exchange. The former has actually been industrialized and 8 plants have been built and operated in the USA since 1976 **[2]**

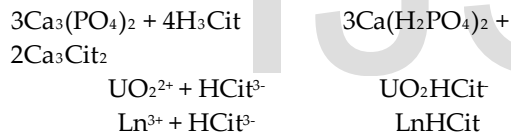[1]Nuclear Materials Authority, P.O.Box 530, El Maadi, Cairo, Egypt.
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in addition to those in Belgium, Canada, Taiwan and China but have however been stopped due to

the decreased U prices. Alternatively, the ion exchange recovery of U^{4+} has been suggested where in France, the Minmet Recherch process used the cationic chelating Duolite C464 resin

containing the hydroxyl-diphosphonic groups while [3,4] have also used the cationic chelating resin Duolite ES 467 with however amino phosphonic groups.

In the selective processing of the phosphate ores; two main trends have been studied; viz, a prior HCl acid leaching of the phosphate values as MCP in the presence of a reductant to keep U^{4+} insoluble [3,5,6]. The second trend, is based on **Krumm findings in 1953 [7]** who has indicated that the presence of calcium citrate and citric acid and using a high liquid/solid ratio would not allow any calcium leaching and is turn phosphate solubilization. This is due to the fact that the ability of the citrate anion to form un-ionized association compounds with calcium ions would be hindered. Thus, it has been possible to first achieve differential leaching of U prior to the phosphate values using a citric acid–calcium citrate mixture under proper conditions from Qatrani phosphate sandstone [8]. On the other hand, both U and the Ln have similarly been leached by the mentioned citric and calcium citrate mixture under proper conditions [9]. The involved reactions are shown as follows:

$$3Ca_3(PO_4)_2 + 4H_3Cit \quad\quad 3Ca(H_2PO_4)_2 + 2Ca_3Cit_2$$

$$UO_2^{2+} + HCit^{3-} \quad\quad UO_2HCit^-$$

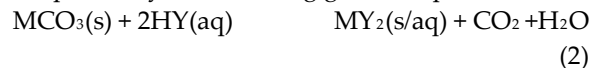$$Ln^{3+} + HCit^{3-} \quad\quad LnHCit$$

On the other hand, it is greatly interesting to refer to the work of several authors who have indeed recommended that it is necessary in the phosphate fertilizer industry that the ore should have a P_2O_5 content exceeding 30% (>70% tricalcium phosphate) and a carbonate content less than 8% [10, 11, 12, 13, 14, 15, 16, 17]. In addition, the CaO/P_2O_5 ratio should be less than 1.6 as well as a MgO content of less than 1% while Fe_2O_3 and Al_2O_3 contents should not exceed 2.5% [17, 18, 19, 20]. Accordingly, the pre-treatment of phosphate rocks prior to fertilizer processing is necessary to reduce the content of the gangue minerals such as carbonates (calcite, dolomite), silicates (feldspar, mica, clays and quartz) in a manner to produce marketable phosphate ores. For sedimentary phosphate ores, the P_2O_5 generally assays 28-36% while for the igneous ores, the latter usually attain up to 35-39%. Several authors have recommended

that calcareous phosphate ores should be beneficiated by organic acid selective leaching of the carbonates prior to manufacture of the [21, 22, 23, 24, 25]. In this regard, **Abu Eishah (1990); Zafar (1993); Abu Eisha and Saddedin (1998) [26, 27, 28]** have applied dilute acetic acid for this purpose and was considered one of the most promising leaching agents for this purpose. The reaction between acetic acid and calcium carbonates can be written as follows:

$$CaCO_3 + 2CH_3COOH$$
$$Ca(CH_3COO)_2 + CO_2 + H_2O \quad\quad (1)$$
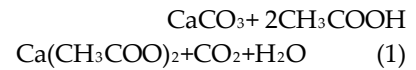
Reaction (1) may include the formation of carbonic acid and then decomposition into CO_2 and H_2O, and reaction for the other impurities depending on the nature and composition of the raw phosphate. The beneficiation of phosphate rock can be simplified by the following general equations:

$$MCO_3(s) + 2HY(aq) \quad\quad MY_2(s/aq) + CO_2 + H_2O \quad\quad (2)$$

$$M_3(PO_4)_2 + 6HY \quad\quad 3MY_2(s/aq) + 2H_3PO_4 \quad\quad (3)$$

where $M = Ca^{2+}$ and/or Mg^{2+}, $Y = H_2C_2O_2^-$ (acetate).

The selectivity should be such that the second reaction does not take place, while the first reaction goes to completion or equilibrium depending on solubility products ($K_{sp}=8.35$, 7.46 for $CaCO_3$ and $MgCO_3$, respectively) and acidity constants for acetic acid ($pK_1=2.21$, $pK_2=3.64$ at 25 °C) and CO_2 ($pK_1=6.35$, $pK_2=10.33$ for H_2CO_3).

In this regard, relevant factors would include reaction time and temperature, S/L ratio, acid type, acid concentration as well as the particle size. While this procedure is environmentally less hazardous than other techniques since the waste organic acids are degradable besides the fact that the applied organic acid can be recovered from the solution by several methods including treatment with sulphuric acid or ion exchange.

Given the fact that the vast resources of Abu-Tartur phosphate ores are relatively of low grade where the collected sample for the present work assays 21.8% P_2O_5 and is associated with 21.3% calcite and 4.6% dolomite, it was found necessary to study its upgrading through leaching of the carbonate minerals prior to phosphate industry using proper organic acids. In this regard, it is interesting to refer to the previous beneficiation

study of Abu-Tartur phosphate by **Malash (2005) [29]** by acetic acid. Using 0.9M of the latter and 60% of the required stoichiometry for 30 min., it was possible to upgrade the rock from 25.6 to 28.6% P_2O_5 with a recovery of 97.2%. Other methods reported in the literature for upgrading the phosphate rock included calcination which is based on the carbonate dissolution after their decomposition; a matter which requires high energy and high cost **[30, 31]**. Alternatively, some workers have also studied the carbonate flotation technique **[32, 33, 34, 35]**.

Accordingly, the present work is concerned with studying the beneficiation of the working calcareous phosphate sample of Abu-Tartur deposit via selective organic acid leaching of its carbonates. For this purpose, 4 organic acids have been chosen; namely acetic acid, tartaric acid, citric acid and oxalic acid to study their efficiency thereupon under different relevant factors. It is interesting to indicate herein that removal of the carbonate gangue would have several economic advantages including the increased P_2O_5 input for the fertilizer plants. On the other hand, while **Farag et al., (2015) [9]** have applied the selective citric acid/calcium citrate mixed reagent leachant for U and Ln leaving both the carbonate gangue and the phosphate values behind, prior elimination of the carbonate would be greatly beneficial in increasing the input assay of both metal values besides P_2O_5 assay; a matter which would be reflected in improving both the capital and operating costs.

Organic acids can be an attractive extracting agent as the extraction is carried out at moderately acidic conditions (pH 3–5) and their degradation is biologically easy **[36]**. In the industrial processes, organic acids may cause a little corrosion effect **[37]**. The use of organic acids at high temperature may be limited because of low boiling temperatures and their decomposition **[38, 39, 40]**.

[9] for its major elements as well as some trace elements together with the study interesting two metal values; viz U and the Ln. From the obtained results shown in Tables (1) and (2), it is evident that P_2O_5 assays only 21.8% while the CaO content attains up to 45.6% and the ignition loss amounts to 9.2% and while U assays only 30 ppm, the Ln attains 1058 ppm. In a trial to translate the chemical composition into a potential mode (Table 3), it was found that while the phosphate mineral did not attain 50%, the carbonate minerals calcite and dolomite assay about 26% which exceeds the triple value of the permissible limit of 8% **[17]**.

Table (1): Chemical composition of the working Abu-Tartur PR sample

Component	Wt. %
SiO_2	5.89
Al_2O_3	1.72
Fe_2O_3	8.08
MgO	1.01
CaO	45.61
Na_2O	0.58
K_2O	0.16
TiO_2	0.29
P_2O_5	21.82
MnO	0.34
F	0.76
Cl	0.17
SO_3	3.88
*L.O.I	9.20
Total	**99.51**

*L.O.I: Loss on ignition

Table (2): Interesting trace elements analysis in the working Abu-Tartur PR sample

Element	ppm	Element	ppm
		U	30
Sc	76	Th	18
V	103		
Cr	77	La	201
Co	54	Ce	337
Ni	40	Nd	176
Cu	24	Sm	42
Zn	72	Yb	19
As	41	Y	283
Cd	2		
Sr	1495	**Total REEs**	**1058**

Table (3): Potential mineral composition of the working Abu-Tartur PR sample

Component	Wt.%	Component	Wt.%
Apatite	49.20	Iron oxides	8.08
Calcite	21.29	Clay	4.30
Dolomite	4.64	Quartz	4.49
Gypsum	8.35		
		Total	**100.35**

2 EXPERIMENTAL

2.1. Material

The working calcareous Abu-Tartur (Egypt) phosphate sample has completely been analyzed

2.2. Experimental procedure

Several organic acid leaching experiments have been performed to eliminate the carbonate content from the study calcareous phosphate rock

of Abu-Tartur deposits. At the beginning, it was found necessary to study the effect of the applied acid type and its concentration upon their efficiency upon the carbonate minerals leaching of the study Abu-Tartur representative phosphate sample. The chosen acid at its optimum concentration was then applied to study the other relevant conditions. In each experiment, a sample weight portion of the study representative sample was agitated in a certain volume of the chosen acid type and concentration for a specific time period and using a proper grain size.

After each experiment, the working slurry was filtered to separate the leached phosphate sample which was then properly washed while both the filtrate and washings were made to volume for the required analysis. The latter involved both phosphorous to insure its insolubilization while calcium analysis was so calculated vs total as well as vs the calcium equivalent of the carbonate minerals.

2.3. Analytical control procedures

2.3.1. Control analysis of P_2O_5

Phosphorous content in the different stream solutions was spectrophotometrically determined via measuring the light absorbance of the yellow molybdo-vanadate phosphoric acid complex at 420 nm using Metertech Inc model SP 8001. The wave length of 420 nm was chosen to provide adequate sensitivity and minimize the effect of iron interference [41].

2.3.2. Control analysis of CaO

For the determination of the calcium content in the different stream solution samples, the compleximetric titration method against a standard EDTA solution in presence of murexide indicator was used [42]. This indicator has a blue violet color in alkaline solution at pH 12. For this determination, it is necessary to add about 30 mg of potassium cyanide and 30 mg of hydroxylamine hydrochloride to 1 ml of each sample solution and adjusting the pH to 12.

2.3.3. Control analysis of U

For uranium analysis in the different working experimental stream solutions, the oxidimetric titration method using ammonium metavanadate procedure has been applied. For this purpose, a prior uranium reduction was performed by $(NH_4)_2Fe(SO_4)_2$ in the presence of diphenylamine sulphonate indicator until it changes to a slightly violet colour [43]. The uranium concentration is thus calculated according to the following equation:

U (g/l) = T.V1 / V. 1000   where   V1: volume taken of NH_4VO_3 solution (ml), V: sample volume (ml) and   T: concentration of NH_4VO_3 to U (g/ml)

2.3.4. Control analysis of Ln

The Ln analysis in the different working experimental stream solutions was spectrophotometically determined by Arsenazo III as a complexing agent and the absorbance was measured at 650 nm against proper standard solutions [44] using a Lambada UV/VIS spectrophotometer (Perkin-Elmer, USA).

3. Results and discussion

3.1. Effect of acid type

To study the effect of the acid type and concentration of the study 4 acids, a certain weight portion of the study representative sample of Abu-Tartur PR was agitated in the concerned acid under specific conditions. The latter involved a S/L ratio of 1/2 for a reaction time of 30 min. at room temperature and using ore samples ground to -150 mesh size while the applied acid concentration involved 3 molarities; namely 0.2, 0.8 and 1.4 M. The obtained results are shown in the Tables (4, 5 and 6) respectively.

Table (4): Effect of acid type (0.2 M) upon the leaching efficiency of U, Ln, P_2O_5 and CaO from the working Abu-Tartur PR sample

Acid type	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
Acetic acid	Nil	Nil	Nil	12.1	46.8
Tartaric acid	2.2	9.4	8.1	16.2	62.6
Citric acid	3.5	12.2	11.2	33.6	100
Oxalic acid	4.4	14.1	12.1	37.1	100

Table (5): Effect of acid type (0.8 M) upon the leaching efficiency of U, Ln, P₂O₅ and CaO from the working Abu-Tartur PR sample

Acid type	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
Acetic acid	Nil	Nil	Nil	23.1	89.3
Tartaric acid	3.3	12.3	12.1	25.5	98.6
Citric acid	3.9	14.9	14.2	39.3	100
Oxalic acid	4.2	22.1	19.3	45.5	100

Table (6): Effect of acid type (1.4 M) upon the leaching efficiency of U, Ln, P₂O₅ and CaO from the working Abu-Tartur PR sample

Acid type	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
Acetic acid	3.0	17.0	16.7	45.2	100
Tartaric acid	4.5	21.1	19.2	49.6	100
Citric acid	6.2	24.6	22.8	52.5	100
Oxalic acid	7.7	30.4	28.1	60.7	100

As a matter of fact, the leaching capability of the organic acids is indeed relatively weak as compared to the inorganic acids. However, application of these weak acids shows an appreciable degree for selective leaching of calcareous material in low-grade phosphate rock [23]. In this concern, it has to be mentioned that using a high molarity of these acids cannot realize the required selectivity and would react with tricalcium phosphate. In the meantime, the study acids have indeed shown variable degrees of leaching the phosphate mineral except acetic acid at 0.2 and 0.8 M concentration. In the latter case, the water molecules tend to decrease the effect of polarity of the OH bond resulting in selective leaching of calcareous material in the rock due to higher degree of ionization [23]. On the other hand, only at 1.4 M acetic acid and at all the study molarities of tartaric, citric and oxalic acids, both the carbonate and the phosphate mineral constituents have reacted to varying degrees. Accordingly, 0.8 M acetic acid was chosen to selectively leach the carbonate mineral while leaving the phosphate mineral intact as will be later shown. After the leaching process, the liquid phase would be later properly treated for regeneration and recycling of acetic acid.

Summing up, it can be concluded from the obtained results that apart from acetic acid at 0.2 M

and 0.8 M, the other 3 studied acids whether at 0.2 M or 0.8 or at 1.4 M together with 1.4 M acetic acid have actually been able to attack the phosphate mineral (together with the contained U and Ln). In this regard, it is interesting to mention that tartaric acid is the least leachant followed by citric and oxalic acids. Thus at 1.4 M oxalic acid, the leaching efficiency of U, Ln and P₂O₅ has only attained 7.7, 30.4 and 28.1 respectively.

Accordingly, in the following experiments, 0.8 M acetic acid will be used to study the selective leaching of the carbonate minerals at different leaching conditions.

3.2. Optimization of acetic acid factors for selective carbonate leaching

3.2.1. Effect of grain size

To study the effect of the particle size of Abu-Tartur PR, different samples of the latter were ground to different particle size ranged from completely passing through mesh sizes 50, 70, 100 and 150. The obtained samples were then leached using 0.8 M acetic acid of S/L ratio of 1/2 for 30 min. at room temperature. From the obtained results shown in Table (7), it is clearly evident that by decreasing the particle sizes from -50 to -150 mesh sizes, the leaching efficiency of the equivalent calcium carbonate mineral has increased from 27.1 to 89.3% respectively.

Table (7): Effect of particle size upon the leaching efficiency of U, Ln, P₂O₅ and CaO by 0.8 M acetic acid from the working Abu-Tartur PR sample

Particle size, mesh	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
-50	Nil	Nil	Nil	7.1	27.1
-70	Nil	Nil	Nil	9.2	35.6
-100	Nil	Nil	Nil	11.6	44.9
-150	Nil	Nil	Nil	23.1	89.3

3.2.2. Effect of acetic acid concentration

The effect of acetic acid concentration upon beneficiation of Abu-Tartur PR through carbonate minerals leaching has further been studied in more details using the ore ground to -150 mesh size. For this purpose, a number of leaching experiments have been performed at room temperature using

different concentrations varying from 0.2 up to 1.4 M with gradual increments of only 0.2 M for 1/2 hr. leaching time and using a S/L ratio of 1/2. From the obtained results shown in Table (8), it is clearly evident that at the acetic acid molarity varying from 0.2 to 0.8 M, neither P_2O_5 nor U and the Ln were leached to any extent while the leached CaO corresponding to the carbonate minerals has ranged from 46.8 up to 89.3% respectively. Only when using an acetic acid concentration of 1 M that U, Ln and P_2O_5 have been leached to the extent of 2.9, 11.1 and 9.7% respectively. Therefore, 0.8 M acetic acid was considered as the optimum acid concentration that does not allow leaching of the latter elements.

Table (8): Effect of acetic acid concentration upon the leaching efficiency of U, Ln, P_2O_5 and CaO from the working Abu-Tartur PR sample

Acetic acid conc., M	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
0.2	Nil	Nil	Nil	12.1	46.8
0.4	Nil	Nil	Nil	16.4	63.5
0.6	Nil	Nil	Nil	19.7	76.3
0.8	Nil	Nil	Nil	23.1	89.3
1	2.9	11.1	9.7	32.9	100
1.2	3.4	13.8	12.6	38.4	100
1.4	4.9	19.5	16.7	45.2	100

3.2.3. Effect of the S/L ratio

To study the effect of the S/L ratio upon the leaching efficiency of the interesting elements, a series of experiments have been performed using an acetic acid concentration of 0.8 M, upon -150 mesh size ore samples for a reaction time of 30 min. at room temperature while the S/L ratio was varied between 1/2 up to 1/6.

Table (9): Effect of the S/L ratio upon the leaching efficiency of U, Ln, P_2O_5 and CaO from the working Abu-Tartur PR sample

S/L ratio	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
1/2	Nil	Nil	Nil	23.1	89.3
1/3	Nil	Nil	Nil	23.9	92.4
1/4	Nil	Nil	Nil	24.1	93.2
1/5	1.4	5.3	4.8	27.4	100
1/6	1.8	8.9	7.3	35.1	100

From the obtained results shown in Table (9), it can be deduced that at the S/L ratios of 1/2 to 1/4, both the phosphate mineral as well as the associated U and Ln values have not been leached and only the carbonate mineral has been leached. Increasing the S/L ratio to 1/5 and 1/6, the phosphate mineral has started to be leached to the extent of 4.8 and 7.3% respectively together with slight amount of U and Ln. In the meantime, the carbonate mineral has been completely leached. Therefore, the S/L of 1/4 would be considered as an optimum value.

3.2.4. Effect of the reaction time

Using an acetic acid concentration 0.8 M and ore samples ground to -150 mesh size in a S/L ratio of 1/4 at room temperature, the effect of the reaction time was studied in the range from 30 up to 80 min. and the obtained results are tabulated in Table (10). From the latter, it was clearly evident that almost all the carbonate has been leached (99.6%) at the reaction time of 50 min. and at which the phosphate mineral has not been attacked. Thereafter, the latter has started to be leached and therefore the reaction time of 50 min. would be considered as an optimum value at which the phosphate mineral will remain intact.

Table (10): Effect of the reaction time upon the leaching efficiency of U, Ln, P_2O_5 and CaO from the working Abu-Tartur PR sample

Reaction time, min.	Leaching efficiency, %				
	U	Ln	P_2O_5	CaO	
				vs total CaO	vs CaO of calcite
30	Nil	Nil	Nil	24.1	93.2
40	Nil	Nil	Nil	24.7	95.7
50	Nil	Nil	Nil	25.8	99.6
60	1.1	3.6	2.4	26.3	100
80	1.3	6.7	4.9	38.8	100

3.3. Acetic acid regeneration

The economy of the studied calcareous leaching process of PR depends mainly on the price of the applied acetic acid and the cost of its recovery. The applied acetic acid can indeed be recovered from the obtained calcium acetate solution by a number of routes as reported [22]. It may thus be recovered by the reaction of calcium acetate solution with any strong acid as sulphuric acid where an insoluble calcium sulphate salt is formed and separated from the recovered acetic acid by filtration. The by-products CO_2 and calcium sulphate may be used or sold to other

industries to meet the cost of commercial acetic acid and its recovery by sulphuric acid.

Finally, all the studied upgrading operations have been translated into an overall generalized proposed flowsheet (Fig. 1). In the latter, both U and Ln have to be later recovered via anionic and cationic exchange resins respectively [9]. In this flowsheet, most of the applied reagents can be properly recycled.

4. Conclusion

Abu-Tartur PR contains about 49.20% apatite mineral (21.8% P_2O_5) and more than 50% of undesirable components including about 26% carbonate minerals besides some siliceous and gypsum minerals. In this study, acetic acid was used to eliminate the carbonate content of the working Abu-Tartur PR in a manner to upgrade both the phosphate value as well as both of the associated metal values; namely U and the Ln. The studied relevant conditions that have realized this objective were found to involve:

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Particle size        : -150 mesh
Acetic acid conc.  : 0.8 M
S/L ratio            : 1/4
Reaction time      : 50 min.
Temperature        : room temperature
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Considering complete removal of the calcite mineral (21.29%), the upgraded Abu-Tartur PR would assay about 28% P_2O_5 together with about 38 ppm U and 1340 ppm Ln.

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