

# Determination of Rare Earth Elements in Products of Chadormalu Iron Ore Concentrator Plant (Iran) from Beneficiation Point of View

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**ABSTRACT:** *Different samples have been prepared from different products in Chadormalu iron ore concentrator plant: Low intensity magnetite separators concentrate (magnetite concentrate), reverse flotation tail (final hematite concentrate), flotation concentrate (apatite concentrate), final tail (L.I.M.S. tail + reverse flotation concentrate+ apatite flotation tail). The samples were used for rare earth elements (REEs) distribution and origin studies. The assay of REEs was determined by ICP-MS spectrometry. The amount of total (light and heavy) REEs were 9631, 291, 199, 2236 ppm and the distributions were 19.3, 3.6, 10.1, 67 % in flotation concentrate (apatite concentrate), reverse flotation tail (hematite concentrate), magnetite concentrate and total tail respectively. About 19.3 % of total REEs were distributed in apatite concentrate with an assay of 9631 ppm. Therefore, further studies have been conducted on this product. According to the Xray studies the minerals of fluorapatite, ankerite and calcite are the main mineral phases in apatite concentrate which the apatite is dominant among them. The scanning electron microscopy studies were shown that the high amount of REEs distributed on fluorapatite mineral. The results have clearly shown that the apatite concentrate that is a by product of iron dressing in Chadormalu plant, with a low economical value and left without any further treatment, can be used as a significant source of REEs. According to this characterization studies, the recovery of a mixed rare earth oxide from fluorapatite is possible either with the treatment of liquors from the total dissolution of the ore in nitric acid or with the proposed treatment of the phosphogypsum by-product from the conventional sulphuric acid route and the recovery of rare earth oxides from phosphoric acid sludges that the detailed flowsheet needs further extraction work.*

**KEY WORDS:** *Rare earth elements, Chadormalu plant, Iron ore, Apatite.*

## INTRODUCTION

The rare earth elements (REEs) are the 15 lanthanides with atomic numbers 57 to 71 that are classified in two

groups: the light or cerium subgroup (LREEs) comprising the first seven elements with atomic numbers 57 to 63

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and the heavy or yttrium subgroup (HREEs), comprising the elements with atomic numbers 64 to 71 as well as yttrium with atomic number 39 [1].

The diverse nuclear, metallurgical, chemical, catalytic, electrical, magnetic, and optical properties of the REE have led to an ever increasing variety of applications. These uses range from mundane (lighter flints, glass polishing) to high-tech (phosphors, lasers, magnets, batteries, magnetic refrigeration) to futuristic (high-temperature superconductivity, safe storage and transport of hydrogen for a post-hydrocarbon economy) [2].

Fiber-optic telecommunication cables provide much greater bandwidth than the copper wires and cables they have largely replaced. Fiber-optic cables can transmit signals over long distances because they incorporate periodically spaced lengths of erbium-doped fiber that function as laser amplifiers. Erbium is used in these laser repeaters, despite its high cost (~\$700/kg), because it alone possesses the required optical properties.

Cerium, the most abundant and least expensive REE, has dozens of applications, some highly specific. For example, Cerium oxide is uniquely suited as a polishing agent for glass. The polishing action of  $\text{CeO}_2$  depends on both its physical and chemical properties, including the two accessible oxidation states of cerium,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , in aqueous solution. Virtually all polished glass products, from ordinary mirrors and eyeglasses to precision lenses, are finished with  $\text{CeO}_2$ . Permanent magnet technology has been revolutionized by alloys containing Nd, Sm, Gd, Dy, or Pr. Small, lightweight, high-strength REE magnets have allowed miniaturization of numerous electrical and electronic components used in appliances, audio and video equipment, computers, automobiles, communications systems, and military gear. Many recent technological innovations already taken for granted (for example, miniaturized multi-gigabyte portable disk drives and DVD drive) would not be possible without REE magnets [2].

Environmental applications of REE have increased markedly over the past three decades. This trend will undoubtedly continue, given growing concerns about global warming and energy efficiency. Several REE are essential constituents of both petroleum fluid cracking catalysts and automotive pollution-control catalytic converters. Use of REE magnets reduces the weight of automobiles. Widespread adoption of new energy-

efficient fluorescent lamps (using Y, La, Ce, Eu, Gd, and Tb) for institutional lighting could potentially achieve reductions in U.S. carbon dioxide emissions equivalent to removing one third of the automobiles currently on the road. Large-scale application of magnetic-refrigeration technology also could significantly reduce energy consumption and  $\text{CO}_2$  emissions [2]. REEs are never found as free metal in earth's crust and their naturally occurring minerals consist of mixtures of various REEs and nonmetals [1]. REEs are found mainly in primary deposits associated with igneous intrusions and associated veins, dikes and pegmatites, and secondary deposit of beach, dune, alluvial placers and residual deposits. REEs bearing deposits minerals may occur as the main valuable component in well individualized deposits as well as potential by-products derived from other minerals, such as apatite. bastansite, monazite and xenotime are three most economically significant minerals to contain essential or significant REEs. Other commercial sources of REEs are apatite, REE bearing clays, allanite, zircon, euxenite and loparite [3].

The magmatic ores of Kola, Palfos and Kovdor with 0.63, 0.48 and 0.14 % lanthanides respectively also the sedimentary ores of Jordan and Morocco with 0.01 and 0.08 % of lanthanides respectively are some of the most important deposits of apatite bearing REEs in the world [4].

Even though, there is not a comprehensive investigation about REEs in central Iran with mining and economical point of view, but the REEs mode of occurrence can be categorized in three main groups, magmatic Iron ores, apatite ores and radioactive metosomatics. Chador Malo, Choghart, Sechahoun and Meydoushan are magmatics deposits [5].

The Chadormalu Iron deposit is located in Yazd province in the center of Iran and the operation is in an open pit mine. The feed of plant consists of different minerals such as magnetite, hematite, martite, quartz, apatite, gypsum, biotite and anhydrite. The plant concentrates are iron ores, hematite and magnetite, and apatite is a by- product [6].

The objective of the present study is to determine the type and distribution of REEs in the products of Chadormalu concentrator plant in order to assess their behavior in the case of extracting the REEs.

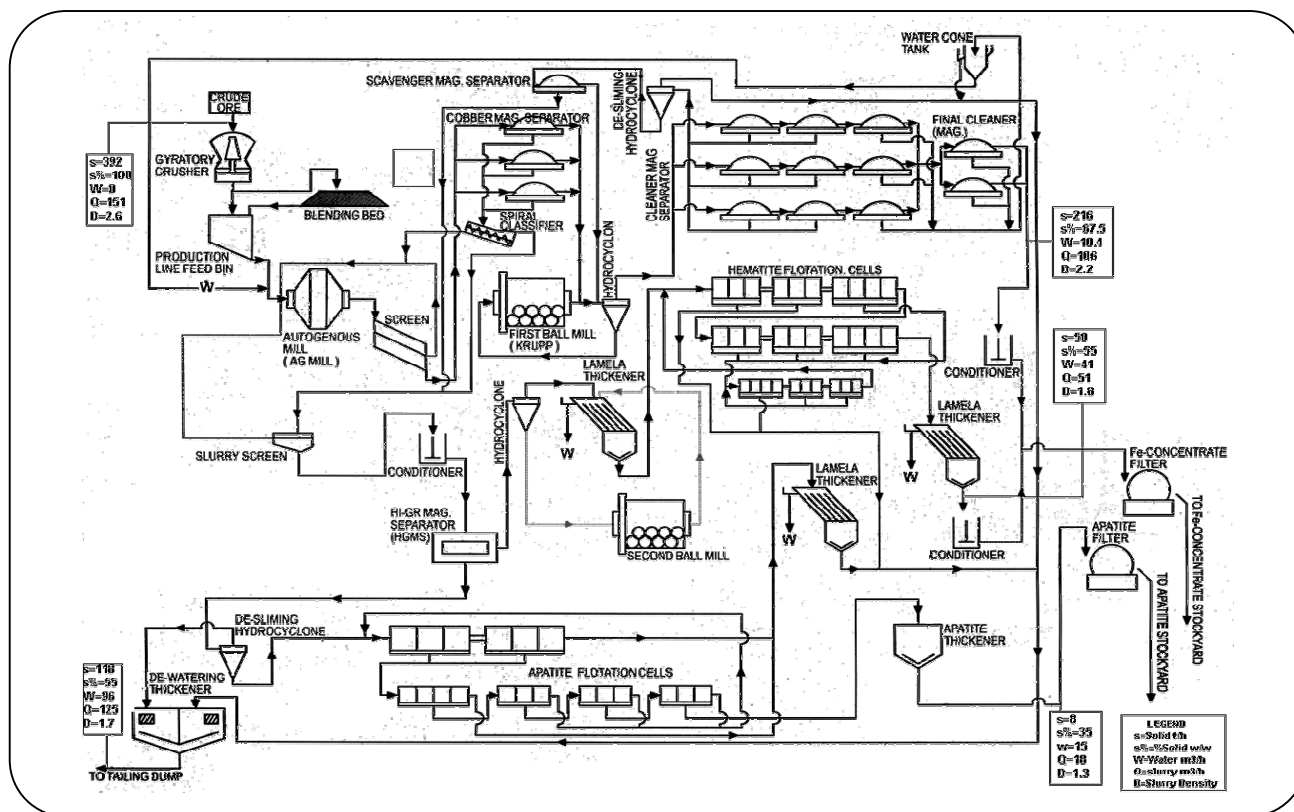


Fig. 1: Process flow diagram of Chadormalu Iron ore concentrator plant.

## EXPERIMENTAL METHODS

### Sampling

In Chadormalu concentrator plant the gyratory crusher and AG mill comprise the comminution system, the LIMS unit produces magnetite concentrate and its tail supplies feed for HGMS and reverse flotation to produce Hematite concentrate. Apatite floatation unit produces apatite from HGMS circuit tail and the tail of LIMS, HGMS and apatite floatation circuits comprise total tail of the plant (Fig. 1).

Different samples were prepared from hematite concentrate, magnetite concentrate, total tail and apatite concentrate during 3 working shifts of plant (shift 2 and 3 of 23 January and shift 1 of 24 January 2005) and representative samples were prepared by means of coning and quartering methods. The representative samples with d80:50 micron were used for further studies without further size reduction.

### Icp-ms Studies of Concentrates and Total Tail

Although there are many analytical techniques used

for determination of REEs in geological samples, inductive coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are the most popular ones [7]. In this study the REEs were detected by means of ICP-MS in ACME analytical laboratories in Canada.

### Scanning Electron Microscopy Studies

The Scanning Electron Microscopy (SEM) a Leo 440i model, was used to determine grain size, shape, mineral intergrowth and the REEs distribution in mineral phases that are important factor for the prediction of suitable method in extraction phase

### X-ray Diffraction and Fluorescence Studies

X-ray diffraction is not used only for identification of minerals and their crystalline character; it was used for assessing the abundance of each mineral phase in sample as well. The Brunker diffraction unit from geological survey of Iran was used in order to identify the mineral constituents of the samples. The X-ray Fluorescence,

Philips pw1480 Model, also was used to determine the Chemical compositions of samples.

## RESULTS AND DISSCUTION

### Icp-Ms Studies

The assay and distribution of REEs in feed and different products of plant are shown in Figs. 2 and 3 respectively. The REEs distribution has been determined by using the assaying of different REEs by ICP-MS and mass balance of different products which are shown in Fig.1.

As it can be seen from the Figs. 2 and 3, although high amount (66%) of total REEs is distributed in total tail, the assay of total REEs in apatite concentrate (9631 ppm) is significantly higher than total REEs assay in total tail (2236 ppm). Motivated by above mentioned, further studies were conducted on apatite concentrate as a feed for future REEs extraction studies.

### Apatite Concentrate Characterztion

#### Detailed Icp-Ms Study

The assay of each light and heavy REEs in apatite concentrate are shown in tables 1 and 2 respectively.

As it can be seen from table 1 and 2, total of light REEs is 8228.5 ppm and total of heavy form is 1402.9 ppm. Cerium and Yttrium, with 51.1 and 60.94 %, are predominant forms of light and heavy REEs respectively on apatite concentrate.

The REEs Distribution in apatite concentrate in contrast to each other are shown in Fig. 4 as well. It is understood from this figure that Cerium with distribution of 43.65 % is predominant form of REEs in apatite concentrate. The ICP-MS studies also showed the absence of radioactive elements (Uranium and Thorium) in the apatite concentrate. This considerably simplifies and cheapens the technology of obtaining the commodity RE products because the REEs extracted from apatite are also not radioactive and, hence, do not require decontamination or raise questions about burying the radio-active wastes.

### SEM Studies of Apatite Concentrate

The SEM microphotograph of apatite concentrate with phosphorus, lanthanum and yttrium distribution is shown in Fig. 5. The total elements distribution in this microphotograph was shown in Fig. 6. As it can be seen

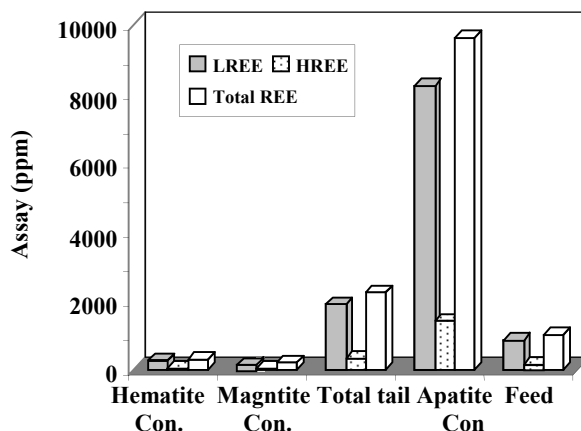


Fig. 2: Assay of total, light and heavy REEs in different products of plant.

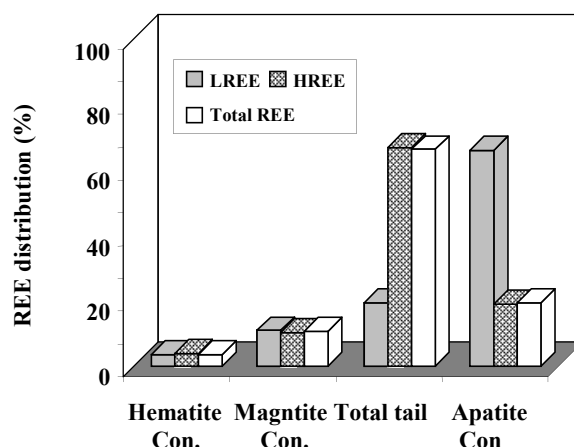


Fig. 3: Light, heavy and total REEs distribution in different products.

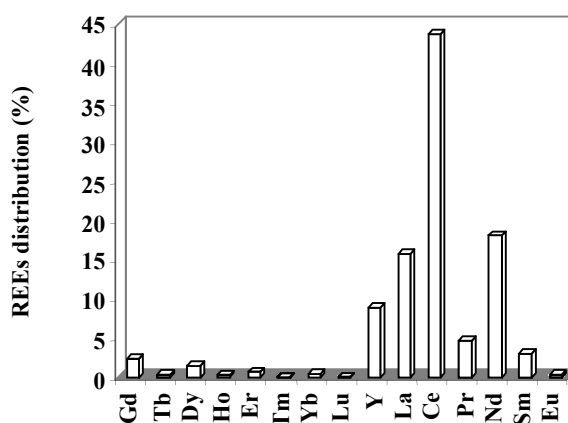


Fig. 4: Distribution of different REEs in apatite concentrate.

**Table 1: Assay of light REEs in apatite concentrate.**

Light Rare earth elements	La	Ce	Pr	Nd	Sm	Eu	Total
Assay (ppm)	1514	4204	455	1738	293	24.5	8228.5
Assay distribution (%)	18.39	51.1	5.52	21.12	3.58	0.29	100

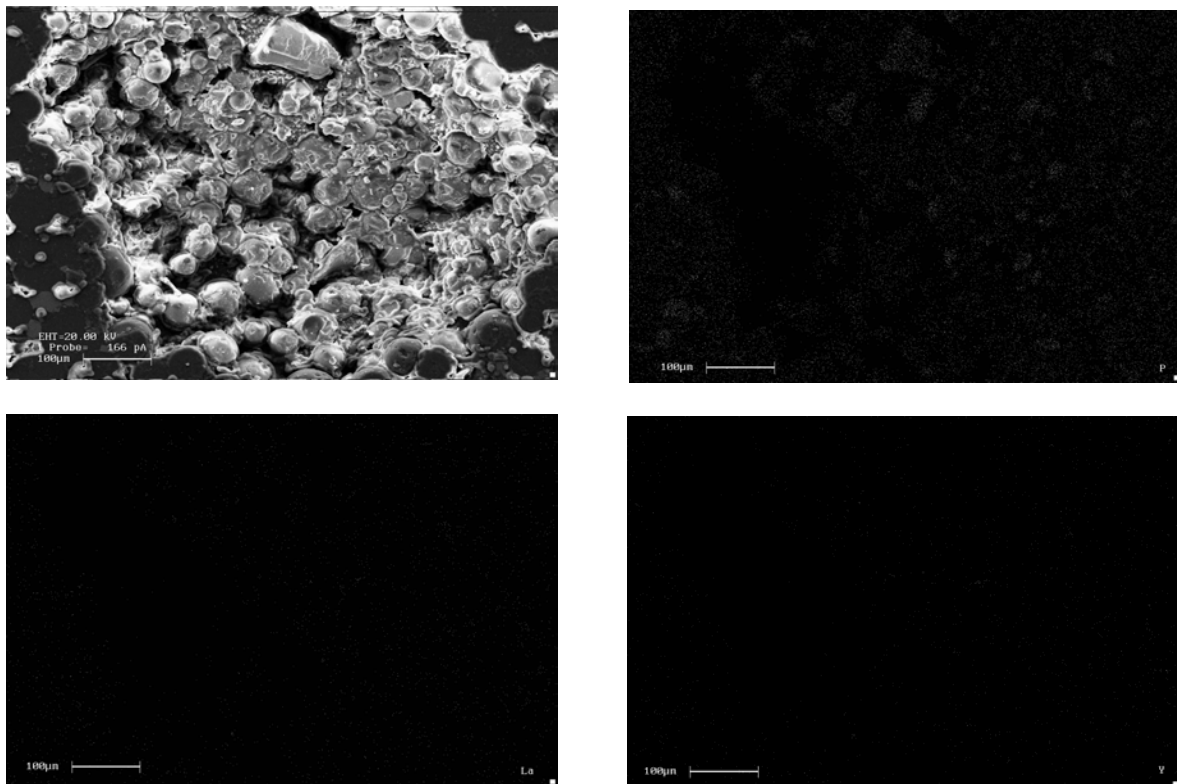
**Table 2: Assay of heavy REEs in apatite concentrate.**

Heavy rare earth elements	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Total
Assay (ppm)	233	28.9	145	24.2	63.2	7.76	40.9	4.94	855	1402.9
Assay distribution (%)	16.61	2.07	10.34	1.73	4.51	0.55	2.9	0.35	60.94	100

**Table 3: Chemical compositions of apatite concentrate.**

Elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	BaO	Cr <sub>2</sub> O <sub>3</sub>
Assay (%)	2.06	0.40	4.85	48.2	0.53	1.37	0.05	0.002	0.111	0.11	0.001
Elements	CuO	SrO	V <sub>2</sub> O <sub>5</sub>	WO <sub>3</sub>	REO*	F	Cl	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	L.O.I	Others
Assay (%)	0.001	0.15	0.026	0.012	0.907	3.05	0.115	0.35	32.9	4.44	0.365

\* REO denotes total of Y, Ce, La, Pr, Nd oxides

**Fig. 5: Microphotographs, SEM: P: Phosphorus distribution, La: Lanthanum distribution, Y: Yttrium distribution.**

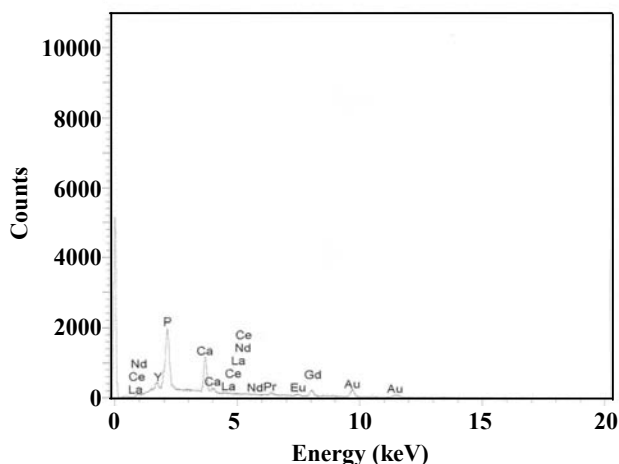


Fig. 6: SEM elemental analysis of apatite concentrate in section is shown in Fig. 5.

from this Figure lanthanum, cerium, gadolinium, calcium, phosphorus, neodymium, yttrium, praseodymium and europium were the elements that characterized in the selected section; It was evidenced that the REEs are distributed in the fluorapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ) mineral. The Fig. 5 clearly shows the strong tendency of the apatite in fine fraction size, lower than 50 micron, which is suitable size for later leaching process.

#### X-ray Studies

The results of XRF and XRD studies of apatite concentrate were shown in table 3 and Fig. 7 respectively. As it can be seen from table 3, total rare earth oxides (REO) consist of Yttrium, Cerium, Lanthanum, Praseodymium and Neodymium oxides was determined in about 0.9 %; Also  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{F}$  and  $\text{P}_2\text{O}_5$  were the significant elements determined by XRF. The measuring condition of L.O.I was 1000 °C for two hours. According to the XRD analysis fluorapatite, ankerite and calcite are the mineral phases of apatite concentrate where the fluorapatite is dominant one.

#### PREDICTION OF REES EXTRACTION METHOD

According to the above mentioned results, the REEs are distributed on economical assay on fluorapatite mineral (9631 ppm in Chadormalu apatite concentrate against 6300 ppm in kola, 4800 ppm in Palfos and 1400 ppm in Kovdor deposits).

Studies on the recovery of a mixed rare earth oxide from apatite have been concerned:

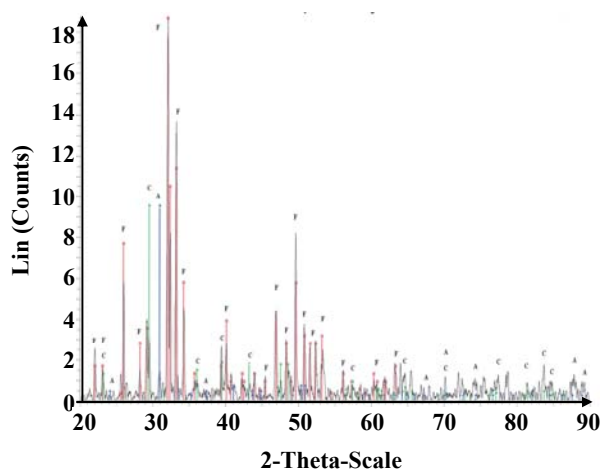
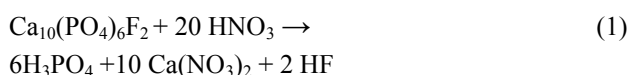


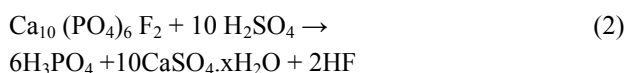
Fig. 7: The XRD diagram of apatite concentrate; F, C and A represent fluorapatite, calcite and ankerite respectively.

a) with the total dissolution of the ore with nitric acid [8-15] as following reaction:

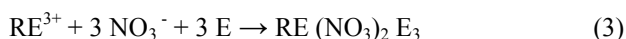


When apatite is leached with  $\text{HNO}_3$ , all the rare earths substituted in the apatite lattice for calcium ions are dissolved and a variety of processes are available for their recovery.

b) With the proposed treatment of the phosphogypsum by-product from the conventional sulphuric acid route [4,9-16] and the recovery of rare earth oxides from phosphoric acid sludges [18, 19] as follows:



In above leaching process most of REEs concentrate in the gypsum by-product. The nitric acid has been used for the recovery of REEs from gypsum. It is well known [11] that rare earth metal cations ( $\text{RE}^{3+}$ ) can be extracted from nitrate media by organic solutions of neutral organophosphorus compounds (E) according to the general mechanism:



Two of the best known commercially available extractants of this type are tri-n-butyl phosphate (TBP) and di-n-butyl n-butylphosphonate (DBBP). Li *et al.*, claimed that it is difficult to separate rare earths from  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$  effectively with TBP because all of them can be extracted by TBP. So They offered dimethyl heptyl

methylphosphonate  $\text{CH}_3\text{PO}(\text{OC}_8\text{H}_{17})_2(\text{P350,B})$  [11].

Finally the precipitation of Mixed REEs can be achieved by oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) solution. The precipitated mixed REEs can be heated to produce REO as a final product.

## CONCLUSIONS

Principal conclusions drawn from this study are as follows:

- REEs studies in different products of plant have shown that assay of total REEs in apatite concentrate (9631 ppm) was significantly higher than REEs assay in other products of plant. So the apatite concentrate was selected to assess its properties in case of extracting the REEs.

- Cerium and Yttrium, with 51.1 and 60.94 %, were predominant forms of light and heavy REEs respectively on apatite concentrate.

- The radioactive elements (Uranium and Thorium) were not present in the apatite concentrate. Therefore, a considerably simpler and cheaper technology is needed to extraction REEs because the REEs extracted from apatite are not radio active and, hence, do not require decontamination or question about burying the radioactive wastes.

- The SEM studies showed that the REEs were distributed in the fluorapatite mineral ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ) and the apatite was distributed in fine fraction size,  $d_{80}:50$  microns that is suitable for later leaching process.

- Fluorapatite, ankerite and calcite were the mineral phases of apatite concentrate where the fluorapatite was dominant one.

- Due to the presence of REEs in fluorapatite, nitric or sulfuric acid leaching procedures, purification by solvents of tri-n-butyl phosphate (TBP) and di-n-butyl n-butylphosphonate (DBBP) or dimethyl heptyl methylphosphonate  $\text{CH}_3\text{PO}(\text{OC}_8\text{H}_{17})_2(\text{P350,B})$ , precipitation of mixed REEs by oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) solution and finally heating to produce REO can be predicted for REEs recovery from Chadormalu apatite concentrate.

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