



Purification of Industrial Phosphogypsum and Separation of Its Embodied Rare Earth Elements

Laila A. Guirguis and Nagwa. I. Fallila

Nuclear Materials Authority, P.O. Box 530 El-Maadi, Cairo, Egypt.

Corresponding author: Laila Attia Guirguis

ABSTRACT:

The purpose of this research is to produce an ecofriendly purified phosphogypsum (PG) and some by product pure rare earth elements (REEs) by cheap, economic and quick method. These activities not only eliminate our need to import valuable REEs from other countries but also reduce the PG deposited in Egypt that have an adverse import on the environment. In this investigation 100ml of 0.5 mol/L sulphuric acid are added to 50 g phosphogypsum. The mixture is heated for 2h at 80-100°C with stirring and air bubbling followed by filtration. The obtained purified PG is processed with a pulp of CaO to a pH of 6.5-7.5. Extraction of total rare earths using 0.5 molar Cyanex 921 in kerosene at an aqueous\ organic phase ratio 1:3 at pH 3, room temperature at an extraction percent of 98%. Stripping of total rare earths is done by 0.5 molar nitric acid of aqueous\ organic phase ratio 2:1 at room temperature. REEs are precipitated by ammonia and oxalic acid, total process recovery was 98.8%. Finally, a technological flow sheet is given for the suggested process and Edex chart of total REEs produced from the studied PG sample is also given.

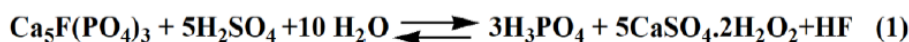
KEYWORDS: Phosphogypsum (PG), REEs Extraction, Gypsum, Cyanex 921.

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I. INTRODUCTION

Phosphogypsum (PG) is an industrial residue from processing phosphate rock using the wet acid process to produce phosphoric acid (H_3PO_4) and Phosphogypsum according to equation (1)



This process is economic; however, it results in the generation of a large amount of PG (for every ton of produced phosphoric acid, about 4-5 tons of PG are yielded). PG consists principally of calcium sulphate but also contains a high level of impurities, such as phosphates, fluorides, and sulphates, naturally occurring radionuclides, heavy metals and other trace elements. Nowadays, PG represents one of the most serious problems faced by the phosphate industry, since commercial uses in the manufacturing gypsum board, ported cement and in agriculture fertilizers or soil consume less than 5% of the world-wide generation of PG. The remaining 85% is disposed of without

any treatment and usually dumped in large scale exposed to weathering. Process occupying a considerable land area and easily a serious environment of contamination of soils, water and atmosphere. On the other hand, rare earth elements (REEs) have a great impact on the development of new technologies, e.g., strategic economy sectors [1–3] are considered to be the flywheel of modern economics and serve as the basis for technological developments. PG contains an overall amount of REES in the interval of 0.343–0.637% by mass and does not show radioactivity level which would exclude it from construction purposes. The presented results serve as the basis for currently available technological directions in the management of apatite PG for useful trade products, which creates a chance for the elimination of its storage necessity by further processing [4]. The solvent extraction of RE with organo-phosphorus reagents, showed that at lower temperature, higher concentration of phosphoric acid and larger liquid/solid ratio were beneficial to REES enrichment in the phosphoric acid. Surfactant additives which enhance the crystal growth of gypsum also enhanced REES leach recovery to about be 75% under optimized conditions. Studies on the solvent extraction of REEs found that D₂EHPA mixtures with neutral organo-phosphorus reagents were antagonistic, and that Fe³⁺ competed strongly over REES. Higher D₂EHPA concentration, larger phase ratio, lower temperature and lower phosphoric acid concentration increased the REES extraction efficiency. A negative enthalpy change was found indicating an exothermic extraction reaction [5]. The authors studied lanthanides leaching from PG waste using Nonyl Phenol Ethoxylate (NPE) associated with HNO₃ and HCl. Further, they reported that in the presence of NPE, the lanthanides leached out better. This study clearly highlights that the association of NPE with HCl or HNO₃ is a potential leaching reagent for the leaching of lanthanides from phosphogypsum waste kouraim et.al., [6]. The research works conducted so far confirm the possibility of applying phosphogypsum for the recovery of lanthanides, and the process enhances the removal of remaining impurities, thanks to which the purified calcium sulphate (gypsum) may find application for the production of construction materials [7]. The research on alternative raw materials for Lanthanides production have been applied among others in modern technologies, the so-called high-tech. cars produced at present, e.g. Toyota Prius, may contain in their mass up to a dozen or so kilograms of rare earths, which exert a beneficial influence on metallic elements enhancing their hardness, crack resistance and general wear. In cars mechanics REES (Rare Earth Elements) compounds are applied in the production of electrical engines (hybrid NiMH battery – contains lanthanum and cerium additives; engine – contains terbium, dysprosium, neodymium, praseodymium), vehicle catalysts (lanthanum, cerium), UV windscreens (cerium), front light glasses (neodymium) and LCD screens (europium, yttrium, cerium) [8-9]. The method for extracting lanthanides with 0.14 mol/dm³ HNO₃ directly from apatite ore or granite rocks is also known. However, the process appears to be economically disadvantageous due to ore pollution, and significant quantities of phosphorus compounds important for phosphoric acid industry [10]. Extraction of rare earth elements from phosphogypsum using sulfuric acid-nitric acid mixture solution at 3.2-1.2 ratio with a concentration of 1-3% by weight and at liquids-solids ratio of 4-5 within 8-12 minutes with simultaneous hydro acoustic action on the extraction suspension agent being mixed succeeded by separation of insoluble gypsum from the extraction suspension agent and by recovery of rare earth elements from extraction solution using a cation-exchange sorption [11].

II. EXPERIMENTAL

Materials and instruments

All chemicals used are of analytical grade, unless otherwise stated. PG samples (of density equals 2.3 g/cm^3) is obtained from Abu-Zaabal Company for Fertilizers and Chemicals.

Chemical, and radiometric analysis are the main experimental methods carried out to investigate the PG sample. Trace concentrations of the different metals in the PG sample is determined using the inductively coupled plasma optical emission spectrometer (ICP-OES) of the model, Shimadzu Sequential Type, Kyoto "Japan". For major elemental analysis, A Shimadzu 160 a Double beam UV spectrophotometer having a wave length range of 200-1100 nm is used for spectrophotometric determination of sulphate, phosphate, and total rare earth elements.

Chemical analysis

The total rare earth content of strip liquor is determined by titration against 0.03 M solution of EDTA using hexamine buffer pH 6 and xylenol orange indicator with formula weight 332 is used for rare earth oxides (Ln_2O_3) based on the extracted distribution of individual elements in the studied sample. The acid content of leach liquors and strip solution is determined against 0.2M NaOH using bromocresol green indicator. [12]

Sulphuric acid leaching

100ml of 0.5mol-1 sulphuric acid is added to 50 gm phosphogypsum. The pulp is heated for 2h at $90\text{-}100^\circ\text{C}$ with stirring and air bubbling. The filtrated precipitate is rinsed with 100 ml of water. Rinsed precipitation is mixed with 0.1 gm of calcium hydroxide to pH 6.5-7.5 and is removed as a purified phosphgypum. Three batches of phosphogypsum are made with some sulphuric acid. Both filtrate and the rinsed precipitation of purified PG are collected and this solution is considered as a starting concentrated raw material for the following REEs separation

Radiometric analysis

Gamma ray spectrometry system having a sodium iodide crystal detector shielded with 7.5 cm thick lead having 100 % relative efficiency and a resolution at 2.1keV of 1.38MeV gamma energy is used.

Solvent Extraction

Extraction experiments are carried out by shaking equal volumes (50 mL) of the aqueous and organic phases using a shaking incubator (GFL 3031, Germany) for 15 minutes at 298 K ($25^\circ\text{C} \pm 2^\circ\text{C}$). The effects of pH of aqueous phase, concentration of extractant in the organic phase, contact time, temp., and A/O phase ratio are investigated. The concentrations of metal ions in the aqueous phase before and after solvent extraction were measured by (ICP-OES) and arsenazoIII. The concentration of metal ions in the organic phase after the extraction is calculated using a mass balance equation. The extraction efficiency (E %) was calculated as the fraction of metal ions extracted into the organic

phase. The extraction distribution coefficient (D_E) is defined as the concentration of species in the organic phase divided by the remained concentration in the aqueous phase and is calculated by the following:

$$D_E = \frac{[C_O]}{[C_A]}$$

Where C_O is the concentration of M in organic phase and C_A is the concentration of M in aqueous phase after solvent extraction.

The extraction percent (%E) is calculated from the following equation:

$$\%E = 100D(P)/1 + (P) \tag{2}$$

Where P is phase ratio=vol of org/vol of aqueous

And D is the distribution coefficient

Percentage stripping (%)

$$\frac{\text{Amount of metal stripped by stripping agent} \times 100}{\text{Amount of metal extracted}}$$

III. RESULTS AND DISCUSSION

Chemical Analysis of PG Sample before and after treatment

Table (1A): Chemical Analysis of PG before and after treatment as well as natural gypsum used in building materials

Compound formula	PG Conc before treatments %	PG Conc after treatments %	Natural gypsum% used in building material [7]
P ₂ O ₅	1.03	0.12	0.02
CaO	31.5	32.5	32.60
Fe ₂ O ₃	0.59	0.32	0.20
Al ₂ O ₃	0.84	0.10	0.08
MgO	0.30	<0.02	0.02
SiO ₂	3.68	3.43	3
Na ₂ O	0.23	0.07	0.23
K ₂ O	0.10	0.04	0.10
TiO ₂	0.12	<0.01	<0.02
F	0.31	0.1	1
SO ₃	42.3	44.7	44.97
L.O.I	20.08	21.05	21.01
pH		5.8-6.5	> 5
Specific gravity		2.76	2.96

Table (1B) Content of impurities in purified PG as determined by (ICP.OES)

Elements	% mass	Impurities	% mass
V	<0.02	Cd	<0.02
Cr	<0.02	Sb	<0.02
MnO	<0.02	Co	<0.02
Hg	<0.02	Ni	<0.02
As	<0.02	Pb	<0.02

Table (1C): Radiometric analysis of PG before and after treatment

Elements	PG Conc before treatment(ppm)	PG Conc after treatment(ppm)
²³⁸ U	4.47	U.D.L
²³² Th	0.04	U.D.L
²²⁶ Ra	44.93	U.D.L
⁴⁰ K	0.5	U.D.L

The obtained PG is nearly depleted from radioactivity isotopes. It is found to fulfil Europeans Commission Concentration of Naturally Accompany Radionuclides for Industrial by product used in Building Materials in the European Union

Table (1D): Determination of total Rare Earth Elements in the studied PG by ICP-OES

Element	Concentration (ppm)
Ce	216.4
La	114
Sm	14
Er	23.1
Pr	5.1
Gd	10.9
Y	8.2
Total REEs	381.7

Light group REEs dominate in PG as the ionic ratio of calcium and light REEs is less than of Ca and heavy REEs. Expect that of Y, moreover different ionic charge limits to inclusion of REEs in PG.

3. Extraction of total REEs from PG solution using Cyanex921 in kerosene

Study of the main relevant factors

Effect of pH on the extraction

Initial pH of the REEs phosphogypsum solution is varied between 0.5 – 6 to show its effect on the extraction percentages of total rare earths. The experimental conditions are conducted using 50 mL of aqueous and organic solutions (phase ratio O/A 1/1), 0.5 M Cyanex 921 in kerosene, room temperature, and 15 min contact. Fig (1) shows the performance of extraction by Cyanex 921 in kerosene as a function of initial aqueous phase pH. As expected, the extraction increases with increasing aqueous pH. High yield of total rare earths elements extraction is at pH 3. There after total REEs extraction decrease gradually.

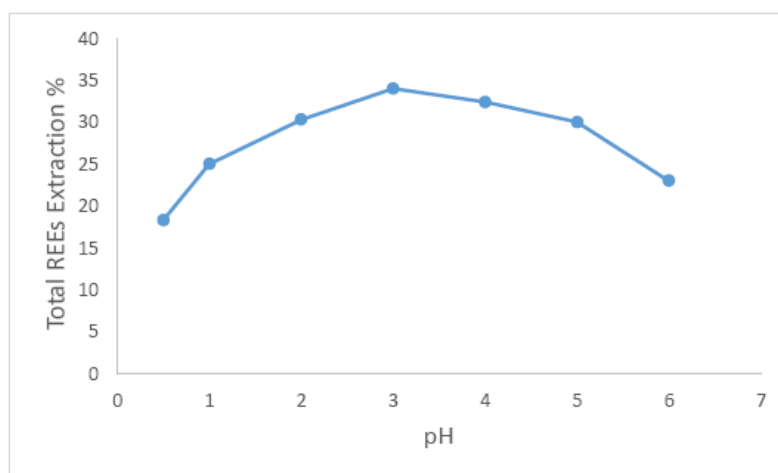


Figure (1): Effect of pH on the extraction process

Effect of different solvent concentration

Cyanex 921 concentration from 0.25 to 1 M is varied in refined kerosene while the other experimental conditions are kept constant (pH=3, room temperature, O/A=1/1 and 15 min contact time). The extraction efficiencies of Cyanex 921 from REES phosphogypsum solution are obtained and given in Fig. (2) These indicate that almost maximum extraction efficiency 98% is reached at 0.5M cyanex921 in refined kerosene.

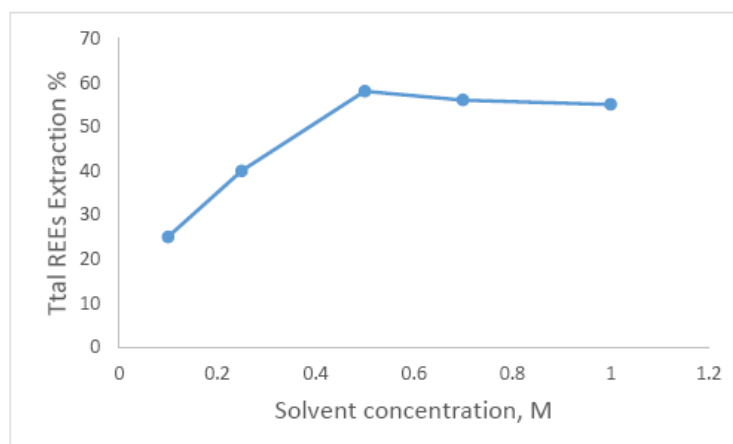


Figure (2): Effect of different concentration of solvent

Effect of O/A ratio

Data given in Fig. (3) represent the effect of changing A/O phase ratio from 1/2 to 5/1 on extraction efficiency from REES phosphogypsum solution by 0.5M Cyanex 921, pH=3 and contact time of 15 min at room temperature. It is noticed that, extraction increased gradually up to 98% at aq/org phase ratio 3/1 than of it decreases.

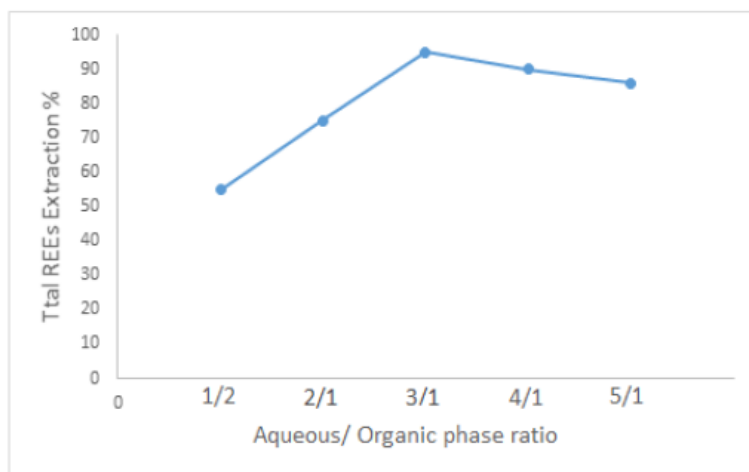


Figure (3): Effect of aqueous organic phase ratio on the extraction process

Effect of contact time on the extraction

This effect is studied at contact time of 5 to 20 min, while other studied factors are kept constant Fig. (4) Shows that 20 min of contact time is an optimum value.

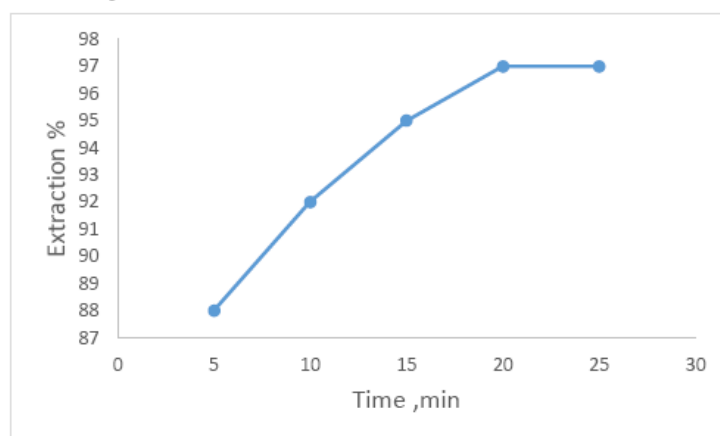


Figure (4): Effect of contact time on the extraction

Effect of temperature

The influence of temperature on extraction process of REEs from phosphogypsum solution is performed at temperatures from 10–40°C, keeping the other extraction conditions constant Fig. (5). It was found that as temperature increased up to room temperature REEs extraction increases then after it decrease. i.e., the optimum temperature is room temperature, an adverse effect is noticed and REEs extraction decreased by increasing temperature from room temp to 40 °C.

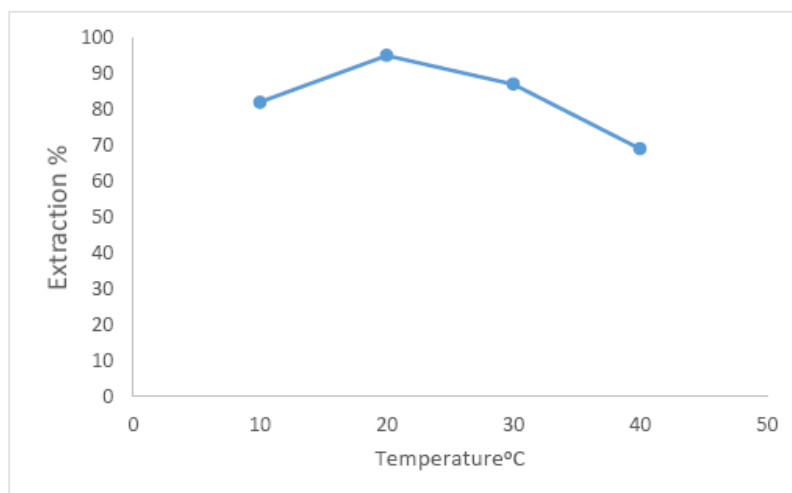


Figure (5): Effect of temperature on the extraction

Extraction Isotherm and construction of Mc-Cabe-thiele diagram for the Extraction process

An extraction isotherm is a plot of the equilibrium concentration of the extracted species in the extraction phase against its concentration in the raffinate phase at a given temperature. Data for the extraction isotherm could be easily obtained from a fixed volume of aqueous phase (leach liquor) with different values of organic feed Cyanex 921 (i.e., the phase ratio variation method) or else by repeated contact of one and some aliquot of the aqueous feed with several aliquot of the fresh organic feed of equal volume. In this study the phase ratio variation method for construction the extraction isotherm of REEs with the solvent is used the process was carried out until saturation of the solvent with REEs is obtained. The obtained data were used to obtain the equilibrium curve. The next step is the construction of the Mc-Cabe-Thiele diagram is to try of a number of operating lines. The slope equal to the ratio of aqueous to organic each operating line the number of stages can be stepped of upon diagram it's clear that one stage extraction stages is quite adequate for REEs extracted Fig (6).

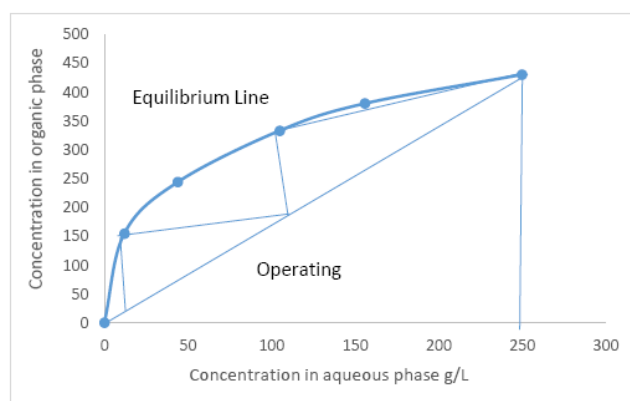


Figure. (6): Mc-Cabe Thiele diagram on the extraction process.

3-Stripping process

Effect of different stripping reagent

Stripping process was carried out on the organic solution consisting of Cyanex 921 in kerosene containing rare earths. The effect of different concentrations of acids and salts on the stripping of metal ions from the loaded organic solvents was studied at 25 °C. The results given in fig (7) show that nitric acid can be considered as a promising stripping agent

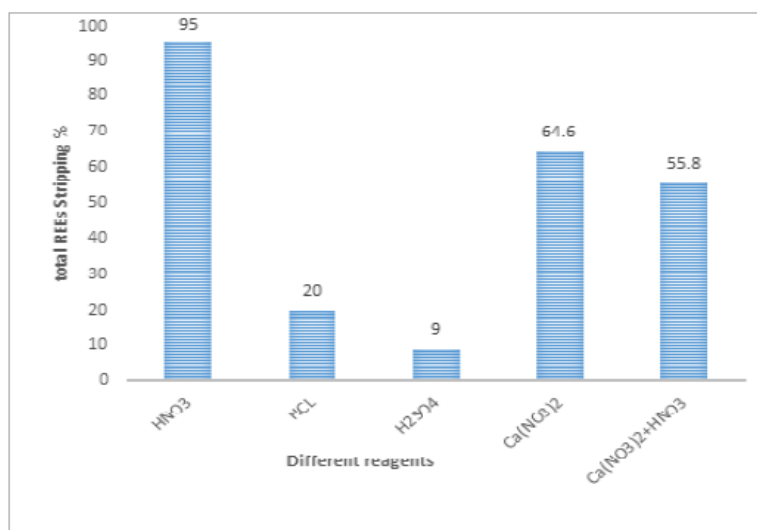


Figure (7): Effect of different stripping reagent

Effect of different concentration of stripping reagent

It is clearly shown from fig. (8) that 0.5 M nitric acid could be taken as an optimum concentration.

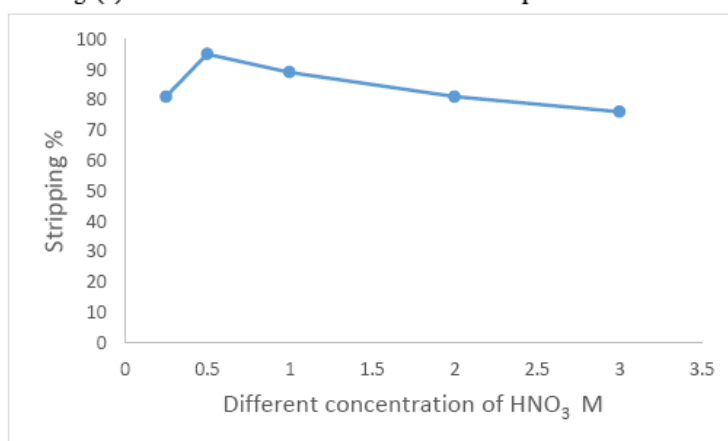


Figure (8): Effect of different concentration of stripping reagent

Effect of O/A ratio on the stripping process

Fig. (9) represented the effect of changing O/A phase ratio from 1 / 2 to 3 / 1 upon stripping efficiency from loaded Cyanex 921 using 0.5M HNO₃, 10 min contact time, and room temperature. It is noticed that, stripping decreased gradually with increase O / A phase ratio. So, the suitable choice maximum rare earths stripping efficiency from loaded Cyanex 921 is 1:1.

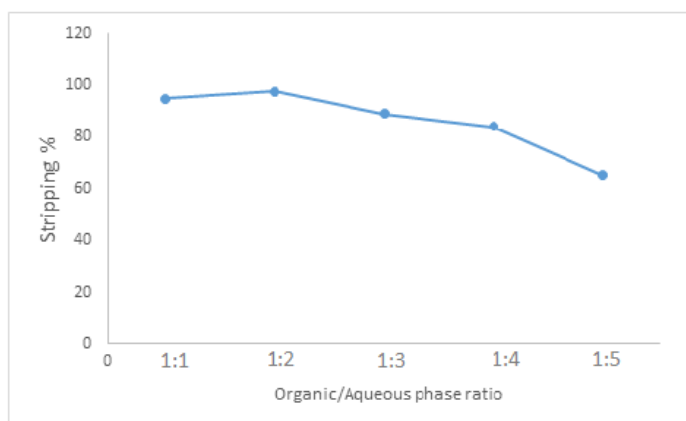


Figure (9): Effect of aqueous\ organic phase ratio on the stripping process

Effect of contact time on the stripping process

Fig. (10) represented the obtained data of varying the contact time periods from 1 to 15 min on the stripping efficiency from the loaded Cyanex 921 upon contacting with 0.5 M HNO₃ solution at an A/O ratio of 2/1, at room temperature. It is observed that increasing the contact time has a remarkable effect on stripping efficiency the maximum achieved value is ten minutes and a contact time greater than ten minutes do not perceptibly increase the metal ions stripping efficiency from the loaded solvent beyond 96 %.

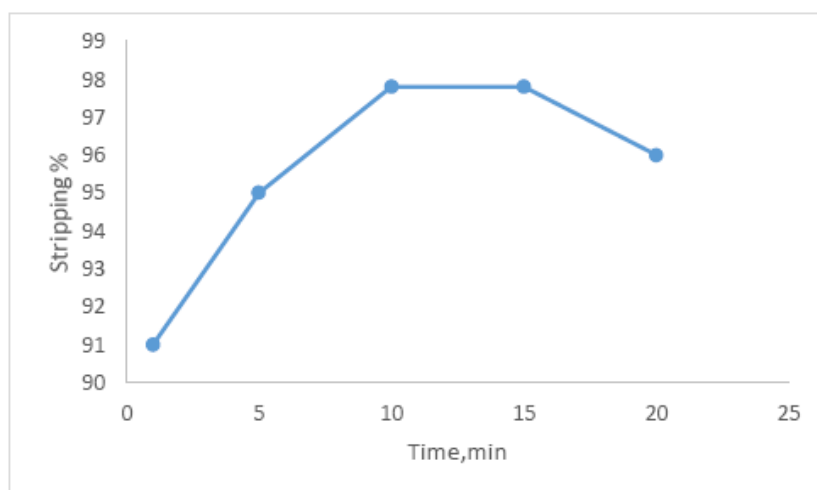


Figure (10): Effect of contact time on the stripping process

Effect of the Temperature

To study the effect of temperature on rare earths stripping efficiency from the loaded Cyanex 921 using 0.5 M HNO₃, a set of experiments has been investigated in the range 10 – 40 °C at an A/O ratio of 2/1, and shaking time of 10 min. Figure (11) represented the effect of temperature on the stripping efficiency. The obtained results reveal that a temperature variation from 25 – 60°C had a slightly impact on the stripping efficiency to 84%. The increase of temperature from 10 – 40 °C, decreases the stripping efficiency from 98% to 84%. From these results, room temperature is chosen for the stripping process.

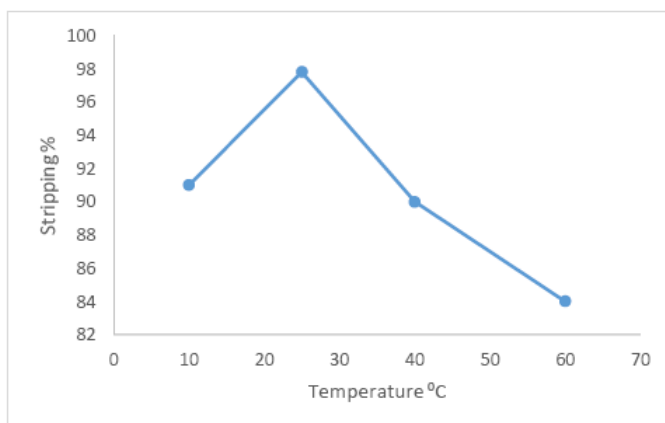


Figure (11): Effect of temperature on the stripping process

Equilibrium line and construction of Mc-Cabe-Thiele diagram for the stripping process

Mc-Cabe-Thiele diagram is a composite plot of equilibrium line and operating line, the latter is readily established by only one point which corresponds mainly to the final raffinate composition and the ratio of aqueous to organic phases that determine the slope of the line as it is a straight line. The diagram can be used to approximate the number of theoretical stages. Another importance of the Mc-Cabe-Thiele Diagram is the evaluation of the obtained results. In this study 10gm of loaded organic (Cyanex921) and 20 gm. of 0.5M HNO₃ stripping reagents contacted 10 minutes at an aqueous organic phase ratio 2/1 at room temp. The optimum determined stripping condition until equilibrium is attained increased portions of the aqueous phase is taken for analysis. Fresh loaded organic phase is added to separation funnel containing the remainder of the aqueous phase to give the same phase ratio as that originally used, the phases are again contacted until equilibrium is attained by the same procedure, this process is carried out until saturation of the aqueous phase with REEs are obtained Fig. (12) illustrate the obtained results whereas two stages is found sufficient for the stripping of REEs from the loaded organic phase.

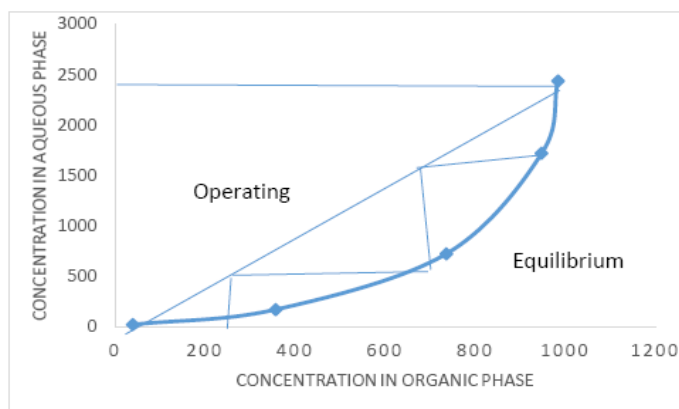


Figure (12): Mc-Cabe-Thiele diagram for the stripping process

4. Precipitation of total REEs

To the strip liquor, concentrated ammonia is added till a residual acidity of 0.8 M is reached followed by 30% excess of crystalline oxalic acid. The mixture is stirred for 1h, leave to settle for 3h. the precipitated rare earth oxalate is filtrated washed with water and dried in air. The oxalate is calcined in the muffle furnace at 750°C for 2hr to convert it to mixed rare earth oxide [13]. Product in Fig. (13) is an EDAX chart of total rare earth oxides obtained from industrial PG after treatment seven rare earth metals in variable concentration is shown in Fig. (13) namely La, Ce, Pr, Er, Sm, Gd and Y.

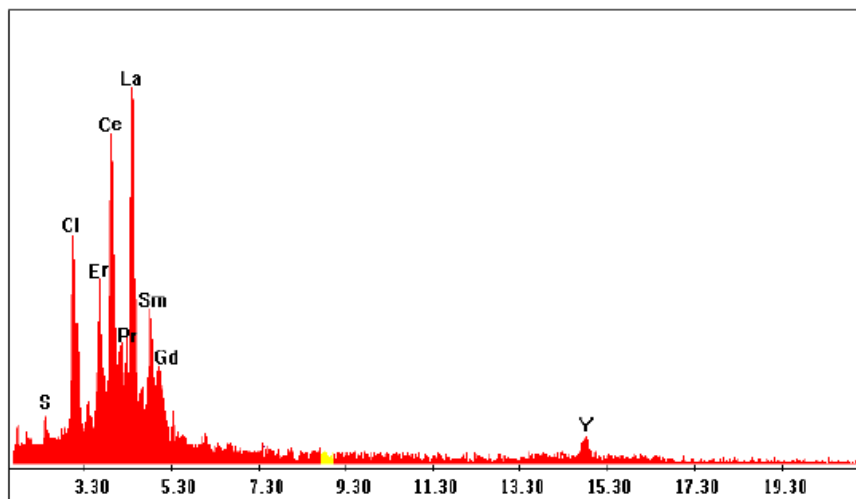


Figure (13): SEM-EDAX chart of total rare earth oxides in PG5. Conclusion

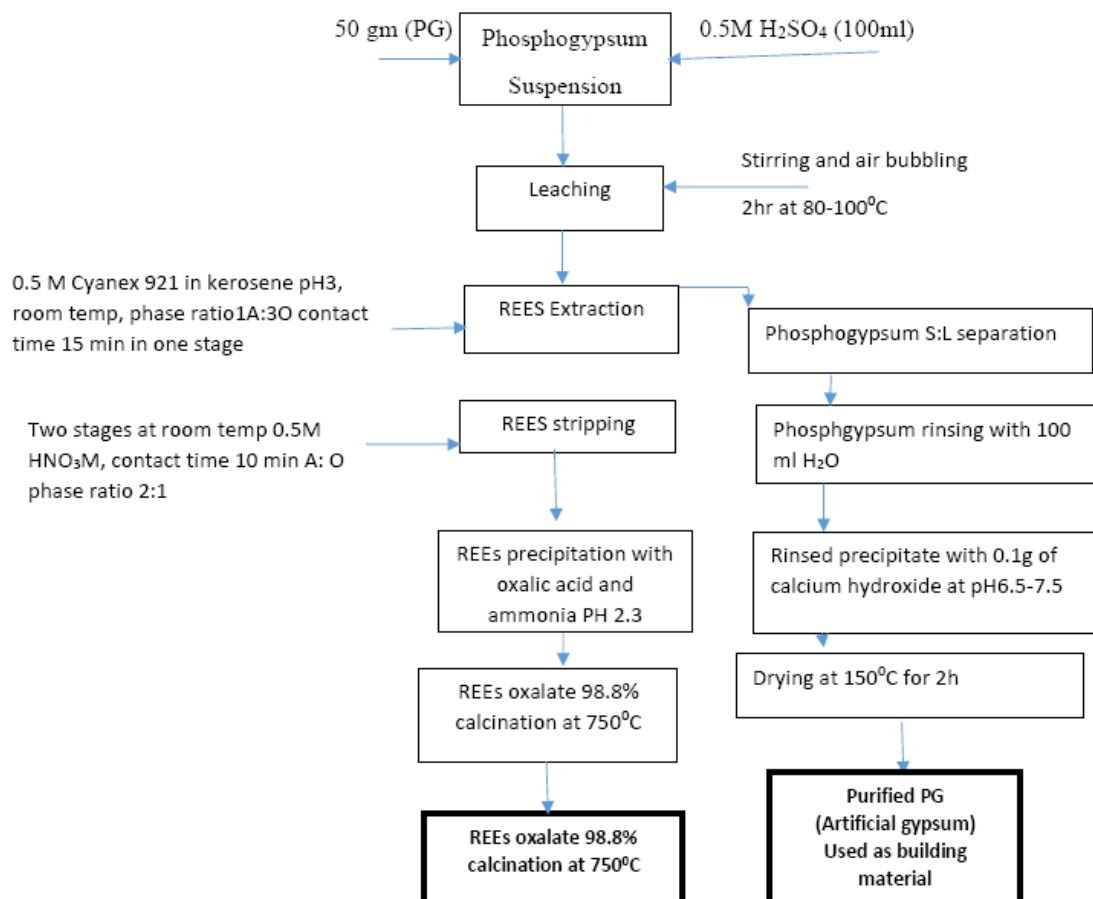


Figure (19): Flow sheet for the studied process

IV. CONCLUSION

Thermal processing of phosphogypsum with dilute sulphuric acid facilitates the recrystallization of PG with crystals of calcium sulphate.

The resulting phosphogypsum contains no harmful impurities or radioactive elements. Accordingly, it can be used in road construction, as additives in the production of cement, and for the production of various building materials.

Economic efficiency of the proposed method is provided by optimal use of all resources as follows

- Sulphuric acid used in the opening of PG is reused up to three times.
- Energy consumption for heating the pulp in the primary processing of PG is reused for the decomposition of phosphate ore.
- No doubt the extraction of the presently found REEs as pure individual elements (Ce, La, Sm, Er, Pr, Gd and Y) are an economic added value to the work.

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