

Some additives as potential alternative sources for lanthanides separation from Abu-Tartur phosphate ore, Egypt

Ahmed R. Bakry*

Nuclear Materials Authority, P.O.Box 530, El Maadi, Cairo, (EGYPT)

E-mail: BakryNma@yahoo.com

ABSTRACT

The lanthanides content of Abu-Tartur phosphate rock deposits (0.18%) have properly been recovered. Using a mixed acid "salt of HNO_3 " $\text{Ca}(\text{NO}_3)_2$ and convenient leaching conditions, it has been possible to obtain a Ln leaching efficiency exceeding 94%. This has been possible after adjusting the leaching conditions in a manner to control the fluoride ion concentrations. From the obtained phosphoric solution, the Ln values were recovered via the cation exchange resin Dowex50W-X8. Under the working conditions the latter was practically saturated with about 35g Ln l^{-1} vsr while its calculated theoretical capacity would attain about 85g Ln l^{-1} . The purity of the final Ln_2O_3 product was found to exceed 91%.

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KEYWORDS

Abu-Tartur;
Phosphate ore;
Additives;
Lanthanides.

INTRODUCTION

Phosphate rocks and mainly used for the production of phosphoric acid which is essentially required as fertilizer as well as in food and pharmaceutical industries. In addition, phosphate rocks are actually considered as an important alternative or secondary resource for both uranium and lanthanides given the fact that their worlds reserves are estimated to be about 18000 million tons. Thus, while the former generally ranges from 50 to 200 ppm, it attains 150 ppm in Florida phosphate rock and up to 0.8% Ln_2O_3 . However, according to several authors, the Ln content in the sedimentary PR attains an average content ranging from 0.1 to 0.4% while in the igneous phosphorites, the Ln can reach average of 0.8 to 3.0%^[1-3]. Considering that more than 100 mil-

lion tons of PR are treated annually for fertilizer production, this means that about 15000 tons of U and 800000 tons of Ln would be annually lost^[4]. With respect to uranium, it has to be mentioned that while many processes for U recovery from phosphoric acid produced by the H_2SO_4 route (WPPA) are known and have been commercially applied on a limited scale, however recovery of the Ln will be difficult during this procedure as they will mostly be lost in the co-produced gypsum. In this trend, it has to be indicated that^[5] have developed a process for Ln recovery from the calcium sulfate sludges of the WPPA of South Africa using nitric acid and which was enhanced by the addition of $\text{Ca}(\text{NO}_3)_2$. Also,^[6] have studied the leaching of Ln from phosphohemihydrate with nitric acid. On the other hand, the use of nitric acid for treating PR for pro-

duction of fertilizers is a well established technology particularly in Europe and would actually eliminate the gypsum disposal problems.

In the meantime, the use of hydrochloric acid did not receive adequate attention and like nitric acid, it will solubilize all the phosphate rock except the gangue minerals. Apart from possible separation of radium, the obtained solution would be then treated to separate calcium and produce ammonium phosphate fertilizer. Calcium can indeed be precipitated by H_2SO_4 acid as $CaSO_4$ and where hydrochloric acid would be regenerated for recycle^[7]. Other advantage of the HCl acid route is the possibility of working under reducing conditions whereby U is kept in the relatively small residue^[8-10]. It is interesting in this regard to mention that while U extraction from phosphoric acid is marginally economic according to the actual market conditions, increasing U prices and “ or technological improvements of its recovery procedures besides possible Ln extraction might indeed result in better economics.

The present work is thus mainly concerned with the processing of Abu-Tartur PR, Western Desert, Egypt for the recovery of its Ln content which attains about 0.18% using nitric acid. However, it was found that its F content (2.8%) present in the fluoroapatite mineral has greatly affected the leaching behaviour of Ln. Thus, while the phosphate mineral has completely been converted into phosphoric acid using 8M HNO_3 , the associated F has been instrumental in Ln precipitation a manner to attain a leaching efficiency of only about 41%. Therefore, it was found quite necessary to defluorinate the leach solution; a matter which would also be greatly advantageous to avoid contamination of the fertilizer and in turn lowering its grade. In addition, this defluorination would permit in the meantime the recovery of F.

The different relevant factors have thus been studied, namely the effect of acid concentration, the S” L ratio, the contact time, the temperature besides calcium nitrate concentration. The latter has proved greatly effective in F precipitation. For the recovery of the Ln, the optimum conditions of these factors were applied and from the obtained phosphoric acid solution, the Ln were recovered by ion exchange

using the cation exchange resin Dowex 50W-X8.

MATERIALS AND METHODS

Material

The studied phosphate rock sample belongs to Abu-Tartur deposit situated in the Western Desert of Egypt. A representative sample portion thereof was properly ground and subjected to complete chemical analysis of its major oxide constituents besides some trace elements as well as the individual Ln contents. From the major oxide contents, the potential mineral composition was calculated (mode).

Recovery procedures of lanthanides

Leaching procedure

The leaching characteristics of the Ln from the studied Abu-Tartur PR have been determined by several experimental series to determine the optimum values of the relevant factors. Thus, after the choice of nitric acid, its concentration, the effect of the S” L ratio, the contact time and the temperature in addition to the effect of salt additive have been studied. In these experiment and except otherwise cited, 20 g sample portions have all the time been used in a S” L ratio of 1/ 2 for 30 min at room temperature.

Ion exchange recovery

For the IX recovery of the leaded Ln from Abu-Tartur PR working sample, a proper solution was prepared thereof using the determined optimum values of leaching using mixed HNO_3 “ $Ca(NO_3)_2$. Dowex50W-X8 cation exchange resin was used by packing 15 ml wsr in a glass column of 1.5 cm diameter and after saturation, the loaded resin column was eluted using 4 M HCl acid. From the obtained eluate, the Ln were precipitated as their oxalates followed by ignition at 850°C to obtain the Ln_2O_3 product.

Analytical procedures

Bulk analysis of the working sample

The representative sample was analyzed to determine the major oxide components and some trace elements as well as the individual Ln contents using

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proper analytical procedures. Thus, for the former the^[11] was adopted while for the trace elements, X-ray fluorescence was used [Philips X Unique-II spectrometer with automatic sample changer, Pw 1510 (30 positions), Holland]. For the individual Ln, ICP-AES Model Philips PV 8490 was used.

Control analysis

For analysis of the different stream solutions of the working experiments, the Ln content was spectrophotometrically determined by the Arsenazo III complex^[12] using Perkin Elmer. In these solutions, the F concentration was determined by the ion selective electrode after adjusting the pH to about 5 using sodium acetate trihydrate and adding TISAB solution to adjust the ionic strength of the solution. On the other hand, the individual Ln content in the final product was also analyzed using ICP-AES.

RESULTS AND DISCUSSION

Characteristics of the Working Abu-Tartur PR Sample

Chemical composition

As previously mentioned, the working sample of Abu-Tartur PR has completely been analyzed by the relevant methods for both the major constituents as well as for some interesting trace elements. From

the obtained results shown in TABLE 1, it was found that the P₂O₅ content in the working sample attains 25.1% while the CaO attains 39.76% together with 2.8% F. In addition, the SiO₂ content amounts to 7.42% whereas SO₃ assays up to 12.32% and Fe₂O₃ attains 6.7% while Al₂O₃ is quite low assaying only 0.47%. On the other hand, the economic metal values in the working sample include mainly the ΣREEs, U and V and were found the attain 1800, 118 and 65 ppm respectively.

The total REEs have also been individually analyzed using the ICP-AES technique and the obtained results TABLE 2 indicate that La and Ce assay 184 and 446 ppm respectively while Pr and Nd attain 110 and 339 ppm respectively. The latter together with Sm, Eu and Gd represent the LREEs in Abu-Tartur PR and would thus attain 1236.5 i.e. about 70% of the ΣREEs. The assay of the HREEs is quite low assaying only 128.9 ppm and among which Tm was under the limit of detection. Analysis of Y indicated an assay of 390 ppm and the ΣREEs (including Y) amount to 1775.4 ppm i.e. about 1800 ppm. The latter total assay of the ΣREEs is indeed quite important to study its recovery which would be quite economic given its association with an important ore material.

Potential mineral composition (Mode)

Proper calculations of the tricalcium phosphate

TABLE 1 : Chemical analysis of the major and trace elements of Abu-Tartur PR

Component	Weight percent, %	Trace elements	ppm
SiO ₂	7.42	Cr	33
Al ₂ O ₃	0.47	Co	4
Fe ₂ O ₃	6.70	Ni	16
MgO	2.10	Cu	13
CaO	39.76	Zn	83
Na ₂ O	1.12	Zr	66
K ₂ O	0.16	Rb	74
TiO ₂	0.72	Ba	147
P ₂ O ₅	25.10	Pb	9
F	2.80	Mn	1080
SO ₃	12.32	Sr	1095
ΣREE	0.18	V	65
H ₂ O ⁺	0.96	*U	118
Total	99.80	*Th	16.5

*U, *Th: measured by Arsenazo III method.

TABLE 2 : Individual analysis of the lanthanides in Abu-Tartur PR

Elements	ppm	Elements	ppm
La	184	Dy	52
Ce	446	Ho	8.4
Pr	110	Er	26.4
Nd	339	Tm	u.d
Sm	80	Yb	28.6
Eu	12.8	Lu	3.3
Gd	64.7	Y	390
Tb	10.2	ΣREEs	1755.4 ≈ (0.18%)

(TCP) content of the working Abu-Tartur PR sample has resulted in an assay of about 55% and to which if the F content is added would amount to 57.8%.

On the other hand, the analyzed SO_3 content of 12.32% is most probably representing previous pyrite (FeS_2) which according to the calculated Fe content (4.7%) would have amounted to 8.8%. Alternatively, the latter pyrite content has been oxidized to Fe_2O_3 (6.7%) and sulfuric acid and which has reacted with previous calcite and dolomite to give gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In other words, the remaining CaO of 9.8% after formation of the TCP would require 14% SO_3 (analyzed 12.32%) to form 23.8% CaSO_4 . Thus, the present gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would attain about 30%. Therefore, it can be mentioned that the potential mineral composition of the working Abu-Taartur PR sample can be represented as follows:

Potential Mineral Wt%

Calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2(\text{F})$]	57.8
Gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$]	30.0
Iron oxides [Fe_2O_3]	6.7
Quartz (chalcedony) [SiO_2]	7.4
Total	101.9

TABLE 3 : Effect of concentration of the mineral acids on the leaching efficiency of the lanthanides from the working Abu-Tartur PR sample

Acid conc., M	Ln leaching efficiency, %		
	HNO_3	HCl	H_2SO_4
2	24	8	5.5
4	33	12	5
6	38	15	4
8	41.6	19.4	5
10	40	18	5.5
12	40	17	5.5

Leachability of lanthanides from abu-tartur PR by mineral acids

Comparable conditions of different concentrations of the three mineral acids have been applied to investigate the leachability of lanthanides from the working Abu-Tartur PR sample. These conditions included a solid to liquid ratio (g:ml) of 1 : 2 using a constant weight sample of 20 g at room temperature with stirring for 30 min.. From the obtained results shown in TABLE 3, it is clearly evident that the obtained leaching efficiencies of lanthanides varied from quite low to moderate values. Thus in case of sulfuric acid, the former has only ranged from 4 to 5.5% while in hydrochloric acid, it varied between 8 and 19.4% and when using nitric acid the leaching efficiency varied from 24 to 41.4% in case of using 2 to 8 M acid respectively.

In other words, using 8 M nitric acid gave a leach liquor containing 0.37 gl^{-1} ΣREEs (41.6% leaching efficiency) while this assay decreases to 0.17 gl^{-1} ΣREEs (19.4% leaching efficiency) in case of 8M hydrochloric acid leaching and down to only 0.045 gl^{-1} ΣREEs (5% leaching efficiency) with 8 M sulfuric acid as shown in (TABLE 3 and Figure 1).

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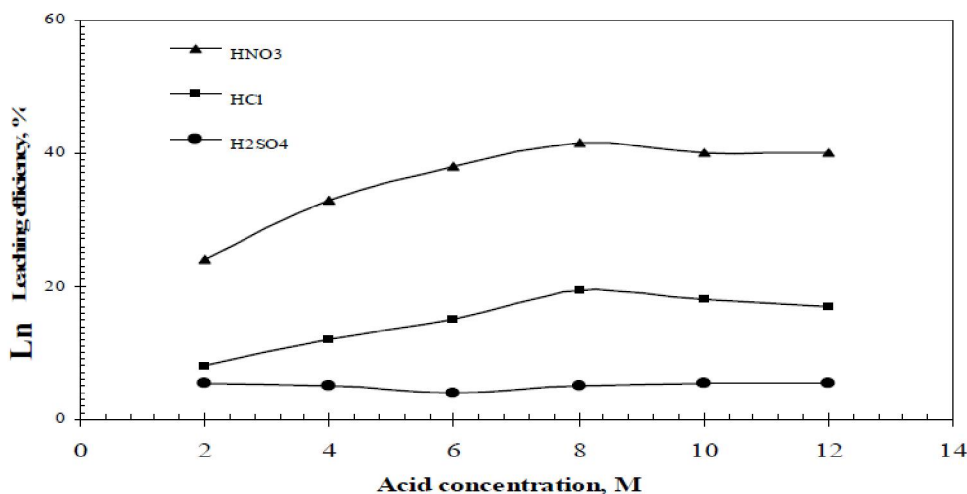


Figure 1 : Effect of the mineral acids concentration on the leaching efficiency of Ln from the working Abu-Tartur PR sample

Further acid increase in the acid molarities has slightly decreased the efficiency as in nitric and hydrochloric acids or else has remained constant as in case of sulfuric acid leaching.

Accordingly, it can be indicated that the theoretical calculation of the acid requirement for the TCP content present in the input 20 g Abu-Tartur PR to form phosphoric acid would be 13.4 g of HNO₃ acid, 8 g of HCl acid and 10.4 g of H₂SO₄ acid. Thus, in case of nitric acid leaching, the input content of the 6 and 8 M acid (15.12 and 20.16 g acid) respectively would be sufficient for phosphoric acid production, however the leached lanthanides was only 38.0 and 41.6% respectively and approximately remained in this range thereafter. With respect to HCl acid, the input acid amount at 6 and 8 M is 8.76 and 11.68 g respectively while the acid required for phosphoric acid production amounts to 8 g HCl acid. However, under both 6 and 8 M HCl, the lanthanides leaching efficiency is only 15.0 and 19.4%. This relatively low efficiency might be due to partial side acid consumption in reaction with the iron oxides content of Abu-Tartur PR. This consumption is most probably more effective in case of HCl acid than is the case in HNO₃ acid; a matter which has resulted in an almost half the leaching efficiency realized with HNO₃ acid.

Concerning the lanthanides leaching efficiency in case of H₂SO₄ acid, it was found that amount required for phosphoric acid production of the input 20 g ore sample attain 10.4 g at 4 M input acid (40

ml), the acid amount attains 15.68 g which is quite adequate for phosphoric acid production, however, the leaching efficiency of the associated lanthanides at these conditions was only 5%. This exceedingly low leaching efficiency of the lanthanides content of Abu-Tartur PR is actually due to co-formation of CaSO₄ which is quite effective in capturing the lanthanides.

It can thus be concluded that the effective acid in leaching the lanthanides from PR would be HNO₃ acid while HCl acid comes next whereas H₂SO₄ is the least effective. It has to be mentioned herein that besides the input acid quantity varied between the 3 acids, the least ability of sulfuric acid to put lanthanides in solution is attributed to the high tendency of the formed gypsum to scavenge most of the leached lanthanides in its lattice.

Apart from the effect of the nature of the working acid in spite of presence of adequate acid amount for the phosphate content, the maximum leaching efficiency of lanthanides was only about 40% in case of nitric acid. This can actually be interpreted as due to co-leaching of the fluoride ion present in the phosphate apatite mineral [Ca₁₀(PO₄)₆F₂]. The latter is indeed quite instrumental in precipitating the leached lanthanides as their fluorides. According to these findings, it was found necessary to study in detail the leaching behavior of both lanthanides and F using HNO₃ acid. In other words, this study would be in the frame nitrophosphate fertilizer production from Abu-Tartur PR.

TABLE 4 : Effect of nitric acid concentration on the leaching efficiency of lanthanides and fluorine from Abu-Tartur PR

HNO ₃ Acid conc., M	Ln		F ⁻ , gl ⁻¹
	Conc., gl ⁻¹	Leaching efficiency, %	
2	0.15	24	3.42
4	0.22	33	3.23
6	0.35	38	2.85
8	0.37	41.6	2.09

TABLE 5 : Effect of solid / liquid ratio (S/L) on the leaching efficiency of the lanthanides and fluorine from Abu-Tartur PR

S/L ratio	Ln		F ⁻ , gl ⁻¹
	Conc., gl ⁻¹	Leaching efficiency, %	
1/2	0.37	41.6	2.09
1/4	0.11	24.4	3.04
1/6	0.08	26.7	3.61
1/8	0.06	26.7	3.80

Nitric acid leaching of Ln and F from Abu-Tartur PR

Effect of nitric acid concentration

The results of the effect of nitric acid concentration (2-8 M) on the leaching efficiency of lanthanides and fluorine from Abu-Tatur PR using 1/2 S/L ratio, an agitation time of 30 min. and at room temperature are shown in TABLE 4.

From these results, it is clearly evident that the leaching efficiency of the lanthanides increased from 24 to 41.6 equivalent to a concentrate of 0.15 to 0.37 gl⁻¹ by increasing the acid molarity from 2 to 8 M respectively. Under these conditions, the F assay has however decreased from 3.42 down to 2.09 gl⁻¹ by increasing the acid molarity from 2 to 8 respectively. It has to be indicated herein that if the leached F has properly been prevented from volatilizing and / or precipitation, it would have assayed up to 14 gl⁻¹. As a matter of fact, several authors have indicated that over 80 % of F in the PR volatilizes during their leaching. This is mainly due that F dissolves mainly as HF and SiF₆²⁻ and while the former is volatile, the latter can dissociate into its volatile components; namely SiF₄ and HF. It can thus be inferred that while the increased acid molarity should have increased the leaching efficiency of Ln above 41.6%, however, such an expected increase has not been manifested due to the precipitation by the leached F whose

assay was decreased due to this effect. In this regard, it is interesting to refer to^[4] who has indicated that during PR leaching, a major part of F volatilizes as HF and SiF₄ and which are usually recovered in industrial applications. Besides contaminating the manufactured fertilizer and thus lowering its grade, the minor part remaining in solution mostly as SiF₆²⁻ would precipitate the leached Ln as their fluorides. According to^[4], the F content that remained in solution and which corresponds to only 6.1% of the F present in Florida PR has been precipitated as Na₂SiF₆ by adding NaNO₃. In case of the obtained results, the effect of the co-leached F has thus decreased the Ln concentration from 0.9 gl⁻¹ (100% Ln leaching) to only 0.37 gl⁻¹.

Effect of solid / Liquid ratio

The effect of the solid to liquid ratio (S/L) (W/Vol) on the leaching efficiency of the lanthanides from Abu-Tartur PR (0.18% ΣREEs) was studied in the range of 1/2 to 1/8. The other experimental conditions were fixed at 8 M HNO₃ and working at room temperature for 30 min. contact time. From the obtained results shown in TABLE 5, it was found that by decreasing the S/L ratio from 1/2 to 1/4, the apparent Ln leaching efficiency has decreased from 41.6 down to 24.4% equivalent to 0.37 down to only 0.11 gl⁻¹ respectively. Further decrease in the S/L ratio to 1/6 and 1/8 has not led to perceptible change

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in the Ln leaching efficiency. In the meantime, the F leaching has increased to about 3-3.8 gl^{-1} indicating that it must have been effective in precipitating the unshown increase in the Ln leaching efficiency. As a matter of fact, it is expected that increasing the acid amount should have led to increase in the Ln leaching efficiency as well as-in the meantime-increase in the F leaching. The latter has thus been instrumental in Ln precipitation. Increase in the F concentration by progressive dilution (decrease in the S/L ratio) might be due to its gradual decreased volatilization and where at the S/L ratio of 1/6 and 1/8, volatilization might not have occurred where complete F leaching would result in a F concentration of 3.5 gl^{-1} . The given assay of 3.6 to 3.8 gl^{-1} at 1/6 and 1/8 S/L ratio (TABLE 5) is mostly due to an analytical error.

Effect of agitation time

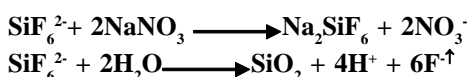
The effect of agitation time on the leaching efficiency of lanthanides and fluorine from Abu-Tartur PR (0.18% ΣREEs) was studied in the range of 10 to 60 min. The other leaching conditions were fixed at S/L ratio 1/2 and using 8M (HNO_3) at room temperature. The obtained results (TABLE 6) indicate that at 10 min. contact time, the lanthanides leaching efficiency has been quite low (12.7%) equivalent to Ln concentration of only 0.11 gl^{-1} whereas the obtained F concentration amounts to 5.5 gl^{-1} . The former has increased to 14.1 and 41.6% while the latter

was decreased to 2.47 and 2.09 gl^{-1} due to increased evaporation by increasing the contact time to 20 and 30 min. respectively. Extending the leaching time to 60 min. has however seriously decreased the apparent leaching efficiency to only 11.1%; a matter which is due to increased Ln precipitation by extension of the contact time.

Effect of temperature

The effect of temperature on the leaching efficiency of the lanthanides and fluorine from Abu-Tartur PR using 8 M nitric acid at a solid to liquid ratio of 1/2 and for an agitation time of 30 min. has been studied in the range from room to 100°C.

From the obtained results (TABLE 7), it was found that while the leaching efficiency of the lanthanides sharply decreased from 41.6% at room temperature down to only 10, 9, 6.7 and 5.6% by increasing the leaching temperature from room to 40, 60, 80 and 100°C. On the other hand, while^[13] have indicated precipitation of SiF_6^{2-} as Na_2SiF_6 by the addition of NaNO_3 is best achieved at 70°C, its hydrolysis can also be achieved under proper conditions^[6]. These reactions can be represented as follows:



Accordingly, the liberated F^- would lead to lanthanides precipitation as their sparingly soluble LnF_3 . Therefore, the net result of increasing the tem-

TABLE 6 : Effect of agitation time on the leaching efficiency of the lanthanides and fluorine from Abu-Tartur PR

Agitation time	Ln		F ⁻ , gl^{-1}
	Conc., gl^{-1}	Leaching efficiency, %	
10	0.11	12.7	5.51
20	0.13	14.1	2.47
30	0.37	41.6	2.09
60	0.10	11.1	2.11

TABLE 7 : Effect of temperature on the leaching efficiency of the lanthanides and fluorine from Abu-Tartur PR

Temperature, °C	Ln		F ⁻ , gl^{-1}
	Conc., g l^{-1}	Leaching efficiency, %	
Room temperature	0.37	41.6	2.09
40	0.09	10.0	2.50
60	0.08	9.0	2.61
80	0.06	6.7	2.73
100	0.05	5.6	2.80

perature would increase the F⁻ in the leaching circuit by increasing its leaching, however, its removal from the leach liquor would be carried out by its precipitation and or hydrolysis. The net result of these two effects is shown in TABLE 7. Accordingly, it can be concluded that the effect of temperature on the leaching efficiency of lanthanides is reversible and thus the room temperature or the ambient temperature would give the highest leaching efficiency of lanthanides (41.6% leaching efficiency).

Effect of additives for F insolubilization

From the above mentioned data of Ln and F leaching efficiencies, it was clearly evident that apart from F volatilization, the remaining fraction has a serious effect upon the leachability of the Ln. In the other words, while during nitric acid leaching of Abu-Tartur PR, a major part of F volatilizes as HF and SiF₄, the remaining minor amount of F is found in solution as SiF₆²⁻. According to^[4, 13] and to^[14] and as mentioned above, it could be possible to precipitate the latter in the form of Na₂SiF₆ by adding of NaNO₃ and heating at 70°C for 30 min. On the other hand, it is according to^[5] that Ln leaching from the CaSO₄ sludges (produced during WPPA production by sulfuric acid) by dilution nitric acid is consider-

ably enhanced by the addition of Ca(NO₃)₂.

In the present work, it was thus found greatly convenient and interesting to try adding some salts to the nitric acid leach liquor that would effectively precipitate the fluorine remaining in Abu-Tartur phosphoric acid and in turn its elimination in a manner to avoid precipitation of the leached Ln as their fluorides and in turn improve their dissolution. Accordingly, 5 different nitrate salts were separately added to the latter in a 0.5 M concentration. From the obtained leaching efficiencies of Ln vs the assay of F in the treated Abu-Tartur PR (TABLE 8), it was found that the leaching efficiency of the Ln has variably increased to a range varying from 58.3 up to 94.4%. The latter correspond actually to the nitrate salts of Na and Ca respectively, while when using the nitrate salt of Fe, Al and NH₄ have resulted in 66.6, 75.0 and 86.1% respectively. In the same time, the F assay increased from Ca to Na from only 0.19 to 2.09 g l⁻¹ while with NH₄, Al and Fe, it increased from 1.33 to 1.17 and 1.90 g l⁻¹ respectively. In spite of presence of Ca(NO₃)₂ in the leach liquor resulting from the dissolution of the TCP [Ca₆(PO₄)₁₀F₆] by nitric acid, it seems that it has not been adequate to precipitate the dissolved F.

In a next step, it was found necessary to study

TABLE 8 : Effect of different nitrate salt additives on the leaching efficiency of lanthanides and fluorine from Abu-Tartur PR

Nitrate salt additive	Ln		F ⁻ , g l ⁻¹
	Conc., g l ⁻¹	Leaching efficiency, %	
Ca(NO ₃) ₂	0.85	94.4	0.19
NH ₄ NO ₃	0.77	86.1	1.33
Al(NO ₃) ₃	0.67	75	1.17
Fe(NO ₃) ₃	0.59	66.6	1.90
NaNO ₃	0.52	58.3	2.09

TABLE 9 : Effect of calcium nitrate additive concentration on the leaching efficiency of lanthanides from Abu-Tartur PR

Ca(NO ₃) ₂ concentration, M	Ln		F ⁻ , g l ⁻¹
	Conc., g l ⁻¹	Leaching efficiency, %	
0.1	0.59	66.6	1.90
0.2	0.62	69.4	2.09
0.3	0.69	77.7	1.52
0.4	0.75	83.3	0.95
0.5	0.85	94.4	0.19
0.6	0.85	94.4	0.19

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the suitable $\text{Ca}(\text{NO}_3)_2$ concentration that would be added to realize the highest removal of F from solution. Thus, the studied concentration was varied from as low as only 0.1 M to 0.6 M and it was found that 0.5 M has been the best value to be added and after which no further improvement was obtained (TABLE 9).

From the above studied leaching factors of the working Abu-Tartur sample, it can be concluded that the optimum leaching conditions for dissolving 94.4% of its lanthanides content would be summarized as follows:

- i- Nitric acid concentration : 8 M.
- ii- solid-to-liquid ratio
(PR wt. /nitric acid vol) : 1/2.
- iii- Agitation time : 30 minutes.
- iv- Temperature : $(22 \pm 1^\circ\text{C})$.
- v- $\text{Ca}(\text{NO}_3)_2$: 0.5 M.

Ion exchange recovery of lanthanides

For the recovery of lanthanides from Abu-Tartur PR nitric acid leach liquor, a proper 1 liter leach liquor was prepared from 0.5 Kg of the PR using the above mentioned determined optimum leaching conditions. Chemical analysis of the leached lanthanides in this liquor was found to assay 0.85 gl^{-1} . For this purpose, the cation exchange resin Dowex 50W-X8 was used where a 15 ml wsr volume was packed in 1.5 cm diameter glass column. The theoretical capacity of the working resin is equivalent to 1.7 meq / ml.

Lanthanides adsorption

The prepared 1 liter of phosphoric acid assaying 0.85 gl^{-1} lanthanides was then subjected to adsorption by the working prepared resin bed using a contact time of about 10 min equivalent to a flow rate of about 0.5 ml / min. The effluent was col-

TABLE 10 : Assay of lanthanides in the effluent of the working Dowex 50W-X8 cation exchange resin column

Effluent sample no. (50 ml)	Effluent lanthanides, conc., gl^{-1}	Lanthanides adsorption efficiency, %
1-10	Nil	100
11	0.26	69.04
12	0.35	57.1
13	0.48	42.8
14	0.61	28.2
15	0.64	23.8
16	0.70	16.6
17	0.77	9.5
18	0.79	7.1
19	0.80	4.7
20	0.81	2.3

Total adsorbed lanthanides $\approx 0.53 \text{ g}$

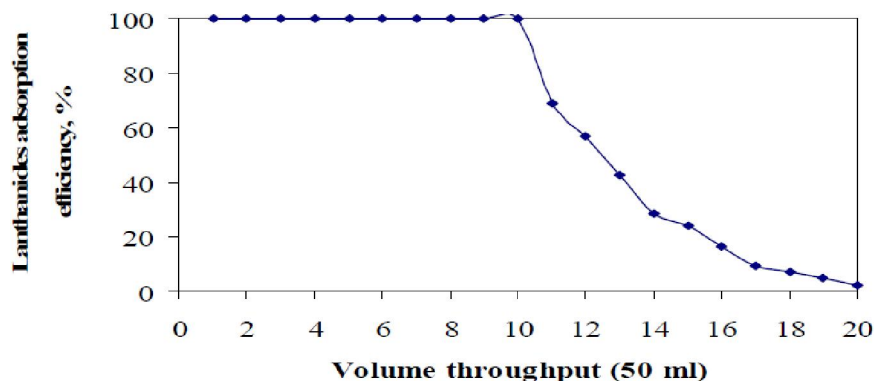


Figure 2 : Adsorption curve of lanthanides effluent from Abu-Tartur PR nitric acid leach liquor using Dowex 50 W-X8 cation exchange resin

TABLE 11 : Assay of Ln in the eluate samples obtained by 4 M HCl elution of the working loaded resin column

Eluate sample no. (10 ml)	Lanthanides conc. gl^{-1}
1	2.65
2	3.15
3	3.87
4	5.58
5	16.31
6	5.21
7	4.48
8	3.42
9	3.07
10	2.23

Total eluted lanthanides $\approx 0.50 \text{ g}$

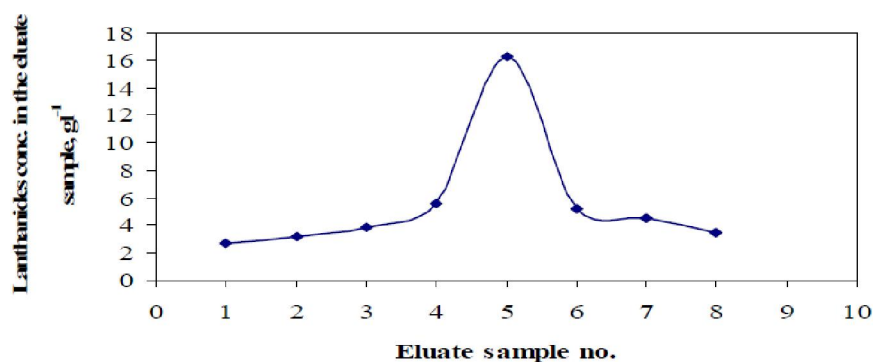


Figure 3 : Lanthanides elution curve using 4 M HCl of loaded Dowex-50 W-X8 cation exchange resin

TABLE 12 : Analytical results of individual Ln_2O_3 in their product obtained from Abu-Tartur PR

Ln_2O_3	Wt, %
La_2O_3	19.80
Ce_2O_3	38.76
Pr_2O_3	5.00
Nd_2O_3	18.60
Sm_2O_3	4.70
Eu_2O_3	0.90
Gd_2O_3	u.d
Tb_2O_3	0.35
Dy_2O_3	1.08
Ho_2O_3	u.d
Er_2O_3	u.d
Tm_2O_3	u.d
Yb_2O_3	u.d
Lu_2O_3	u.d
Y_2O_3	2.20
Total	91.39

lected every 50 ml and analyzed for its lanthanides content and the obtained results are shown in TABLE 10 and plotted in Figure (2).

Proper calculation of the adsorbed Ln content was found to attain 0.53 g/ 15 ml wsr of Dowex 50W-X8 indicating that the realized capacity

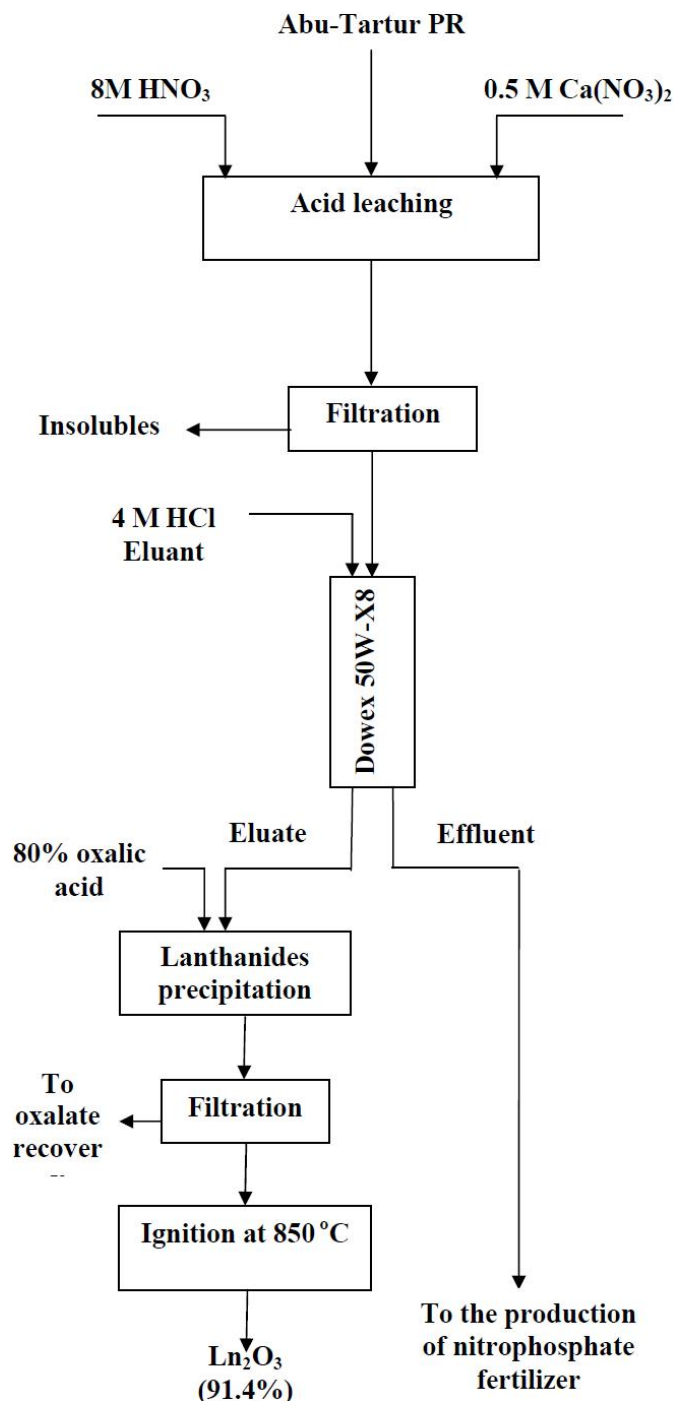


Figure 4 : Schematic flowsheet for the recovery of lanthanides from Abu-Tartur PR via its leaching with mixed HNO_3 - $\text{Ca}(\text{NO}_3)_2$

amounted to 35.3 g Ln/l of the working wsr. Assuming an average molecular weight of the LREEs of about 150, the approximately calculated theoretical capacity of the working resin for Ln would attain 85g l^{-1} wsr. However, the attained practical (saturation) capacity of the Ln from the nitrophosphoric acid attained 41.5% of the former. This is most prob-

ably due to the high acidity of the working Abu-Tartur phosphoric acid besides its high Ca content.

Lanthanides elution

Before lanthanides elution using 4 M HCl at a contact time of 10 min, the loaded resin column was first washed with 2 M HCl to remove any adsorbed possible impurities. From the obtained elution data

shown in TABLE 11 for the obtained eluate sample (10 ml each), the elution curve was plotted (Figure 3). The latter exhibits the famous bell-shaped with a major peak at the 5th throughput sample, which assayed up to about 16.3 g Ln l. Proper calculation of the Ln content in the eluate samples has indicated elution efficiency of 94.3% where a total of 0.50 g Ln has been collected.

Preparation of Ln₂O₃ Product

The obtained eluate samples in the form of lanthanides chloride were collected and subjected to precipitation by oxalic acid followed by filtration and proper washing. The washed precipitate was ignited at 850°C to obtain Ln₂O₃. The latter was then analyzed by ICP-AES and from the obtained results shown in TABLE 12, it is clearly evident that a purity exceeding 91% has been realized. On the other hand, it is interesting to compare the obtained content of the individual lanthanides with their input values in the working Abu-Tartur PR.

Finally, all the results concerning, the studied procedure of Ln recovery from Abu-Tartur PR using nitric acid are schematically represented in the overall flowsheet shown in Figure (4).

CONCLUSION

An alternative procedure for the recovery of the lanthanides content from Abu-Tartur PR assaying 0.18% has successfully been applied. In this procedure, a leaching efficiency exceeding 94% for the Ln has been achieved using 8M HNO₃ mixed with 0.5M Ca(NO₃)₂ to ensure precipitation of the remaining fluoride ion species. The relevant leaching factors have been properly optimized. Also, it has been possible to recover the leached Ln from the obtained nitro phosphate liquor with Dowex-50W-X8 cation exchange resin. The obtained Ln₂O₃ product was found to attain a purity of about 91.4% and where the first 4 LREEs attain 82.2% besides 2.2% Y₂O₃.

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