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Recovery of Lanthanides Cake from Industrial Phosphogypsum Waste

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Abstract
Phosphogypsum (PG), a residue of the phosphate fertilizer industry that has relatively harmful concentrations of rare earth elements (as lanthanides) is accumulated in large stockpiles and occupies vast areas of land. The present work was oriented to decrease the concentration of lanthanides by leaching of PG using the synergism of methyl iso-butyl ketone (MIBK) and Tri-octyl amine (TOA) in kerosene modified by 1-octanol. The factors which affect the leaching process such as agitation time, concentration of the solvent, liquid/solid ratio, and temperature were optimized. Based on the experimental results, about 92.1% of lanthanides were successfully transferred from the PG into the solvent phase. Nitric acid has been used to strip the lanthanides from the organic solvent. The precipitation of 93.4% of lanthanides was carried out using oxalic acid under the desirable conditions. A decontaminated product that can be safely used in many industrial applications was obtained.

1. Introduction

Industrially, phosphoric acid is mostly produced from phosphate ores in the so-called, wet process. Phosphogypsum (PG) is a by-product in the manufacture of phosphoric acid by acidulation of phosphate rock with 70 % sulfuric acid as in the following reaction [1,2]:

$$Ca_{10}(PO_4)_6.F_2.CaCO_3 + 11H_2SO_4 \rightarrow 6H_3PO_4 + 11CaSO_4 + 2HF + H_2O + CO_2$$

The amount of PG exceeds the mass of the product, because this amount was produced in the ranges from 4.5 to 5.5 tons per ton P_2O_5 in terms of dry matter depending on the method of production. This PG is mostly disposed off without any treatment, which represents serious disposal problems with the phosphoric acid production unit. PG is considered as a source of lanthanides elements [3,4]. During the wet-process phosphoric acid, the main part of lanthanides (80-85%) passes to the phase of dihydrate $CaSO_4.2H_2O$. Generally, in natural apatite Ca^{2+} is often substituted by REE^{3+} and charge compensation is done by (a) intrinsic electron defects, (b) depletion of the constituent ions, and (c) a coupled substitution of the constituent ions by REE^{3+} [5,6,7]. In spite of the fact that phosphate rocks are considered as a poor source of uranium and lanthanides, attention has been directed to phosphate deposits as a potential source of these elements. In refining, it is necessary therefore to treat the phosphate ores to separate or dissociate free lanthanides compound from its other components. This separation or dissociation step has therefore been carried out purely chemically. Thus, phosphates have been treated with sulfuric acid, nitric acid and hydrochloric acid to yield the lanthanides [2].

Arocena et al. (1995) found that, the enrichment of traces and lanthanides was in the fine size fraction (< 20μm) compared to bulk PG, the coarse and medium size fractions, and compared to soil and shale [8]. El-Didamony et al. (2013) studied the leaching of PG waste (produced from the El-Sebaiya & Abu-Tartur region) from radionuclides (^{226}Ra, ^{210}Pb, ^{238}U, and ^{40}K) and ∑REE using suitable organic extractants such as tribuytl phosphate, trioctyl phosphine oxide, triphenyl phosphine oxide, and diethyl hexyl phosphoric acid dissolved in kerosene. The results show that, the leaching of PG using organic extractants enhances the removal efficiency of the studied radionuclides and ∑REE in appreciable way [9, 10, 11].

Ali and Mohammed (1999) studied a process for the treatment of Abu-Tartur phosphate rock using HNO_3. The results show an assessment of complete dissolution of the lanthanides occurs in the phosphoric acid produced by H_2SO_4. A significant benefit of Abu-Tartur phosphate rock processes lies in their relatively high content of lanthanides (averaging 1200 ppm), while the produced fertilizer would pollute the environment less with radioactive materials due to the low uranium content (averaging 25 ppm) [12]. Pessac et al. (1987) mentioned that during the acidulation of the phosphate rock, the leaching efficiency of REEs was increased to 56% by introducing aluminum and/or iron and/or silica minerals into the slurry. However, this may lead to difficulties in subsequent stages of phosphoric acid production [13].

The rare earth-metals group comprises the lanthanides elements (from lanthanum to lutetium) plus lanthanum, yttrium and scandium. They are essential in many and relevant applications in chemical, metallurgical, optical, electronic and ceramic products [14]. The application of lanthanides in geochemistry has been widely used to investigate petrogenetic problems of igneous and metamorphic rocks. One of the important effects of lanthanides on the corrosion resistance of Mg is the so-called “scavenger effect”, i.e., some impurity elements in Mg, such as Fe, severely deteriorates its corrosion resistance [15].

The main objective of the present work is oriented to study the leaching and recovering of lanthanides from a by-product PG, after the production of phosphoric acid in the Abu-Zaabal Company for fertilizers and Chemicals, using adequate leaching agents. The leaching processes were performed using the synergism of MIBK and TOA in kerosene modified by long chain alcohol. The factors affect the leaching operation such as: contact time, liquid/solid ratio, temperature, and concentration of the leaching agents were optimized. The stripping of lanthanides from the solvent as well as the precipitation from the aqueous solution was carried out. The obtained product was subject to analyses.

2. Experimental

2.1. Materials and Apparatus

The PG (of density 2.48 g/cm^3) was received from the Abu-Zaabal Company for fertilizers and Chemicals, Egypt. It was first washed with hot distilled water to remove excess H_3PO_4 and left to be air dried. Tri-octyl amie (TOA), methyl iso-butyl ketone (MIBK), kerosene, and 1-octanol were obtained from El-Nasr Chemicals Company, Egypt. Metertech UV/VIS SP8001 Spectrophotometer, China, was used for measuring the concentrations of major oxides and lanthanides [16]. Inolab pH meter, Germany, was used for pH determination. Sherwood flame-photometer 410, England was used for Na and K analysis. ICP-AES spectrometry was used for measuring the concentration of individual lanthanides [17].

2.2. Analysis of the Phosphogypsum

The chemical analysis of major and trace contents in the PG provided from the Abu-Zaabal Company for fertilizers and Chemicals is presented in Table 1.

Table 1. *Chemical analysis of phosphogypsum (PG) sample.*

Components	Concentration	Components	Concentration
(wt, %)			
CaO	27.3	Na_2O	0.09
SO_3	32.5	K_2O	0.04
SiO_2	8.82	TiO_2	0.30
P_2O_5	2.01	Fe_2O_3	4.50
F	1.14	Ignition Loss	22.1
(wt, ppm)			
Lanthanides	1470	Uranium	21.0

Morphologically, PG is yellowish brown color and relatively soft grains [18]. Chemically, the received PG mainly contains about 81.9% as a $CaSO_4.2H_2O$, (32.5%, SO_3, 27.3% CaO, and 22.1% ignition loss) with some impurities of SiO_2, Fe_2O_3, and P_2O_5 as well as traces of Na_2O, K_2O, TiO_2, U, and F. It has considerable concentration (1470 ppm) of rare earth elements as lanthanides.

2.3. Pretreatment of PG

Since water exists in PG in both a combined and a free form, consideration must be given to the methodology of drying of these types of water before analysis. Free water is difficult to be removed completely by air drying samples at room temperature because the samples are influenced by humidity. Sample of PG was washed with hot distilled water, after dryness and grinding, the bulk sample was carefully quartered into different homogenous smaller samples for chemical and radiometric analysis as well as work's experiments. One kg of the bulk PG was fractionated into six homogeneous fractions with different particle sizes ranging from 37 to 250 µm to show the effect of particle size on the distribution of lanthanides in these fractions. The enrichment factor (En) was calculated as a ratio of particular lanthanides content in a certain fraction to its content in the bulk PG:

$$En = A_n / A$$

Where A_n is the concentration of lanthanides (ppm) in the given fraction (n), and A is its concentration (ppm) in the bulk. The portions were prepared for chemical analysis and the results were shown in Fig 1.

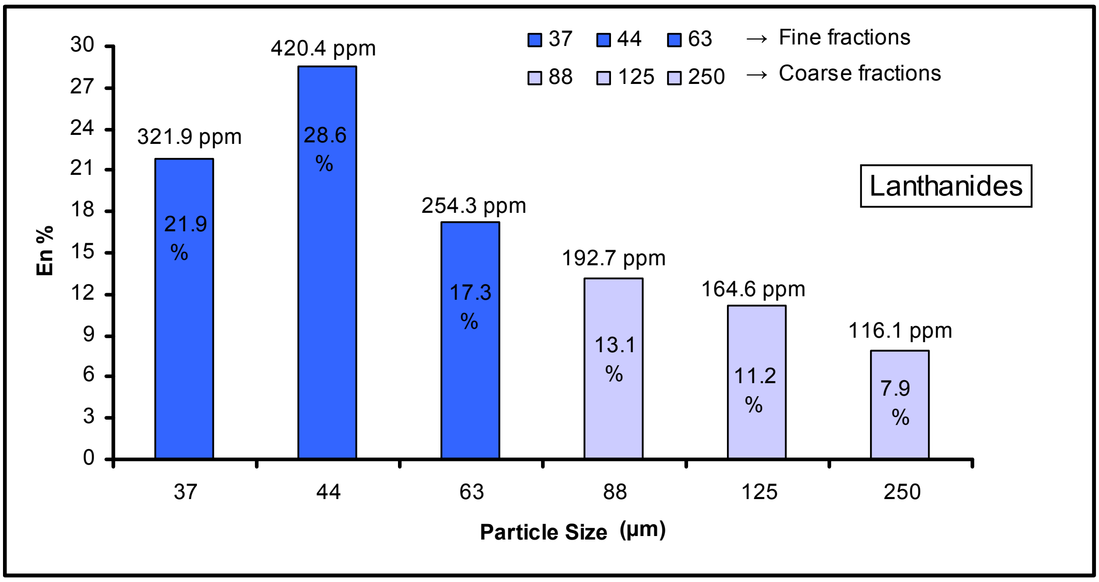

Fig. 1. *Effect of particle size fractionation on the distribution of lanthanides in PG.*

The results indicate that most lanthanides are enriched in the fines particle sizes of PG comparable to that found in the bulk of phosphogypsum sample. The distribution of lanthanides content into the different portions was determined in which about 32.2% of lanthanides were incorporated into coarse portion (88-250μm). On the other hand, about 67.8% were captured into the fine portion (37-63μm). The distribution of lanthanides decreases with particle size greater than 63μm. Therefore, for the extraction of lanthanides from PG waste, the particle size of PG should be < 44μm in which 742.3 ppm of lanthanides were concentrated. It is clear that, the fractionation process can be considered as a physical separation of the lanthanides in the PG sample.

The results for distribution of lanthanides under fractionation of PG into fine size are considered as positive results in comparison with those reported by Arocena et al (1995) [8].

2.4. Analytical Procedure

In general, leaching is the process in which inorganic, organic contaminants are extracted and released from the solid phase into the liquid phase under the influence of mineral dissolution [19, 20, 21].

In different 250 ml measuring beakers, a known amount of PG was taken, with the addition of certain volume of organic extractants at room temperature and mixed thoroughly for a predetermined period. The factors affect the desired leaching materials (such as contact time, concentration of solvent, liquid/solid ratio, and temperature) were optimized. For the analysis of the lanthanides, the concentration of initial sample was measured (C_o) before leaching. After each leaching process, the solution was separated by centrifugation from the solid. The residue was washed with hot distilled water, dried, and analyzed for lanthanides contents. The removal efficiency percent (E%) can be calculated as follow:

$$\text{Removal efficiency (E) \%} = [(C_o - C_f)/C_o] \text{ X } 100$$

Where, C_o is the initial concentration of the received PG and C_f is the concentration of treated PG. The removal efficiency (E) was expressed as leaching percent (%) of waste materials.

Total rare earth elements (as lanthanides) were determined by Arsenazo-III method [16]. In weakly acidic solution, the reagent was violet, whereas their complex with the rare earth elements was green. To the acidic sample solution (pH ≈ 1) 1 ml of 1% ascorbic acid solution was added. After few minutes, 1 ml of the format buffer and 2 ml of Arsenazo-III solution were added. The solution was diluted with distilled water to ≈ 20 ml and the pH was adjusted to ≈ 2.6. The solution was transferred and diluted with water in 25 ml standard flask. The absorbance was measured at 650 nm against reagent blank solution.

3. Results and Discussion

The leaching of lanthanides from PG is essentially important in many industries. The E% depends on many factors such as type of leaching materials and conditions at which the process was carried out.

3.1. Effect of Leaching Materials

A series of experiments were carried out using trioctyl amine (TOA) and/or methyl isobutyl ketone (MIBK) in kerosene. In one experiment, MIBK or TOA was added alone in kerosene. In the other experiments both of them were added together to show the effect of synergism, Fig. 2. The results show that, the synergism of both organic extractant gives the highest E% of 20.6%.

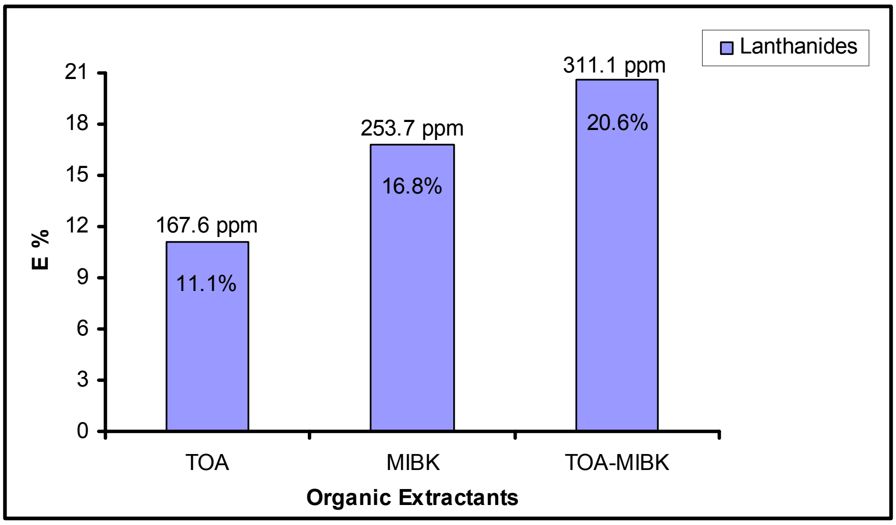

Fig. 2. *Effect of types of organic extractant on leaching process.*

During contacting different concentrations of TOA and/or MIBK with PG a "third phase" of an insoluble viscous brown-reddish was formed. Several experimental conditions such as aqueous acidity, extracted metal, diluents and extractant structure can affect the formed third phase. This phenomenon is more important for extraction systems containing extractants of amine type and solvents with low polarity and leads to the increase of separation duration simultaneously with the diminution of its efficiency. The formation of the third phase can be avoided by addition of a "phase modifier" in the organic solvent [22].

Generally, this compound should be an alcohol with an aliphatic chain of at least 8 carbon atoms and modifies the polarity of the solvent, promoting the breakage of the stable emulsion and solubilization of its content. Adding a modifier (a long chain alcohol) to the organic phase is the most common method of preventing third phase formation. Tests were carried out to determine the best modifier and its volume of those needed in the organic phase as shown in Fig. 3:

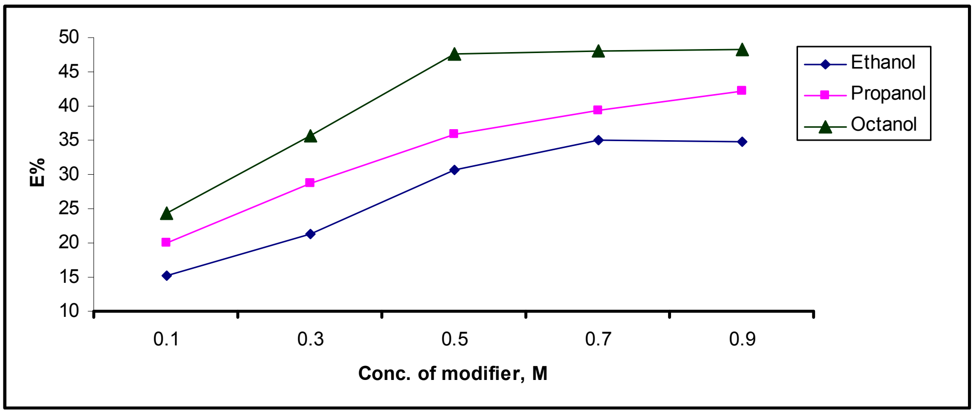

Fig. 3. *Effect of addition of modifier on leaching of lanthanides from PG using TOA-MIBK.*

From Fig. 3, the concentration of 0.5 M 1-octanol gives higher E% of lanthanides, than the other modifiers, which equals 47.6% (about 718.8 ppm), and then a slight increase was occurred after this value. The addition of 1-octanol induced the increase of the extraction efficiency, the most important influence being recorded for the solvent with lower polarity. Moreover, the volumetric fraction of alcohol controls the number of extractant molecules participating in the interfacial product formation [11].

So the synergism of TOA-MIBK in kerosene modified by 0.5M 1-octanol was choice for leaching of lanthanides from PG waste.

3.2. Synergistic Leaching of PG with TOA-MIBK

Methyl iso-butyl ketone (MIBK) is a major extractant and modifier with many applications in hydrometallurgy. The addition of TOA to MIBK in kerosene can improve the removal efficiency and the mass transfer of leaching process. The factors affect the synergism of TOA-MIBK such as: contact time, concentration of leaching materials, liquid/solid ratio and temperature were optimized as the following:

3.2.1. Effect of Agitation Time

The effect of agitation time on the leaching of lanthanides from PG using TOA-MIBK in kerosene with 0.5M 1-octanol was investigated. The reaction was carried out at room temperature by the addition of equal ratio of (0.1M) TOA-MIBK in modified kerosene & PG in time ranged from 15 up to 75 min. The results were illustrated by Fig. 4.

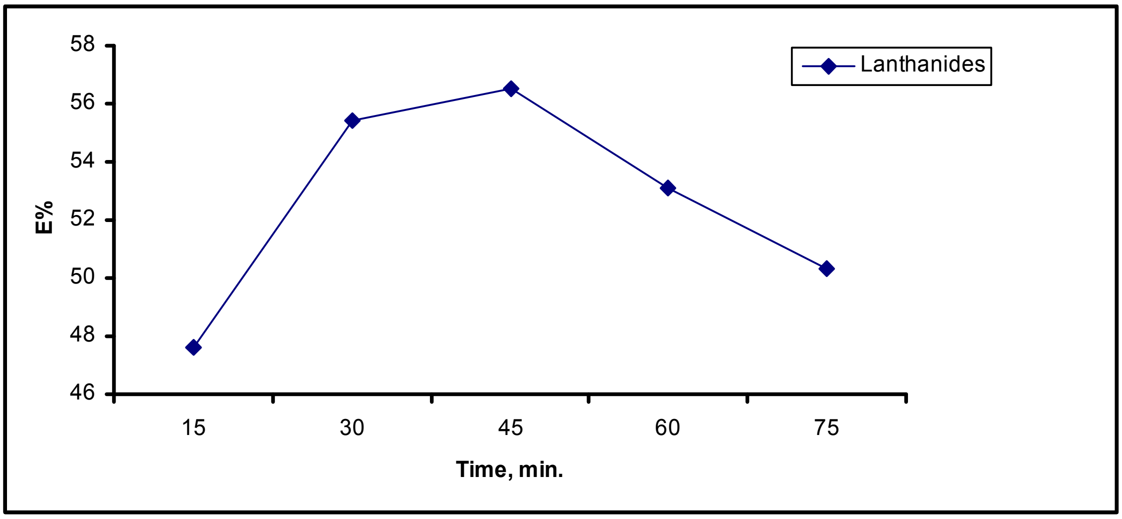

Fig. 4. Effect of agitation time on leaching of lanthanides from PG.

The removal efficiency E% increases by the time up to 30 min. with slightly increase up to 45 min. then decreases gradually to reach the minimum values at 75 min. At the agitation for 30 min. the E% of lanthanides equals 55.4% respectively. In general, for leaching process, the extracted solid matter must be prepared in the way that the extracted substance can be solved (by the solvent) in short time; this was achieved by grinding the PG to a fine particle size. After grinding, the capillary ways in PG become short so that only a short distance has to be overcome by diffusion and a direct contact of solvent and extracted substance becomes possible in an appreciable time [11, 21]. Therefore, the desired time for leaching process depends upon the particle size at which the extracted material was milled and fractionated (< 44μm).

For leaching of lanthanides from PG waste using mixed solution of TOA-MIBK in 0.5M 1-octanol with kerosene, the agitation time for 30 min. was considered as a sufficient time to reach the maximum values of the removal efficiency.

3.2.2. Effect of TOA-MIBK Concentration

At room temperature the PG samples were agitated under equal L/S ratio for 30 min. using different concentrations of modified organic extractant (ranged from 0.05 to 1M). The effect of mole ratio on the E% can be divided into three parts of: equal, low-high, or high-low TOA-MIBK mole ratio. The relation between the E% and the different concentrations of solvents was shown in Fig. 5.

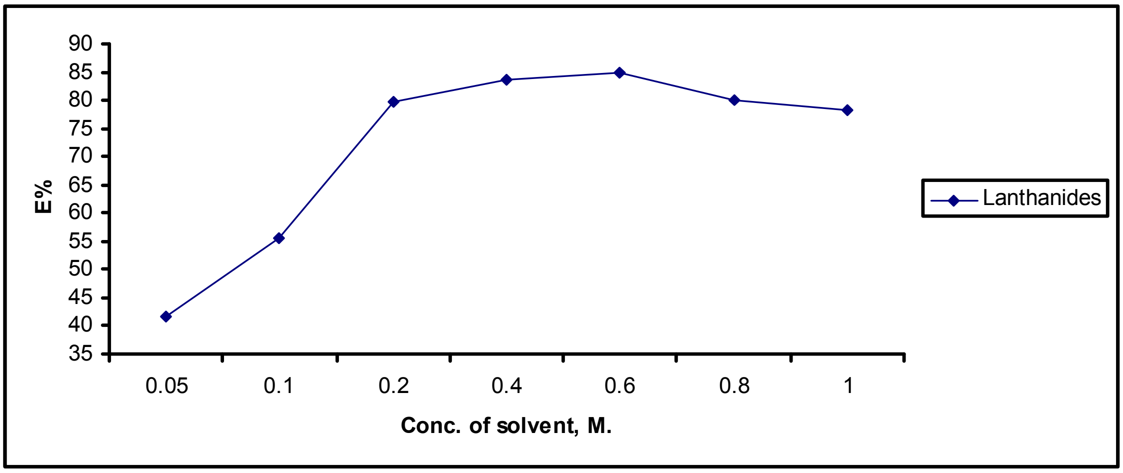

Fig. 5. Effect of concentration of TOA-MIBK on leaching process.

For equal concentration of TOA-MBK, the results indicate that, the leachability percent (E%) increases with concentration from 0.2M up to 0.6M then decreases slightly after this value. For the E% the highest values occur at concentration 0.6M which equal 85%. Based on the above data, the best removal efficiency concentrates between 0.2M and 0.6M of TOA-MIBK in kerosene with 0.5M 1-octanol. The effect of different mole ratio of TOA-MIBK for leaching of lanthanides was studied. The concentrations of 0.2M up to 0.6M for both TOA and MIBK were used in exchangeable way to determine the maximum removal efficiency of lanthanides. The relation between leachability percent and different molar ratios of TOA-MIBK is diagrammatically plotted in Fig. 6.

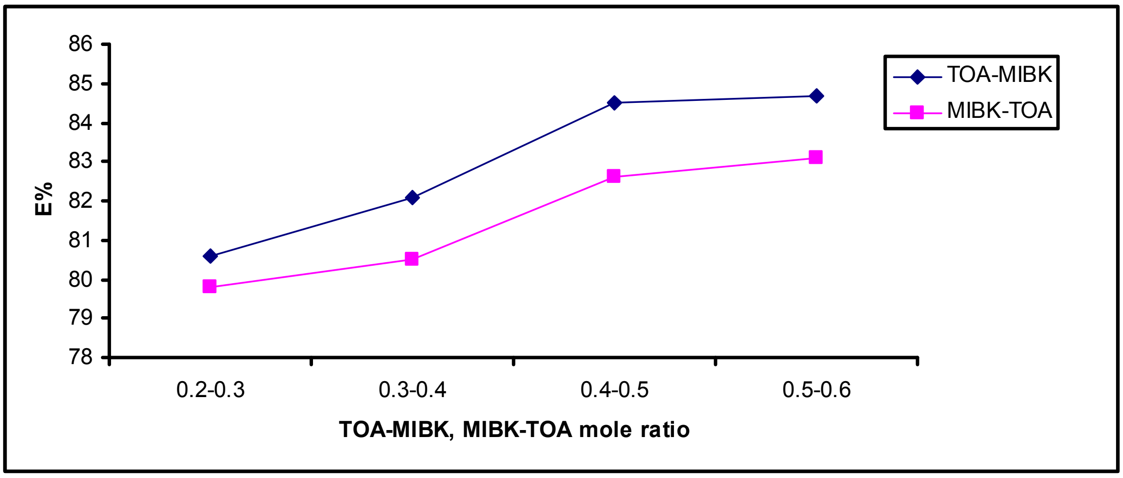

Fig. 6. *Effect of TOA-MIBK molar ratio in kerosene on leaching process.*

The increase in the concentration of MIBK than that of TOA (0.2-0.3, 0.3-0.4, 0.4-0.5M, and 0.5-0.6) was accompanied by increase in the E% of lanthanides that reaches the maximum values of 84.5% at 0.4-0.5M. On the other hand, by increasing the concentration of TOA than that of MIBK (0.3-0.2, 0.4-0.3, 0.5-0.4, and 0.6-0.5), the E% for lanthanides shows a slightly increase and reaches the maximum values of 83.1% at 0.6-0.5 M.

Using the synergism of TOA-MIBK in modified kerosene for leaching of lanthanides from PG waste the concentration should be 0.4-0.5 M.

3.2.3. Effect of Liquid/Solid Ratio (L/S)

The volumes of TOA-MIBK solution (0.4-0.5M) in the modified kerosene range from 50-300 ml (which corresponding to 0.5:1 up to 3:1 liquid/solid ratio) were agitated with 100 g of PG samples at room temperature for 30 min. The values of removal efficiency E% of lanthanides were shown in Fig. 7.

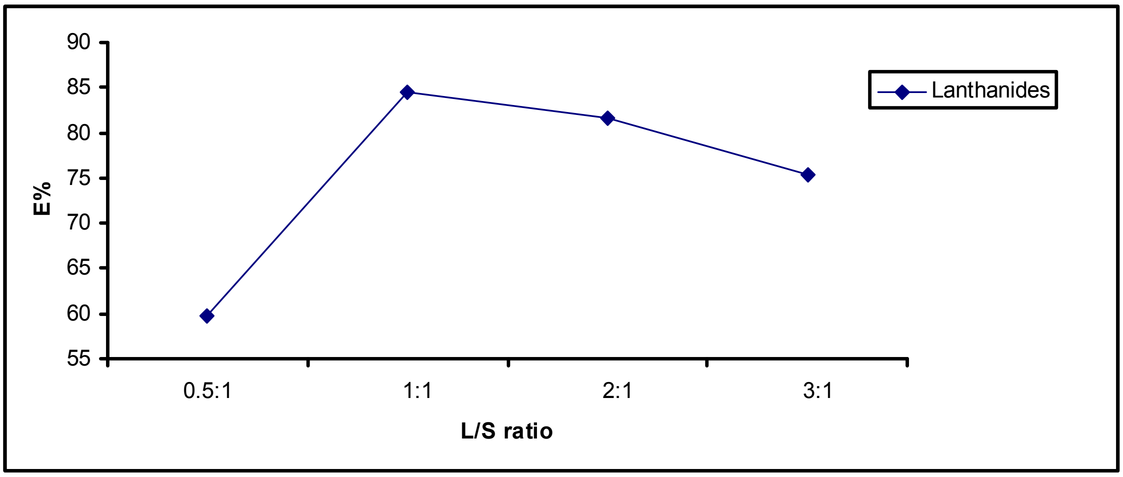

Fig. 7. *Effect of liquid/solid ratio on leaching of lanthanides from PG.*

The data show that there is a general increase in the E% of lanthanides till L/S ratio equal 1. After this ratio the effect of L/S on the leaching process was reversible, i.e. by increasing L/S ratio gradually, the leachability decreases. This behavior indicates that the leaching was affected by the viscosity of the solvent as the low viscosity leads to low pressure drop and good mass transfer [19,21].

It is observed that, equal liquid/solid ratio improves the leaching percent of lanthanides to reach the highest values of 84.5 %.

3.2.4. Effect of Reaction Temperature

The effect of reaction temperature on the leaching process was studied. About 100 g of PG (particle size < 44μm) were agitated with 100 ml of TOA-MIBK in modified kerosene (0.4-0.5 M) for 30 min. at temperature ranged from 30 to 60°C. The relation between temperature and leachability of lanthanides & from PG is plotted in Fig. 8.

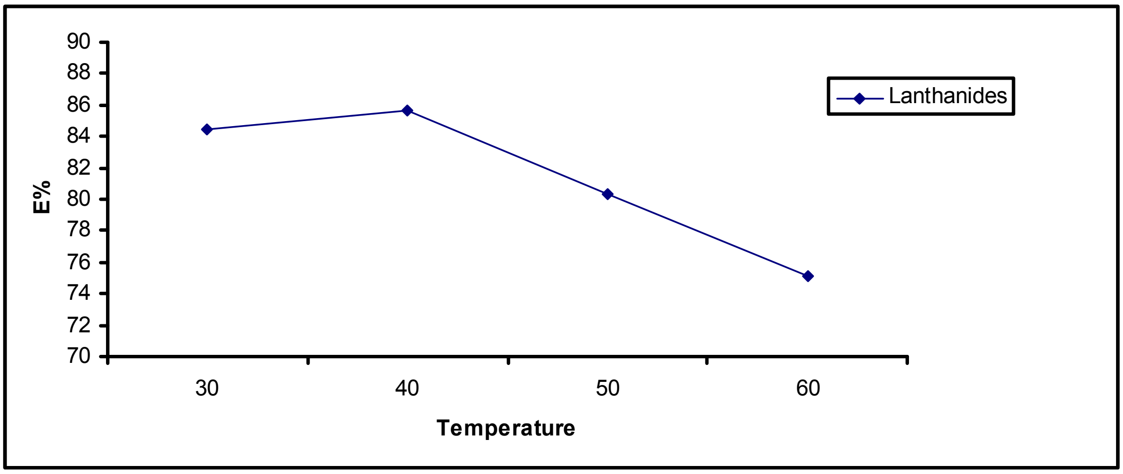

Fig. 8. *Effect of temperature on leaching process by TOA-MIBK in kerosene.*

The results indicate that a remarkable increase in the removal efficiency (E%) occurs at 40°C. By increasing the temperature, the E% decreases as the concentration and viscosity of TOA-MIBK were increased. Thus, 30°C is the applicable temperature required to give the maximum removal efficiency of lanthanides from PG samples which equals 84.5%.

Based on the above results, the high temperature has unappreciable effect on the leachability of lanthanides as the solvent has been concentrated [19,21].

3.2.5. Choice of the Optimum Conditions

The optimum conditions required for the leaching of lanthanides from homogenous PG (<44μm), using TOA-MIBK in kerosene with 1-octanol, were summarized as follows:

01- Agitation time equals 30 minutes.
02- Concentration of TOA-MIBK: 0.4-0.5 M
03- Concentration of 1-octanol: 0.5M.
04- Liquid: solid ratio equals (1:1) (volume of solvent per weight of PG).
05- Reaction temperature of 30^{o}C.

3.3. Successive Leaching Processes

The leaching operation of lanthanides from the PG (particle size <44μm) using modified TOA-MIBK in kerosene, was carried out three times under the previously optimum experimental conditions. The results are graphically represented in Fig. 9.

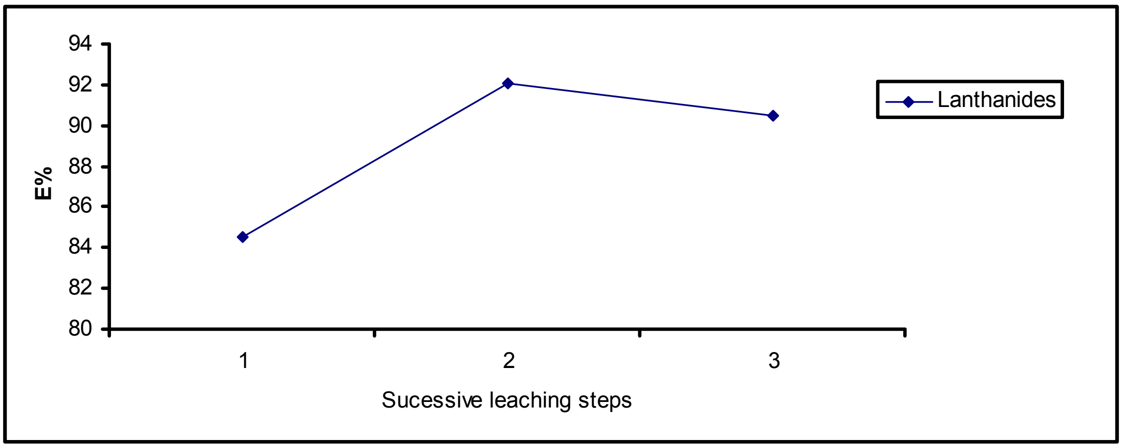

Fig. 9. *Effect of Successive leaching steps by TOA-MIBK in kerosene.*

The results indicate that, the E% of lanthanides increases after the second successive step which becomes 92.1%, while in the third leaching process, the E% was decreased to become 90.5% [11, 21].

3.4. Analysis of the Product

After the separation of leaching products by centrifugation, the treated PG was filtered, washed, and dried. Chemicals analysis of the lanthanides in phosphogypsum before and after leaching processes measured by ICP-AES apparatus is given in Table 2.

Table 2. *Chemical analysis of lanthanides in the PG (initial and treated) samples (ppm) measured by ICP-AES apparatus*.*

Elements	Initial	Treated	E%
La	174.5	9.60	94.5
Ce	367	17.8	95.1
Pr	96.0	9.40	90.2
Nd	265.5	12.9	95.1
Sm	57.0	8.60	84.9
Eu	10.2	2.40	76.4
Gd	61.6	7.60	87.7
Tb	8.50	3.50	58.8
Dy	42.2	7.90	81.3
Ho	6.70	1.40	79.1
Er	22.8	3.70	83.7
Yb	26.4	6.30	76.1
Lu	2.60	0.10	96.2
Y	329	24.9	92.4
Σ Lanthanides	1470	116.1	92.1

*All ICP-AES analysis was carried out in hot laboratories center in the Egyptian Atomic Energy Authority

From Table 2, the initial PG sample contains a higher concentrations of Ce, Y, Nd, and La of about 367, 329, 265.5, and 174.5 ppm respectively, than the other components of lanthanides. The treated PG contains lanthanides of 109.6 ppm which corresponding to remove about 92.1% of theses materials from the origin concentration.

3.5. Stripping Processes

The stripping investigations were carried out to choose the best conditions that can successfully strip the lanthanides elements from the organic solution. The factors affect the stripping process such as: type of acid, shaking time and organic to aqueous phase ratio were studied. Habashi [23] studied the stripping of lanthanides from organic extractants using different acids and alkalis. The results showed that stripping by acidic solutions was always higher than any alkaline solutions.

3.5.1. Effect of Acid Solution

The effect of type of acid on the stripping of lanthanides from TOA-MIBK solution was investigated using different concentrations of H_2SO_4, HCl, and HNO_3 ranged from 0.02 to 0.1M. The process was performed at room temperature for 15 min using equal organic: aqueous phase ratio, Fig. 10.

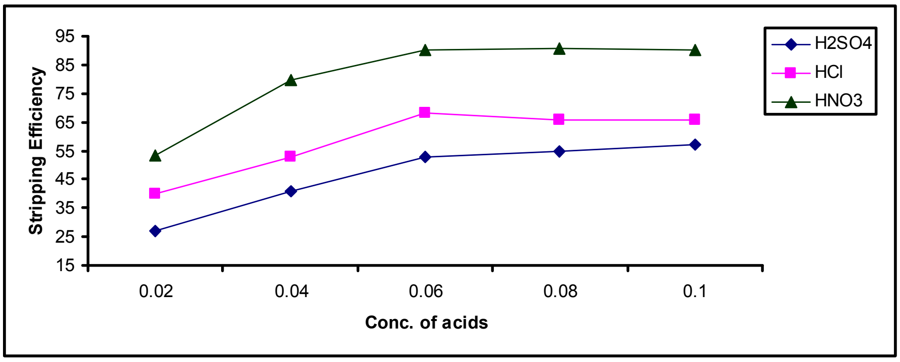

Fig. 10. *The effect of type and concentrations of acid on the stripping of lanthanides.*

The results show that, the stripping efficiency reaches the maximum values of 90.6, 68, and 57% at concentration of 0.06M HNO_3, 0.06M HCl, and 0.1 H_2SO_4 respectively. This indicates that the stripping process was enhanced by using HNO_3 solution.

3.5.2. Effect of Shaking Time

The effect of shaking time on the stripping of lanthanides from TOA-MIBK solution was investigated using 0.06M HNO_3. The process was performed using equal organic: aqueous phase ratio at room temperature, while the shaking time was ranged from 5 to 20 min.

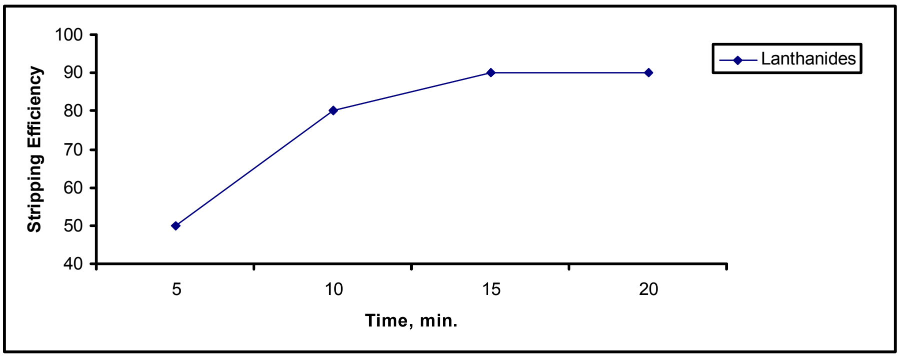

Fig. 11. *Effect of shaking time on the stripping of lanthanides from organic phase.*

The results in Fig. 11 indicate that, the stripping efficiency slightly increases from 5 to 15 min. and then remains constant at 20 min. This indicates that the process is rapid, i.e. is not a diffusion controlled process [26]. At 15 min. the stripping percent of lanthanides equals 90%.

3.5.3. Effect of Organic/Aqueous Ratio (O/A)

The effect of organic/aqueous phase ratio has been studied using 0.06M HNO_3 at room temperature. The shaking time was 15 min., while organic/aqueous phase ratio was varied from 1/1 to 4/1, Fig. 12.

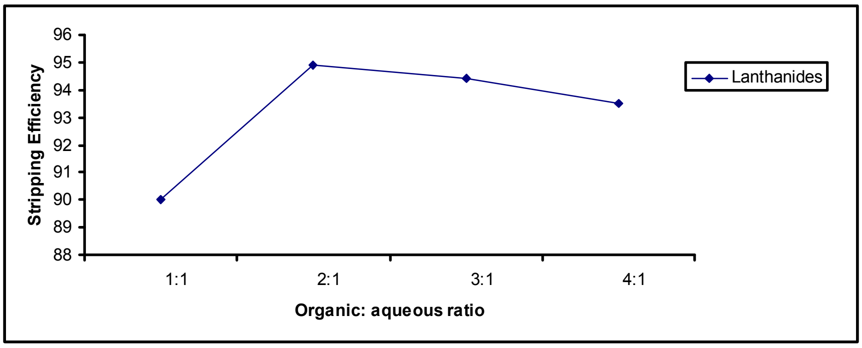

Fig. 12. *Effect of organic: aqueous ratio on the stripping of lanthanides.*

By increasing organic/aqueous ratio, the stripping efficiency was slightly increased and reached a maximum at 2:1 which corresponding to stripping 94.9% of lanthanides. Further increase in organic/aqueous ratio was associated with a very slight increase in stripping percent. Accordingly, 2:1 organic/aqueous phase ratio is recommended for stripping when using HNO_3 solution.

For the stripping of lanthanides from TOA-MIBK in modified kerosene, the process should be performed using 2:1 phase ratio of 0.06M HNO_3 at room temperature for 15 min. shaking time.

3.6. Precipitation of Rare Earth Elements

In the bench-scale work, the mixed lanthanides were precipitated from the strip liquors by the addition of 50% excess of crystalline oxalic acid to the mixture. The mixture was stirred for 1h then the precipitated rare earth oxalate was filtered and washed with water and dried. The oxalate was calcined in a muffle furnace at 950°C for 2 h to convert it to a mixed rare earth oxides (REO) [24,25]. The excess of oxalic acid is favorable for the elimination of, Cr (III), Ti (IV) and Fe (III) as well as Zr (IV), Al (III), Ta (V) and UO_2^{2+} [13]. The chemical analysis of composition of rare earth oxide (ΣREO) product by ICP-AES apparatus was shown in Table 3.

The mixed rare earth oxide was in the form of light brownish powder. Analysis of the rare earth oxides in about 0.25g of the product gave a ΣREO content of 93.4%. It is observed that the most important conclusion is that high recoveries are obtained for the valuable light rare earths (cerium, lanthanum, yttrium, neodymium, and praseodymium). Also, it is expected that the ΣREO product contain some impurities such as P_2O_5, CaO, MgO, Fe_2O_3 and U [24].

Generally, the lanthanides have played an important role in our lives, such as in the television industry: It has been found that if a small amount of europium oxide (Eu_2O_3) is added to yttrium oxide (Y_2O_3), it gives a brilliant-red phosphor [2]. The flow sheet for the treatment process was illustrated in the following Fig. 13.

Table 3. *Composition of the sum rare earth oxide (ΣREO) measured by ICP-AES apparatus*.*

Rare Earths Oxides	Wt (%)
La_2O_3	21.6
Ce_2O_3	39.3
Pr_2O_3	5.72
Nd_2O_3	11.5
Sm_2O_3	1.48
Eu_2O_3	0.96
Gd_2O_3	ND
Tb_2O_3	0.79
Dy_2O_3	0.47
Ho_2O_3	ND
Er_2O_3	ND
Yb_2O_3	1.18
Lu_2O_3	ND
Y_2O_3	10.4
ΣREO	93.4

*All ICP-AES analysis was carried out in hot laboratories center Egyptian Atomic Energy Authority

4. Conclusion

A successful leaching procedure of phosphogypsum, a by-product from the Abu-Zaabal Company for fertilizers and Chemicals after the wet process phosphoric acid, has been developed in the present work. This was possible through leaching of lanthanides using TOA-MIBK in kerosene. The corresponding relevant factors were studied and the conclusions can be summarized as follows:

1. Leaching of homogenous PG (< 44μm) using TOA or MIBK in kerosene gives the E% of 11.1 and 16.8% respectively. While in case of the synergism of TOA-MIBK in kerosene, the removal efficiency (E%) of lanthanides becomes 20.6%. When using (0.5M) 1-octanol as a modifier, the E% reaches the maximum value of 47.6% for the removal of lanthanides from PG.

2. The best conditions for using TOA-MIBK in the modified kerosene are; agitation time of 30 min., solvent concentration of 0.4-0.5 M, under equal liquid/solid ratio (TOA-MIBK in kerosene volume/ PG weight) at room temperature. These conditions removed 92.1% respectively of lanthanides from PG waste after two successive steps respectively.
3. The best conditions for the stripping of lanthanides using 0.06M of HNO_3 were organic: aqueous phase ratio of 2:1 for 15 minutes which leads to recover 94.9% of lanthanides from the extracted solution. For the precipitation of lanthanides as oxalate a high recovery is obtained, for the valuable light rare earths (yttrium, lanthanum, cerium, praseodymium, neodymium and samarium), which equals 93.4% of total obtained weight. Generally, lanthanides in the organic phase can be easily stripped using suitable stripper then introduced in many useful processes.
4. Use of TOA-MIBK with kerosene in the reduction of lanthanides from PG waste is found more economic to produce local material that can be used in the preparation of many industrial applications.

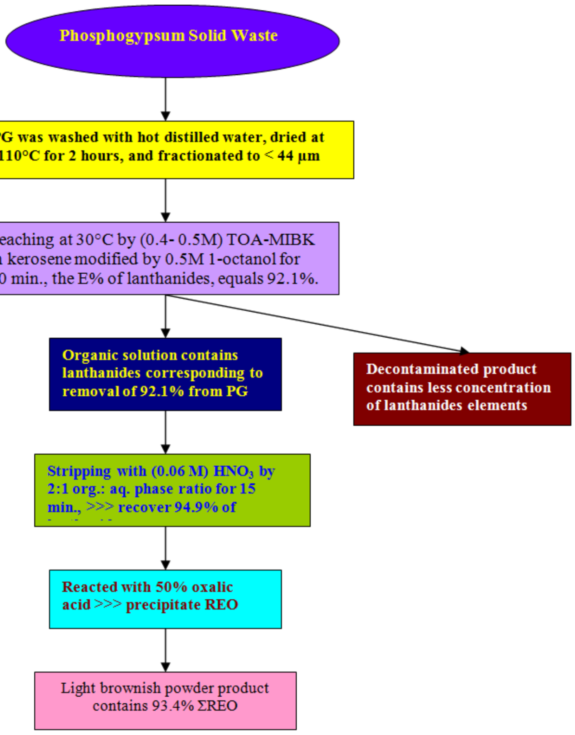

Fig. 13. *Flow sheet of PG treatment.*

The 1 ton of PG requires the following materials to be purified from lanthanides:

- 89-32L (TOA-MIBK) → as an organic extractant for leaching processes

- 1000 L Kerosene → as a diluent for the used organic extractant

- 40L 1-Octanol → as a modifier for the used solvent

- 22L HNO_3→as a for stripping of lanthanides from organic solution

The total costs for the treatment of PG wastes depending on the type and quality of the used reagents.

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References

[1] Abdel-Aal, E.A., Mahmoud, M. H., El-Shall, H., and Ismail, A. K. (2007): Increasing the filtration rate of phosphogypsum using surfactant, Hydrometallurgy, (85), 53-58.

[2] Habashi, F. (1985): The recovery of the lanthanides from phosphate rock, Journal of Chemical Technology and Biotechnol, (35), A, 5-14.

[3] Abalı, Y., Mehmet, A. Y., Sadrettin, Z. M., and Ahmet, A. K. (2007): Using phosphogypsum and boron concentrator wastes in light brick production, Construction and Building Materials., (21), 52-56.

[4] Langholtz, M., Douglas, C. R., Donald R. L., and Janaki, A. R. (2007): The economic feasibility of reclaiming phosphate mined lands with short-rotation woody crops in Florida, J. Forest Economics., (12), 237-249.

[5] Reijnders, L. (2007): Cleaner phosphogypsum, coal combustion ashes and waste incineration ashes for application in building materials: A review, Building and Environmental, (42), 1036-1042.

[6] Papastefanou, C., Stoulos S., Ioannidou A., and Manolopoulou, M. (2006): The application of phosphogypsum in agriculture and the radiological impact, J. Environ. Radioactivity, (89), 188-198.

[7] De Oliveira, S. B., da Silva, P. C., Mazzilli, B. P., Favaro, D. T., and Saueia, C. H. (2007): Rare earth elements as tracers of sediment contamination by phosphogypsum in the Santos estuary, southern Brazil, J. Applied Geochemistry, (22) 837-850.

[8] Arocena, J., Rutherford, P., Dudas, M. (1995): Heterogeneous distribution of trace elements and fluorine in phosphogypsum by-product", J. The Science of the Total Environment, (162), 149-156.

[9] El-Didamony, H., Ali, M. M., Awwad, N. S., Fawzy, M. M., and Attallah, M. F. (2013): Radiological characterization of phosphogypsum waste produced from phosphate ore processing, J. Hazardous Materials, (245), 596-602.

[10] Fawzy, M. M. (2012): Radiological characterization and treatment of phosphogypsum waste produced from phosphate ore processing, Faculty of Science, Ph.D Thesis, Zagzig University, Egypt, 250p

[11] El-Didamony, H., Ali, M. M., Awwad, N. S., Fawzy, M. M., and Attallah, M. F. (2013): Radiological characterization and treatment of Egyptian phosphogypsum, J. Radiochemistry, (Issue 4) 607-615.

[12] Aly, M. M., Mohammed, N. A. (1999): Recovery of lanthanides from Abu Tartur phosphate rock, Egypt, Hydrometallurgy, (52), 199-206.

[13] Pessac, J. F., Lambert, A. P., Tognet, J. P. (1987): Acidification, aluminum and iron compounds, U.S. Patent, 4636369A.

[14] Tanaka, K., Takahash. Y., and Shimizu, H., (2007): Determination of rare earth element in carbonates using laser-ablation inductively-coupled plasma mass spectrometry: An examination of the influence of the matrix on laser-ablation inductively-coupled plasma mass spectrometry analysis, Analytica Chimica Acta, (583), 303-309.

[15] Wang, L. M., Qin Lin, Yue, L. J., Liu L., Feng Guo, and Wang, F. M. (2007): Study of application of rare earth elements in advanced low alloy steels, J. Alloys and Compounds, (451), 1-6.

[16] Marczenko, Z. (1986): Spectrophotometric determination of elements, John Wiley and Sons, Inc., New York, USA, 708p.

[17] Zhao-Hui, W., Xiu-Ping, Y., Zhi-Peng, W., Zheng-Pu, Z., and Li-Wen, L. (2006): Flow Injection online solid phase extraction coupled with inductively coupled plasma mass spectrometry for determination of trace rare earth elements in environmental materials using maleic acid grafted Polytetrafluoroethylene fibers as sorbent, J. Am. Soc. Mass Spectrum, (17), 1258-1264.

[18] El-Gamal, E. (2007): Studies on the treatment of solid wastes produced during purification of phosphoric acid at phosphoric acid purification pilot plant in Egyptian Nuclear Materials Authority, M.Sc. Thesis, University of Al-Azhar, Egypt, 135p.

[19] Simpson, N. (2000): Solid-phase extraction: principles, techniques, and applications, Varian Associates, Inc., Harbor City, California, USA, 315p

[20] Ramachandran, V., Paroli, R., Beaudoin, J., Delgado, A. (2002): Handbook of Thermal Analysis of Construction Materials, Noyes Publications, New York, USA, 524p.

[21] Savova1, M., Bart, H., and Seikova, I. (2005): Enhancement of mass transfer in solid-liquid extraction by pulsed electric field, J. Chem. Technol. Metall. (40), 329-345.

[22] Galaction, I., Kloetzer, L., and Cascaval, D. (2010): Separation of p-amino-benzoic acid by reactive extraction in the presesnce of 1-octanol as phase modifier, Chem. Biochem. Eng. Q., (24) 2, 149-157.

[23] Habashi, F. (1996): The recovery of uranium and the lanthanides from phosphate rock, Third Arab Conference on the Peaceful Uses of Atomic Energy, Damascus, 9-13 December.

[24] Gupta, C. K., and Krishnamurthy, N. (1992): Extractive Metallurgy of Rare Earths, International Materials Reviews, (37) 5, 204-216.

[25] Preston, J. S., Cole, P. M., Craig, W. M., and Feather, A. M., (1996): The recovery of rare earth oxides from a phosphoric acid by-product, Hydrometallurgy, (41), 1-19.