

# Recovery of Rare Earth Elements in The Hydrometallurgical Processes of Phosphate Rock- A Critical Review

Shengxi Wu<sup>a,b,c,d</sup>, Liangshi Wang<sup>a\*</sup>, Longsheng Zhao<sup>a</sup>, Patrick Zhang<sup>b</sup>, Hassan El-Shall<sup>c</sup>, Brij Moudgil<sup>c</sup>, Xiaowei Huang<sup>a\*</sup>, Lifeng Zhang<sup>d</sup>

<sup>a</sup> National Engineering Research Center for Rare Earth Materials, Beijing, 100088, PR China

<sup>b</sup> Florida Industrial And Phosphate Research Institute, Bartow, FL, USA

<sup>c</sup> Particle Engineering Research Center, Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA

<sup>d</sup> School of Metallurgical and Ecological Engineering University of Science and Technology Beijing (USTB) Beijing, P.R. China

## Corresponding author:

Liangshi Wang: Tel.: 0086-010-82241180; E-mail: wls1657@163.com

Xiaowei Huang: Tel.: 0086-010-82241180; E-mail: hxw0129@126.com

## Highlight:

1. Technologies for rare earth elements (REEs) recovery in the decomposition processes of phosphate rock are reviewed.
2. Methods for REEs recovery from high-phosphorus leaching solutions are reviewed.
3. Recommendations for further development for REEs recovery from phosphate rock are given.

## Abstract:

Generally, phosphate rock contains about 0.05wt% rare earth elements (REEs) on average. And the world commercial phosphate rock production is estimated to be 200 million tons per year, that makes phosphate rock a potential new REEs resource. However, low content of REEs in phosphate rock leads to the technical challenges and cost overages, that hindered the commercial recovery of REEs. In this paper, an overview of achievements aiming at solving the challenges is given. Based on the

decomposition processes of phosphate rock by  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ , various REEs recovery processes via crystallization, precipitation, solvent extraction and ion exchange methods are systematically reviewed.

In  $\text{H}_2\text{SO}_4$  processes, REEs are recovered based on the removal of impurities from phosphoric acid and phosphogypsum since the main challenge is the diluted content of REEs in these products. In the case of  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  processes, REEs are entirely transferred into leaching solution and the recovery research are mainly focused on REEs extraction from leaching solutions. For REE extraction from high phosphorus content leaching solutions, crystallization, precipitation, and ion exchange methods are currently inconsiderable due to the high energy consumption, impurity involvement and low efficiency, respectively. Solvent extraction seems to be the potential promising method in terms of its good overall performance. Finally, recommendations to promote the development of REEs recovery technologies from phosphate rock are provided.

## Abbreviations

REEs, rare earth elements; REO, rare earth oxides; PG, phosphogypsum; PHH, hemihydrate phosphogypsum; PDH, dihydrate phosphogypsum; DH, dihydrate process, HH, hemihydrate process; HDH, hemi-dihydrate process; HRC, hemi-dihydrate recrystallization process; WPA, wet process phosphoric acid; D2EHPA, di-(2-ethylhexyl) phosphoric acid (TOPS-99); TBP, tri-butyl phosphate; TOPO, tri-n-octyl phosphine oxide; Cyanex301, bis(2,4,4-trimethyl pentyl)di-thiophosphinic acid; Cyanex272, bis(2,4,4-trimethyl pentyl) phosphoric acid; PC-88A, 2-ethyl hexyl 2-ethyl

hexyl phosphonic acid; MOPPA, mono-octyl phenyl phosphoric acid; DOPPA, di-octyl phenyl phosphoric acid; DNPPA, di-nonyl phenyl phosphoric acid; Nacure1052, di-dodecyl naphthalene sulfonic acid; Cyanex923, a mixture of four trialkyl-phosphine oxides; MGA, merchant grade phosphoric acid; NPE, nonyl phenol ethoxylate; NPA, nitric-phosphoric acid solution; HPA, hydrochloric-phosphoric acid solution; NP, nitrogen-phosphorus fertilizer; NPK, nitrogen-phosphorus-potassium fertilizer.

**Keywords:** Rare earth elements; Phosphate rock; Phosphoric acid; Phosphogypsum; Recovery technologies;

---

## Content

### 1. Introduction

#### 1.1 Rare earths resource

#### 1.2 Phosphorous resource and REEs distribution

### 2 Recovery of rare earth elements in sulfuric acid processes

#### 2.1 Distribution of REEs in the sulfuric acid processes.

#### 2.2 Recovery of REEs from phosphoric acid solution

##### 2.2.1 Crystallization methods

###### 2.2.1.1 Crystallization by evaporation

###### 2.2.1.2 Crystallization with seeds

##### 2.2.2 Precipitation methods

###### 2.2.2.1 Ammonia neutralization precipitation methods

###### 2.2.2.2 Double sulfates precipitation methods

###### 2.2.2.3 Fluorides precipitation methods

##### 2.2.3 Solvent extraction methods

##### 2.2.4 Ion exchange methods

#### 2.3 Recovery of REEs from evaporation sludge

#### 2.4 Recovery of REEs methods from phosphogypsum

##### 2.4.1 Recovery of REEs from dihydrate phosphogypsum

###### 2.4.1.1 Leaching REEs from PDH with $\text{H}_2\text{SO}_4$

###### 2.4.1.2 Leaching REEs from PDH with $\text{HCl}$ and $\text{HNO}_3$

###### 2.4.1.3 Leaching REEs from PDH with organic liquid

## 2.4.2 Recovery of rare earths from hemihydrate phosphogypsum

### 2.4.2.1 Leaching REEs from PHH with $\text{H}_2\text{SO}_4$

### 2.4.2.2 Leaching REEs from PHH with $\text{HNO}_3$

## 2.5 Recovery of REEs in HDH and HRC processes

## 3 Recovery of REEs in nitrophosphate processes

### 3.1 Crystallization and Precipitation methods

### 3.2 Solvent extraction methods

### 3.3 Ion exchange methods

## 4 Recovery of REEs in hydrochloric acid processes

## 5 Recovery of REEs in phosphoric acid process

## 6 Conclusions and recommendations

---

# 1. Introduction

## 1.1 Rare earths resource

The rare earth elements (REEs) are a series of elements with similar physiochemical properties which includes 15 elements of lanthanides and scandium, yttrium. The industrial applications of these elements have been extended to metallurgy, magnets, ceramics, electronics, chemical, optical, medical, agriculture and nuclear technologies in the past century owing to their unique properties[1-4]. The production of REO has gone through three main eras throughout the development of rare earths industry (Fig. 1), at present, REEs products mainly originate from bastnasite, monazite, ion-absorbed clay, xenotime and loparite[5-11]. However, contradiction between the shrinking easy-processing REEs resources and the increasing demand, especially from green energy and new materials[11-15], makes the exploration of new origins of REEs become an urgent subject, especially for heavy rare earth elements (HREEs)[16-18].

So far, efforts for sustainable development of REEs resources have been paid on following aspects: (1) Recycle REEs from manufacturing rare earth scrap/residues[19]; (2) Reclaim REEs from End-of-Life products[20-22]; (3) Extract REEs from landfill mining of industrial wastes or residues[23-26]. While, up to now, most of them are limited to academic research due to the difficulties of collection, technique and economy[19, 27]. Besides, an enormous amount of research have focused on (4) REEs recovery from trace REEs associated minerals such as uranium(U) ore[28], fluorite[29], sea sediments[30, 31], and phosphate rocks[32], etc.. Among them, phosphate rocks

was considered as one of the most promising potential new recourses of REEs in terms of the following advantages for REEs recovery from phosphate rocks[33, 34]:

- i. The mature phosphoric acid and phosphate fertilizer industries consume about 250 million tons of phosphate rocks per year[35]. Generally, phosphate rocks contains 0.046wt% REEs on average[36], which means about 125kt of REEs potential yearly production and the value is relative high due to the high HREEs proportion.
- ii. The cost of mining and processing of minerals has been covered by the industries of phosphoric acid and fertilizers[37].
- iii. The increasing demand of REEs and the strengthening restrictions of environment requires the removal of REEs and other hazardous elements from phosphoric acid, phosphogypsum, and phosphoric acid sludge.
- iv. Combine REEs recovery with uranium extraction from phosphate rock seems promising because uranium recovery from wet process phosphoric acid has ever been achieved in industry. Furthermore, profit of REEs recovery may partly compensate the gap between high cost of U recovery and low price of U product.

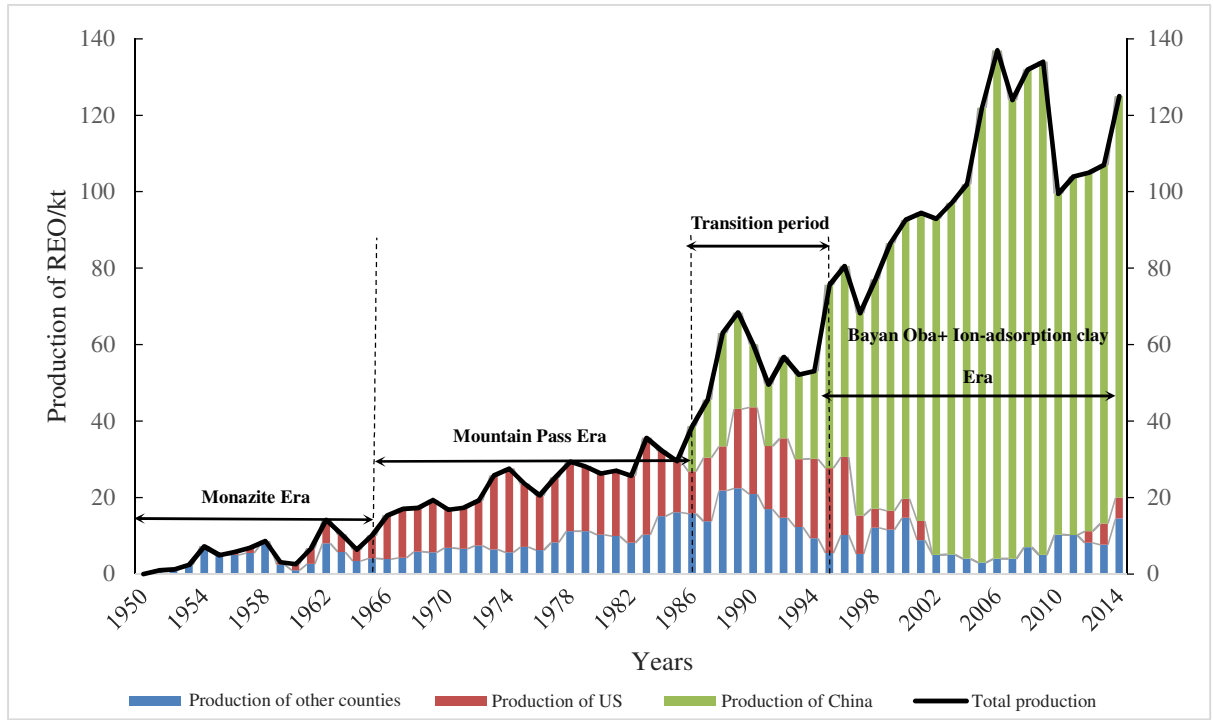


Fig. 1 World production of REO from 1950-2014, source-USGS ( Monazite era (1800s-1964), Mountain Pass era (1965-1984), Bayan Obo and ion absorbed clay era (1991-present))

## 1.2 Phosphorous resource and REEs distribution

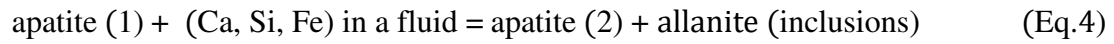
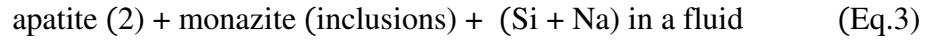
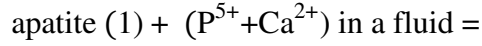
Phosphate rock, formulated as  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$  that can be classified as igneous apatite and sedimentary phosphorite according to their mineralization mechanism[38].

In phosphate rock, REEs are majorly presented in the form of isomorphous substitution and deposit as the REE-francolite that can be easily released into leaching solution by mineral acids. The substitution is dominated by following equations:





While small amount of REEs occurred as particle inclusions such as monazite, xenotime, allanite and carbonate in apatite and they are originated from REEs-apatite via ore forming reaction, for example[39, 40]:



where apatite (1) represents the REEs-rich apatite, apatite (2) represents the REEs-poor apatite. Furthermore, in some cases, large amount of inclusions were generated and led to difficulty in REEs dissolution during the leaching process, especially for the high REEs content ores. The typical phosphate rock with relative high REEs content (>0.046wt%) were listed in Table.1.

Table.1 Typical REEs containing phosphate rocks

Origin	Countries	REEs (wt%)	Mineralogy (reserves)	Refs.
Kola	Russia	0.80-1.00 <sup>‡</sup>	Igneous apatite, REE-carbonates (11.50Mt <sup>‡</sup> )	Zielinski et al.[41]
Khibiny		0.35-0.4 <sup>‡</sup>		Zaitsev et al.[42]
Zhijin	China	0.05-0.13 <sup>‡</sup>	/ (1.45Mt <sup>‡</sup> )	Nie et. al.[43]
Florida	America	0.06-0.29 <sup>‡</sup>	REE-francolite	Patrick[44]
Negev	Israel	~0.03 <sup>‡</sup>	REE-francolite	Soudry et al.[45]
Kaiserstuhl	Germany	0.12-1.69*	Monazite and allanite inclusions	Puchelt et. al.[46]
Abu Tartur	Egypt	0.05-0.11*	Monazite, xenotime inclusions/(0.87Mt*)	Awadalla G.S.[47]
Whistler member	Canada	~0.11 <sup>‡</sup>	--	Simandl et al[48]
Fernie formation	Canada	~0.13 <sup>‡</sup>		Simandl et al[49]
Nolans Bore	Australia	~2.78 <sup>‡</sup>	Monazite inclusions (1.22Mt <sup>‡</sup> )	Jaireth et al.[50]

Esfordi	Iran	0.2~1.5*	Monazite and bastnasite inclusions	Jami[51]
Posht-e-Badam	Iran	0.10 -2.50*	Magnetite-apatite ore	Mokhtari et. al.[52]
Love Hollow	America	~1.80*	REE-francolite	Emsbo et al.[53]
Kiirunavaara	Sweden	0.07-0.83 <sup>‡</sup>	Monazite and xenotime inclusions	Harlov et al.[54]
Southern Mongolia	Mongolia	1.36-6.15 <sup>‡</sup>	Magnetite-apatite (0.30Mt <sup>‡</sup> )	Kim et al.[55]
Bou Craa	Morocco	~0.09*	REE-francolite	Christmann[33]
Gloserheia (Forland)	Norway	0.06-0.36 <sup>‡</sup>	Monazite and xenotime inclusions	Aur-r[56]

Note: where \* is the average weight percent of REEs, <sup>‡</sup> represents REO (rare earth oxides).

Various mineral acids have been used for the decomposition of phosphate rock that corresponding to the hydrometallurgical processes of phosphate rock including H<sub>2</sub>SO<sub>4</sub> processes, HNO<sub>3</sub> processes, HCl processes, H<sub>3</sub>PO<sub>4</sub> processes. Based on these processes, REEs recovery has been extensively investigated in the past century (Fig. 2).

The history of REEs recovery from phosphate rocks dates back to the 1930s, USSR firstly began the investigation of recovery of REEs byproduct from wet process phosphoric acid[57]. And since then, researchers from Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Russian Academy of Sciences has devoted to the studies of REEs recovery from phosphate rock, phosphoric acid, phosphogypsum (PG). Many literatures demonstrated that REEs recovery from phosphate rock has ever been achieved in industrial scale in Russia, and the most possible process was the one that decomposes phosphate rock with HNO<sub>3</sub> and recovers REEs by solvent extraction with TBP[58, 59].

In 1965, researchers from Romania decomposed phosphate rock with HCl, precipitated REEs from chloride-phosphate by precipitation with lime milk, and obtained REO concentrate with a purity about 87.9% by further treatments including acid redissolution,

---

oxalic acid precipitation, and calcination[60, 61]. However, due to the relative low recovery of REEs (65%), no further research was reported. During 1965-1972, it was reported that REEs were recovered commercially by Kemira Oy from phosphate rock in Finland[62]. In the 1970s, researchers from China conducted kg-scale experiments on REEs recovery from Tangdu phosphate rocks using stepwise neutralization method with lime milk from the leaching solution in HCl process[61]. In the late 1970s beginning of the 1980s, Solvay did a lot experimental work on U and REEs extraction from WPA with mixture of D2EHPA+TOPO and went a full industrial scale pilot in Rouen[63].

During 1987-1996, pilot scale experiments of REEs recovery via  $\text{HNO}_3$  leaching and solvent extraction from the evaporation sludge was carried out in South Africa[64-67]. While due to certain reasons the process was not used in industry. In 1993, pilot scale of REEs recovery from hemihydrate phosphogypsum via solvent extraction during the hemihydrate-dihydrate recrystallization process was reported [41].

During 2000-2016, plenty of research focused on REEs recovery from WPA and PG via various methods. And particular attention has been paid on the solvent extraction method. Recently, The United States Department of Energy sponsored a huge project aiming at recovering REEs from phosphate rock and PG, etc. which may greatly promote the research progress on REEs recovery from phosphate rock and PG. In 2014, Russia began the cooperation with Finland to recover REEs from PG and the pilot scale experiments was going to conduct[68]. In 2016, Researchers from MISiS National Research Technology University developed a technology that recovers REEs from PG

in plant scale[69].

So far, most pilot scale experiments were failed to achieve the extension of commercial recovery of REEs. It can be attributed to the technical challenges and cost overage caused by the low content of REEs in phosphate rock. In this review, an overview of research aiming at solving the technical challenges is given. Based on the decomposition processes of phosphate rock by  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ , various REEs recovery processes via crystallization, precipitation, solvent extraction and ion exchange methods are reviewed. Finally, recommendations to promote the development of REEs recovery technologies from phosphate rock are proposed.

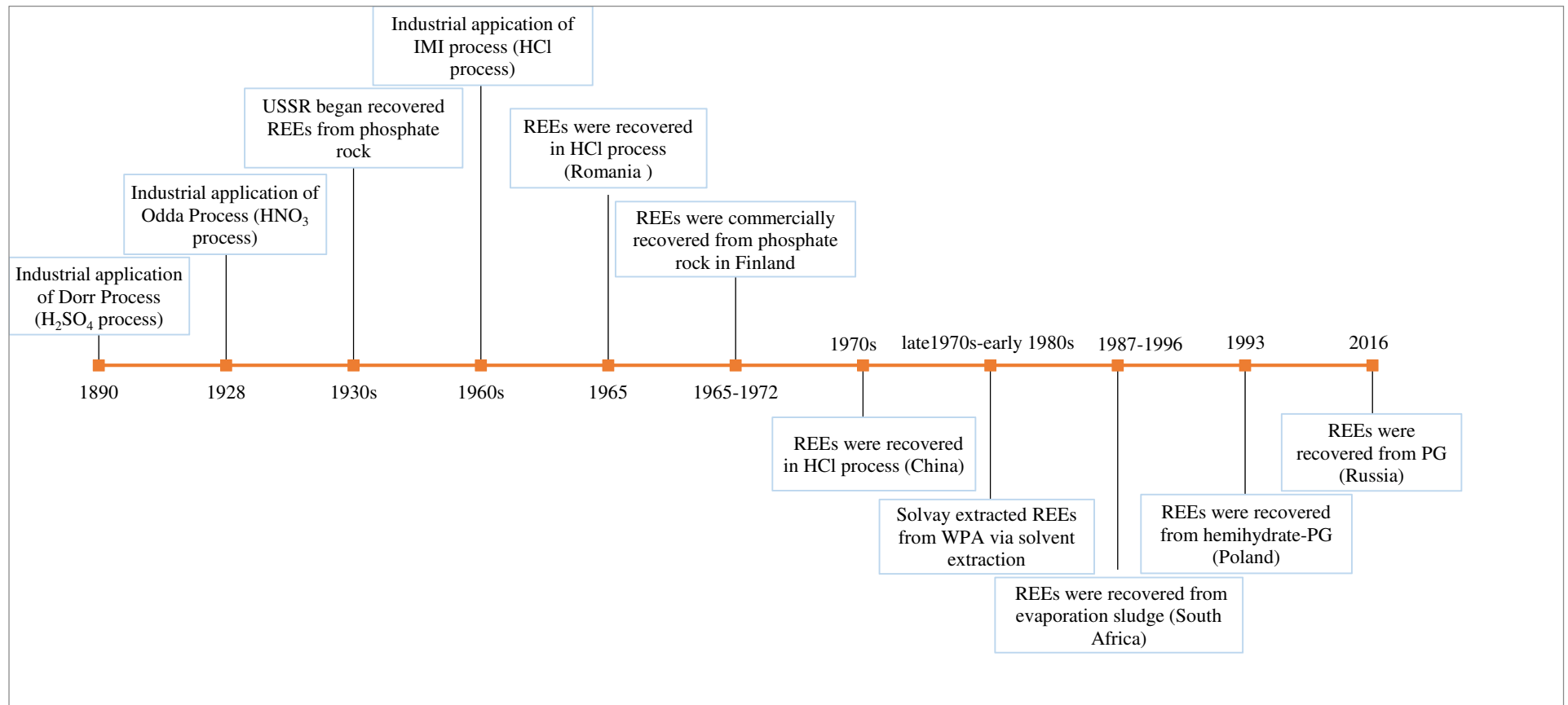
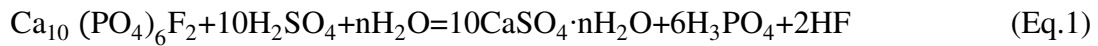


Fig. 2 Pilot scale experiments of REEs recovery from phosphate rock in the past century

## 2. Recovery of REEs in sulfuric acid processes

### 2.1 Distribution of REEs in the sulfuric acid processes

Processes for phosphate rocks decomposition using sulfuric acid (Eq.1) can be classified as: dihydrate process, hemidihydrate recrystallization process, hemihydrate process, Anhydrate process, hemidihydrate process, and dihemihydrate process[70]. So far, investigations on rare earth elements recovery have been found in processes of dihydrate, hemihydrate, hemidihydrate and hemi-dihydrate.



Where  $n=0, 0.5, 2$ , depends on the reaction temperature during the decomposition of phosphate rocks.

Dihydrate process (DH) is the most widely used phosphoric acid process at present due to its simple design and easily operation[70]. In this process, 28%-32%  $\text{P}_2\text{O}_5$  phosphoric acid and dihydrate phosphogypsum( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -PG) are produced at 72-83°C, then PG is removed from phosphoric acid by filtration (Fig. 3). Phosphoric acid produced by dihydrate process is also called wet process phosphoric acid (WPA). Generally, the WPA will be concentrated to 54%  $\text{P}_2\text{O}_5$ -commercial grade phosphoric acid by evaporation to meet the requirements for further applications. In dihydrate process, REEs were distributed into two parts, about 15-30% of REEs enter phosphoric acid solution and eventually reprecipitate in sludge during the evaporation procedure[65], while 70-85% REEs are transferred into PG in the form of isomorphous substitution

with calcium ion ( $\text{Ca}^{2+}$ ) in the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  crystal lattice[65, 71, 72].

Optimizing leaching for REEs during the decomposition of phosphate rocks have been investigated with Fanshan phosphate rocks. About 60-65% leaching efficiency of REEs was obtained under a relative lower phosphoric acid concentration (20-25%  $\text{P}_2\text{O}_5$ ). Moreover, the optimum REEs leaching efficiency of 75% was achieved with the addition of Non-ionic surfactant NS-2[73]. Solvay's experience shown that perlite, porosil or sodium silicate have a significant improvement on leaching efficiency of yttrium and europium from phosphate rocks with sulfuric acid[63].

Hemihydrate process (HH, Fig. 4) attacks phosphate rocks at elevated temperature of 90-110°C and produces 40-52%  $\text{P}_2\text{O}_5$  phosphoric acid[74]. In this process, calcium sulfate is crystallized as hemihydrate phosphogypsum( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ -PHH). For REEs distribution, up to 95% of REEs enters into PHH and mainly present as rare earth hydrate phosphates precipitation ( $\text{REEPO}_4 \cdot x\text{H}_2\text{O}$ ) due to the high concentration of phosphate ions and elevated temperature[75, 76]. Normally, solubility of  $\text{REEPO}_4 \cdot x\text{H}_2\text{O}$  increases with the increasing the degree of hydration which is represented as the value of x and it depends on the temperature of HH process[77, 78].

Hemi-dihydrate process (HDH, Fig. 5) consists of two main sections: hemihydrate section and hemi-dihydrate transformation section. Separation of phosphoric acid is conducted in hemihydrate section and the concentration of phosphoric acid ranges from 40 to 52%  $\text{P}_2\text{O}_5$ . More than 90% of REEs is transferred into the hemihydrate gypsum and then be released during the recrystallization process but finally ended into dihydrate

---

phosphogypsum[79].

In hemi-dihydrate recrystallization process (HRC, Fig. 6), decomposition of phosphate rock is conducted under the same conditions of HH process but without filtration, followed by recrystallization to dihydrate and filtration to produce 30-32% $P_2O_5$  phosphoric acid. Distribution of REEs in HRC is similar to that in HDH.

From the view of practicability that more than 80% phosphate rock were treated by  $H_2SO_4$  processes at present. About 100kt of REEs go into the material flows of wet-process phosphoric acid production and this potential production of REEs seems considerable compared with the world REEs production (126kt REO[80]). Therefore, it is the urgent practical requirement for REEs recovery from phosphoric acid, phosphogypsum, and phosphoric acid evaporation sludge regarding the concern of environment protection and resources utilization.



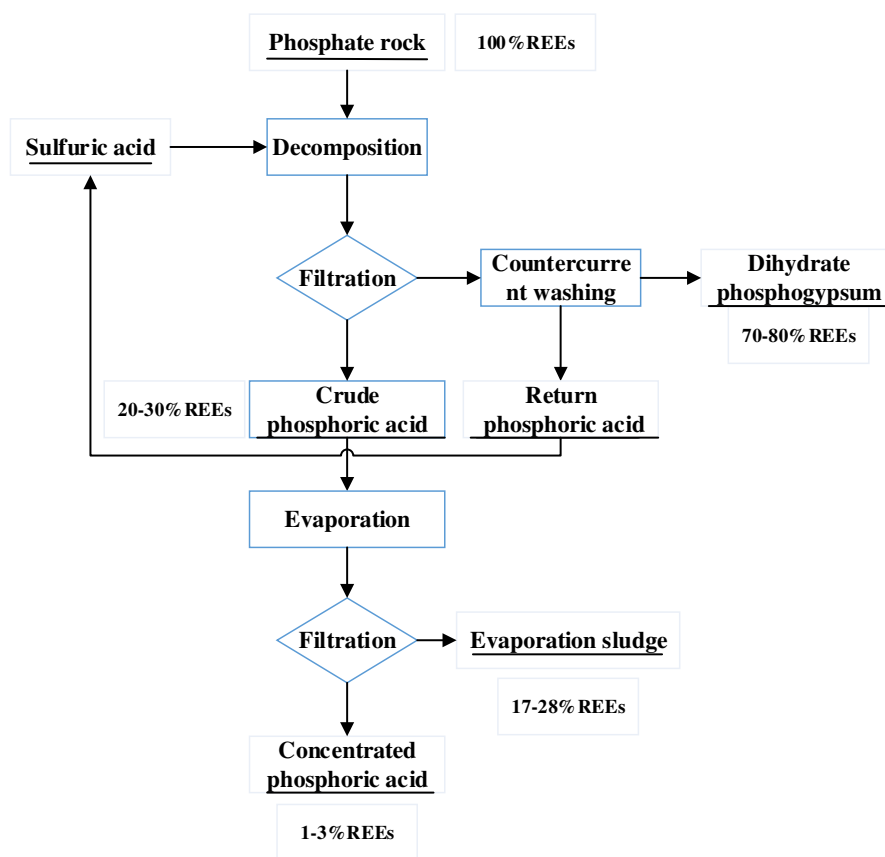


Fig. 3 Flowsheet of dihydrate process and the distribution of REEs

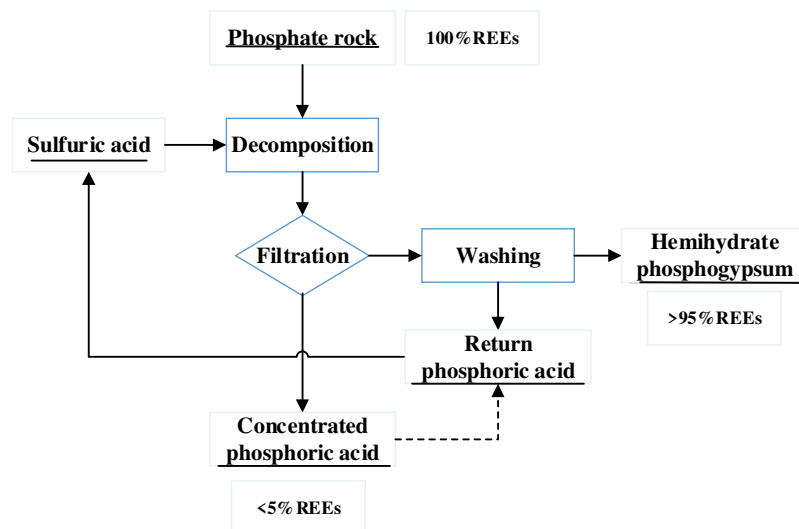


Fig. 4 Flowsheet of hemihydrate process and the distribution of REEs

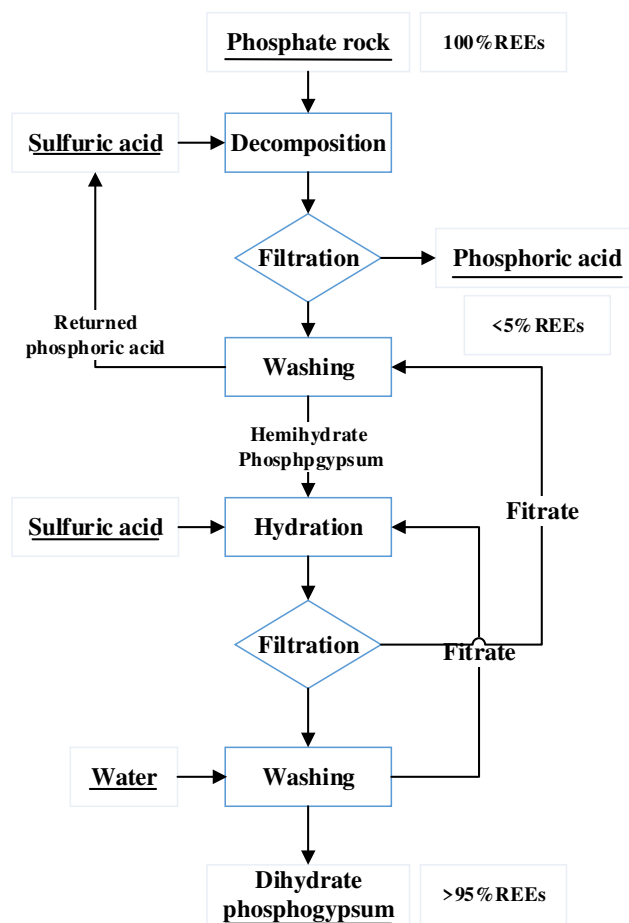


Fig. 5 Flowsheet of hemi-dihydrate process and the distribution of REEs

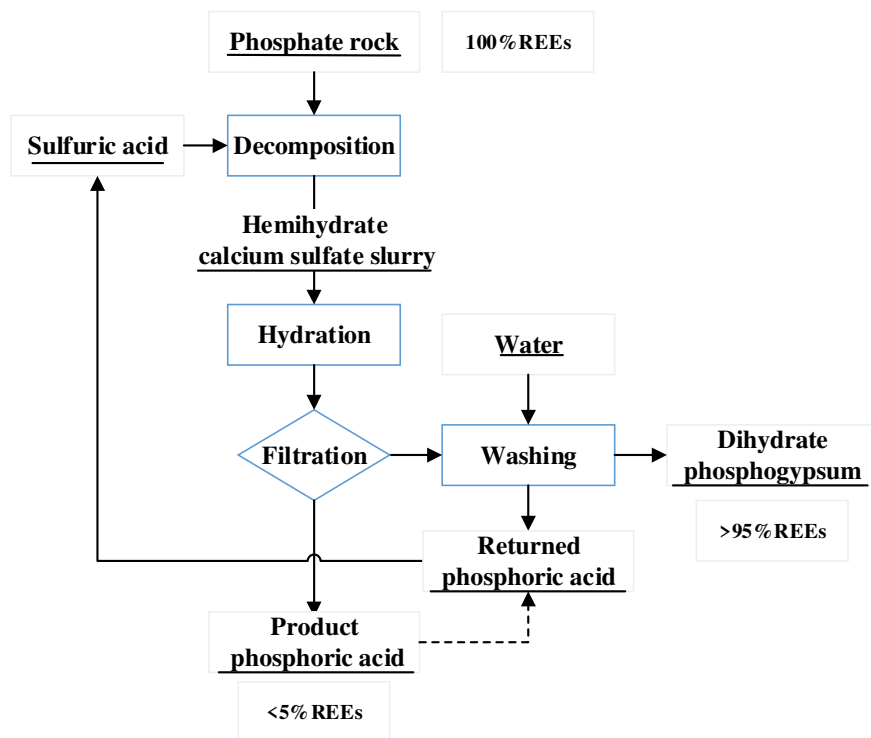


Fig. 6 Flowsheet of hemi-dihydrate recrystallization process and the distribution of REEs

## 2.2 Recovery of REEs from phosphoric acid solutions

Phosphoric acid solution (WPA) is an intermediate product of dihydrate process, which has a concentration of 26-32wt%P<sub>2</sub>O<sub>5</sub>, equal to about 4-6mol/L H<sub>3</sub>PO<sub>4</sub>, and containing a small amount of sulfuric acid (less than 3wt%). REEs concentrations in WPA vary from several ug/g to one thousand ug/g depends on the REEs content in phosphate rocks and the decomposition conditions of wet processes. So far, methods of crystallization, precipitation, solvent extraction, ion exchange have been used for REEs recovery from WPA and features of these processes were compared in Table.2.

Table.2 Comparison of methods for REEs recovery from phosphoric acid solutions

Methods	Operations or Reagents	Technical Characteristics	Challenges
Crystallization	Evaporation at 200°C for 2h	High REEs recovery (98%).	High energy consumption. Pressure resistant apparatus.
	Seed addition with CePO <sub>4</sub> and CeF <sub>3</sub>	Relative high purity (54wt%REO). Concentrating REEs via cycle leaching.	Passivation of seeds. Low REEs recovery (~50%). Expensive seeds.
Precipitation	Ammonia neutralization, NaOH to pH=2.0-3.0	Simple process. Relative high REEs recovery(>90%). Fe, Al removal achieved at the same time.	Large amount of reagent consumption. Low REEs purity (2.5wt%REO).
	Fluorides: partial neutralization (20%) and adding 15.4g/L F <sup>-</sup> in WPA	High REEs recovery (99.8%) Coprecipitation and removal of U.	Impurity issue caused by fluorine introduction (>15g/L F <sup>-</sup> left in WPA)
	Double sulfates: 10-15wt% H <sub>2</sub> SO <sub>4</sub> +23-35g/L Na <sub>2</sub> SO <sub>4</sub> or NaCl	Relative high REEs recovery (91%). Easy available and low-cost material reagents.	Impurity issue of H <sub>2</sub> SO <sub>4</sub> in WPA (>10wt%). Low REEs purity (5wt%REO).
Solvent extraction	MEHPA,D2EHPA, D2EHAP+TBP/TOPO	Mature technology (for U). Simultaneous recovery of U and HREEs.	Insufficient for LREEs. Optimal conditions of U extraction are adverse to REEs. Extra process is needed for REEs separation from U (green cake).
	DOPPA, DNPPA+TOPO DOPPA+TOPO	Simultaneous recovery of U, HREEs, and LREEs with high efficiency. Good extraction performance.	Extra process is needed for REEs separation from U (green cake).

---

Ion exchange	Tulsion CH-90, 93, 96, and T-PAR DOWEX-50WX4, 8	Simple process.	Low recovery for REEs (<60%).
--------------	-------------------------------------------------------	-----------------	-------------------------------

---

### **2.2.1 Crystallization methods**

REEs recovery from phosphoric acid solution via crystallization is based on the poor solubility of rare earth phosphates in phosphoric acid solution. The solubility products of REEs are on the level of  $10^{-25}$ - $10^{-27}$  under 25 °C in neutral aqueous solution[79, 81, 82]. Hence, it is possible for rare earth phosphates nucleation and growth if the active concentration of  $\text{REE}^{3+}$  or  $\text{PO}_4^{3-}$  were elevated to certain level which can be achieved by evaporation and recycle leaching.

#### **2.2.1.1 Crystallization by evaporation**

It was found that the solubility of rare earth phosphates in phosphoric acid solution decreases with increasing temperature[62]. Thus, a evaporation method was suggested to recover REEs from defluorinated phosphoric acid solution by heating up the acid to 200°C and kept for 1h in an autoclave. Rare earth phosphates crystal contains 15-24% REO, 15% $\text{P}_2\text{O}_5$  was obtained and high recovery of 98% for REEs was achieved[83, 84]. Whereafter, REO product was obtained after dissolving the crystal with  $\text{HNO}_3$ , and then precipitated with oxalic acid, redissolved by  $\text{HNO}_3$ , and reprecipitated by  $\text{NH}_4\text{OH}$  followed by calcination (Fig. 7). However, REEs recovery by evaporation requires high-output, high temperature and pressure resistant apparatus and great energy consumption which severely limited its application.

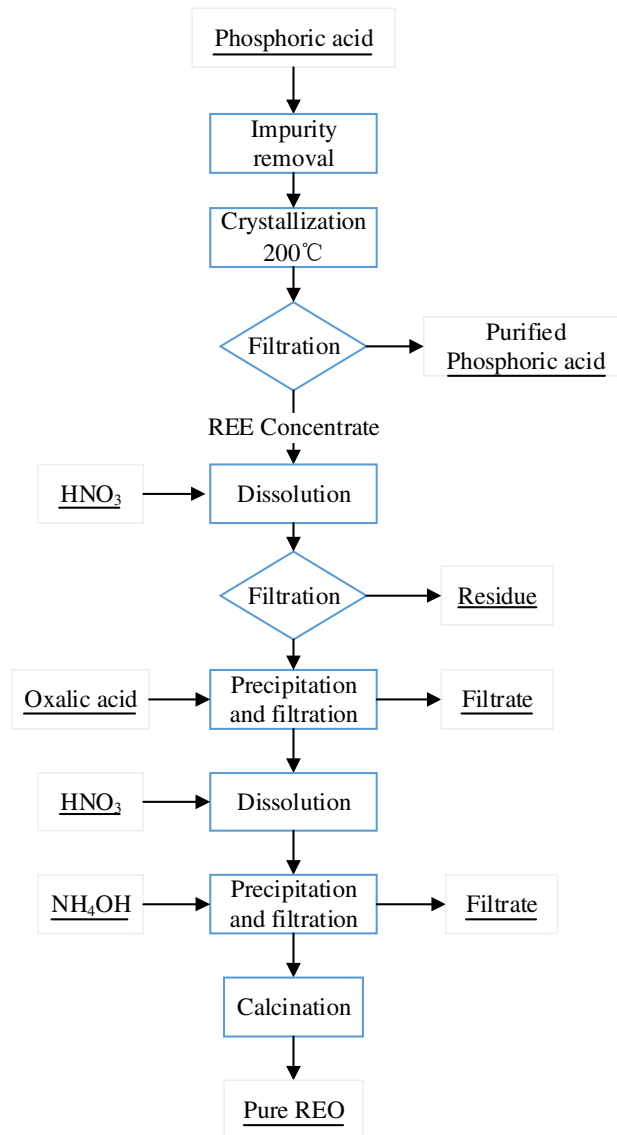


Fig. 7 Recovery of pure lanthanide oxides from wet process phosphoric acid by crystallization[62]

### 2.2.1.2 Crystallization with seeds

Rare earth phosphates and fluorides were introduced as seeds for the crystallization of REEs from phosphoric acid. Melikhov[85] separated REEs from 2-5mol/L H<sub>3</sub>PO<sub>4</sub> by crystallization with CePO<sub>4</sub>·0.5H<sub>2</sub>O seed under 60-90°C. The study shown that the distribution coefficients between the crystals and the solution are  $1.1 \times 10^4$  for cerium and  $4 \times 10^3$  for europium. In addition, calcium phosphate seeds shown a salting-out effect and

enhanced the crystallization process of rare earth phosphates.

Dibrov et al.[86] investigated the crystallization process of rare earth phosphates from WPA produced by Kingisepp, Nevinnomyssk, and Balakovo factories with seed of  $\text{CePO}_4$ . The WPA contains 0.08-0.11 wt% REEs and it is 2-4 times more than the solubility of rare earth ions in WPA which means rare earth phosphates own a high supersaturation. Moreover, the activation energy of crystallization process was reduced from  $119.7 \pm 3.0 \text{ kJ/mol}$  to  $37.3 \pm 1.02 \text{ kJ/mol}$  by adding seeds of  $\text{CePO}_4$ , and the standard Gibbs energy difference was  $-31.1 \text{ kJ/mol}$ . Therefore, about 50% REEs recovery was readily achieved for this method. In addition, thermodynamic calculation illustrated that REEs presented in the form of soluble dihydrophosphates ( $[\text{REE}(\text{H}_2\text{PO}_4)]^{2+}$ ) complexes in WPA. Crystallization processes with rare earth fluorides seeds were also studied[87], and the results shown that the composition of the rare earth crystals depended on the content of seeds (Table. 3).

Table. 3 Composition of crystals with different seeds[83]

Seeds	REO	$\text{P}_2\text{O}_5$	F	$\text{SO}_3$	MgO	CaO	$\text{Sr}_2\text{O}$
Phosphate (wt%)	50.67	27.7	<0.1	5.13	1.24	2.59	5.91
Fluoride (wt%)	66.70	4.40	24.80	0.37	--	2.59	0.56

Crystallization with seeds were generally conducted under temperature range of 60-90°C which makes the apparatus introduction easily and has a relative low energy consumption. However, the crystallized rare earth phosphates or fluorides attached and covered the surface of seeds which results in severely passivation during the crystallization process. Furthermore, preparation of rare earth phosphate seeds requires

---

a preliminary conversion of rare earth phosphates or fluorides into a water-soluble form, and the cost of this process is rather high. However, this method may be attractive if a persistent effective seed were used such as fresh rare earth hydrate-phosphates.

### **2.2.2 Precipitation methods**

Precipitation method has been considered as a simple and economic way for REEs recovery from aqueous solutions. REEs precipitation from WPA is based on the sparingly soluble of rare earth compounds in WPA. According to the constitution of precipitate, precipitation methods can be categorized as: neutralization methods, double sulfate salts methods, and fluoride salts methods.

#### **2.2.2.1 Ammonia neutralization precipitation methods**

In phosphoric acid solution system, weak alkali of ammonia was introduced as the precipitant for REEs precipitation. REEs were reported to co-precipitated in the process of uranium recovery from WPA by partial neutralization with  $\text{NH}_4\text{OH}$  and a concentrate contains 2.5wt% REO, 47.1wt% U was obtained[62]. Zakharova et al.[88] studied the effect of temperature, pH, and presence of impurities on the precipitation process of REEs from WPA with ammonia. Colloidal precipitate of rare earth phosphates was formed (Eq. 2), and 90% lanthanides, 45% Sc, and 29%Y were precipitated when the pH was adjusted to 2.0. Another study[83] achieved fully REEs precipitation by neutralizing the pH of WPA to 3.0 with ammonia and obtained the concentrate contains 1.73–2.30% REO. However, due to the buffer effect of phosphoric acid solution, neutralization with ammonia leads to a large consumption of alkali reagents and the



precipitate formed in this process was difficult to filtrate. Even worse, concentrate obtained from ammonia neutralization method has a low REEs content (<3%REO), it seems to be uneconomic for industrial application. But this method maybe feasible in the case of nitrogen-phosphorus fertilizer production. In the process, ammonia is used to neutralize WPA and REEs can be precipitated via stepwise precipitation at the pH=2.0-2.5.



#### 2.2.2.2 Double sulfates precipitation methods

Method of precipitating REEs in form of double sulfates from aqueous solution has been widely applied in REEs hydrometallurgy because of the poor solubility of rare earth double sulfates even in acidic aqueous solution[89-91]. It has been reported that REEs can present as double sulfates with alkali metal elements and ammonia and their formulas are written as:  $\text{NaREE}(\text{SO}_4)_2$ ,  $\text{NH}_4\text{REE}(\text{SO}_4)_2$ ,  $\text{KREE}(\text{SO}_4)_2$ ,  $\text{RbREE}(\text{SO}_4)_2$ ,  $\text{LiREE}(\text{SO}_4)_2$ ,  $\text{CsREE}(\text{SO}_4)_2$ [92]. Sodium sulfate and sodium chloride were generally used as the precipitant for rare earth double sulfates in terms of their high efficient, easily available, and low-cost[93, 94]. Solubility of REEs in phosphoric acid increases significantly by introducing sulfuric acid, while decreases sharply after sodium compounds were added. Further research demonstrated that REEs can be effectively precipitated from phosphoric acid with 10-15wt% of sulfuric acid in form of Na/K-REE double sulfates (Eq. 3)[95].



---

Lokshin et al.[83] achieved a REEs recovery of 91% by adding 15wt%  $\text{H}_2\text{SO}_4$  with 25-35g/L  $\text{Na}_2\text{SO}_4$  into WPA and produced ~5wt% REO concentrate without washing. The low content of REEs in the concentrate was mainly attributed to the co-precipitation of a large amount of sodium fluosilicates. Therefore, after removal of  $\text{Na}_2\text{SiF}_6$  by sodium compounds, about 19wt% REO in concentrate was obtained. Precipitation efficiencies of REEs from WPA with  $\text{Na}_2\text{CO}_3$  and  $\text{NaCl}$  were also tested.  $\text{NaCl}$  is the optimal precipitant because of the relative high REEs recovery and the shortest crystallization time with the same dosage of sodium. However, even precipitating with  $\text{NaCl}$ , REEs concentrate contains large amount of phosphorus and fluorine. Therefore, A process consisted of distillation and water leaching (Fig. 8) was proposed in order to remove phosphorus and fluorine from concentrate[96]. More than 99% fluorine was removed in form of  $\text{SiF}_4$  by a two stages of distillation and REO concentration in the final concentrate was increased by 3.5 folds.

In summary, precipitation REEs from WPA by double sulfates leads to a high rare earth recovery with  $\text{H}_2\text{SO}_4$  and  $\text{NaCl}$ . However, it is insufficient for the recovery of more valuable HREEs due to the relative high solubility of Na/K-HREE double sulfates. Furthermore, this method requires a condition of 10-15wt%  $\text{H}_2\text{SO}_4$  which may bring significant interference to the production of phosphoric acid.

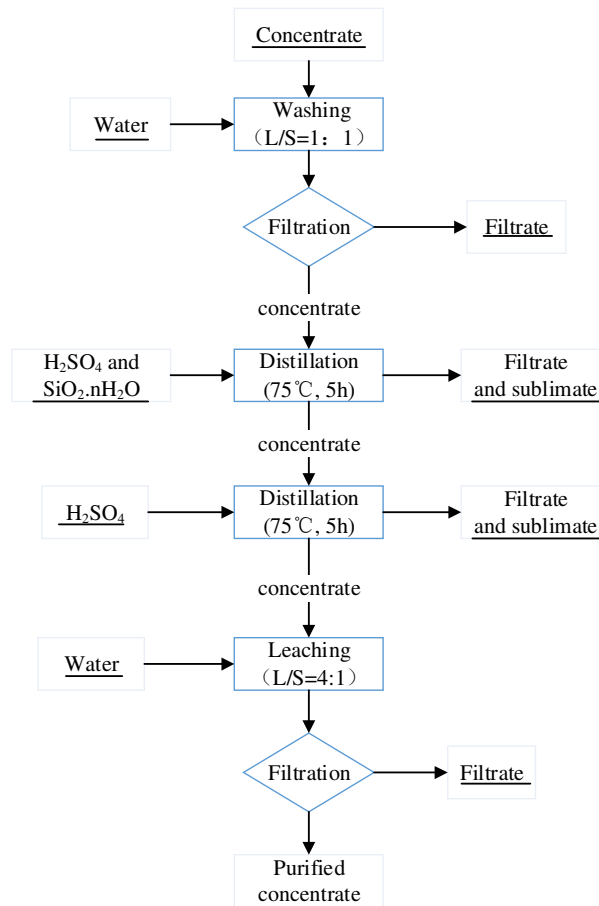


Fig. 8. Treatment flowsheet of the concentrate to remove phosphates and fluorides from REE concentrate[96]

### 2.2.2.3 Fluorides precipitation methods

In aqueous solution, rare earth fluorides have very low solubility products about  $10^{-16}$ - $10^{-20}$  equal to solubility level of  $10^{-2}$ - $10^{-3}$  g/L REO [78, 97, 98]. Even in pure 20wt%  $P_2O_5$  phosphoric acid, solubility of rare earth fluorides located 0.001-0.7 g/L in terms of REO. Therefore, REEs recovery by fluorides precipitation can be achieved when adequate amount of fluorine were added into WPA. It is noticeable that REEs does not precipitate even in the high fluorine concentration WPA since fluorine can form strong complex anions with silicon and some other impurity ions[99]. In this case, extra fluorine is required for REEs precipitation after satisfying the need of all fluoride complex ions formation. Lokshin et al.[100] investigated the precipitation efficiency of REEs from

WPA with various fluorides at 70–75°C and the precipitation efficiency shown an decrease order as  $\text{NaF} > \text{NH}_4\text{F} > \text{NH}_4\text{F} \cdot \text{HF} > \text{HF}$ . However, precipitation efficiency of REEs might reduce with much excess NaF due to the formation of rare earth double fluorides.

In order to achieve high recovery of REEs, a large amount of fluorine ion is required: 19.5g/L  $\text{F}^-$  for 92.8%, 39.0g/L  $\text{F}^-$  for 93.6%, 58.5g/L  $\text{F}^-$  for 97.0%. Thus partial neutralization method with  $(\text{NH}_4)_2\text{CO}_3$  was introduced and 98.8-99.8% REEs recovery was achieved with a low fluorine ion concentration of 10.3-15.4g/L  $\text{F}^-$  under the optimal neutralization ratio  $\alpha = 21\%$  ( $\alpha$  was defined as the molar ratio of amounts of the introduced ammonia and first proton of  $\text{H}_3\text{PO}_4$ ). But partial neutralization also stimulated the precipitation of impurities such as aluminum, iron and calcium and diluted the concentration of REEs in precipitate. In order to increase REEs content in concentrate, deposition time needed to be controlled to 50-60min according to the kinetics study, about 99% recovery and 16.9wt% content of REEs in concentrate were achieved[101]. It has been proved that REEs presented as fluorophosphate compounds in the concentrate obtained by fluoride precipitation from WPA[102]. Therewith a process (Fig. 9) was proposed to recover REEs from the fluorophosphate concentrate. In this process, REEs were extracted by sulphocationite resin through water washing, acid washing and sulfuric acid leaching.

Weterings and Janssen[103] precipitated REEs from both 30wt% and 52wt%  $\text{P}_2\text{O}_5$  phosphoric acid when recovered U by  $\text{NH}_4\text{F}$  with the dispersant of acetone. Then uranium and REEs were concentrated via further treatments (Fig. 10). However, REEs

content in the precipitate is relative low and a costly extra process of impurities removal is required. Besides large amount of excess fluorine introduced in WPA for REEs precipitation was left in acid solution, leading to the interference to WPA production. These two challenges are the key ones that limited the further application of fluorides precipitation methods in industry.

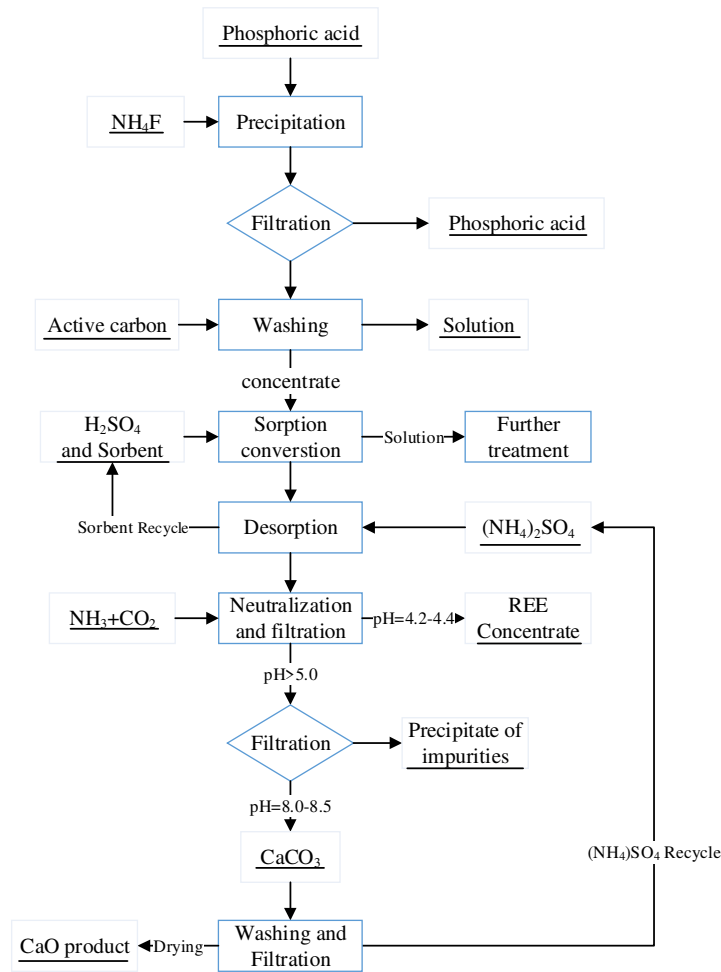


Fig. 9 Technological scheme of REEs extraction from WPA by  $\text{NH}_4\text{F}$  precipitation[101].

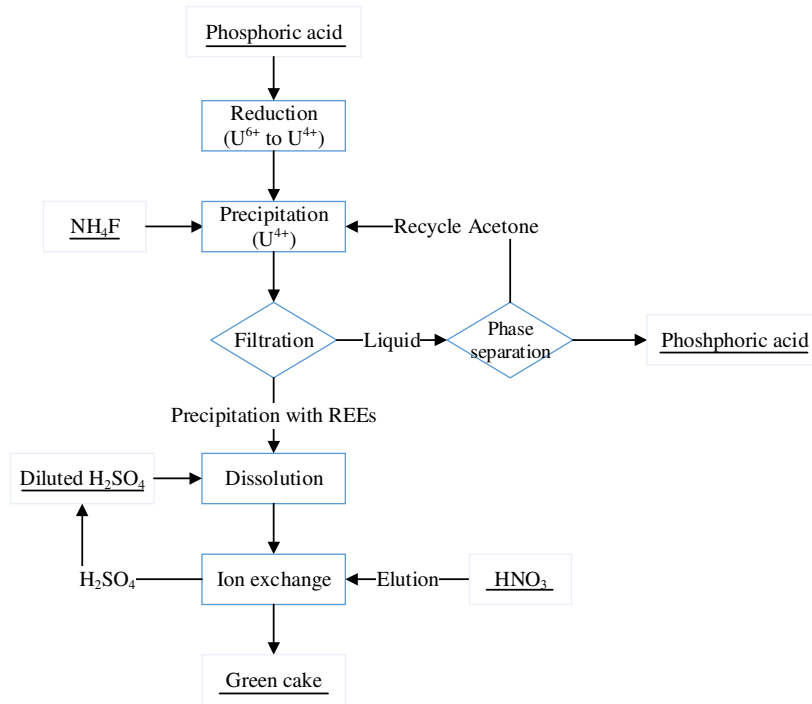


Fig. 10 Process of uranium recovery from phosphoric acid by precipitation[124]

### 2.2.3 Solvent extraction methods

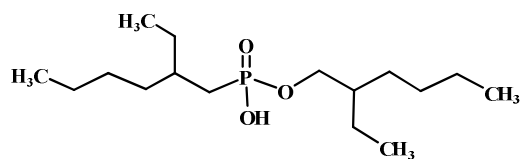
Solvent extraction is the most commonly method for REEs recovery from acidic mineral decomposition solution[18, 104]. Solvent extraction for REEs recovery from bastnasite and monazite are mainly conducted in sulfate, nitrate and chloride solution systems. On the contrast, rare earth containing solutions in apatite processing are phosphate ions dominated aqueous solution system. In phosphate solutions, rare earth ions are poorly soluble and easily to form complexes. Generally, phosphoric acid produced by dihydrate process contains 100~1200ug/g REEs depends on the REEs content in phosphate rocks (Table. 4).

Table. 4 REEs concentration in wet phosphoric acid (WPA) of different district

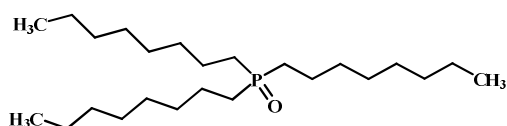
Origin of WPA	Proportion of HREEs	Concentration of REEs	Reference
Florida	75.5%	237.2ug/g	Al-Thyabat[105]
Kola	18.5%	1000~1200ug/g	Lokshin[100]
Annaba (Algeria)	--	115ug/g	Krea[106]

In 1956, part of REEs were reported to co-extracted with uranium(U) by Octyl pyrophosphoric acid (OPPA) from WPA[107]. However, at that period of time, most studies were focused on uranium recovery, while little attention has been paid to REEs recovery. Until 1990s, series of research begun to focus on simultaneous recovery of REEs and uranium[106, 108, 109], rare earth recovery alone[110], and individual rare earth separation from phosphoric acid[111-114]. During this period of time, lots of extractants, especially, organic-phosphorus based extractants were introduced in such as di- (2-ethylhexyl ) phosphoric acid (D2EHPA/TOPS-99), tri-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO), bis(2,4,4-tri-methyl pentyl)di-thiophosphinic acid (Cyanex301), bis(2,4,4-trimethyl pentyl) phosphoric acid (Cyanex272), 2-ethyl hexyl 2-ethyl hexyl phosphonic acid (PC-88A), mono-octyl phenyl phosphoric acid (MOPPA), di-octyl phenyl phosphoric acid (DOPPA), di-nonyl phenyl phosphoric acid (DNPPA), di-dodecyl naphthalene sulfonic acid (Nacure1052), Cyanex923 (a mixture of four trialkyl-phosphine oxides) etc. (Table. 5).

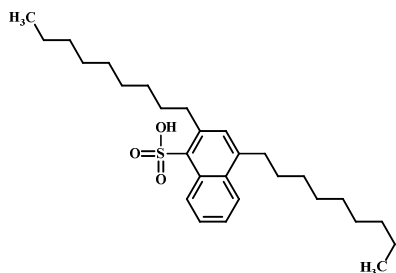
Table. 5 Structures of REEs extractants used in phosphoric acid solutions



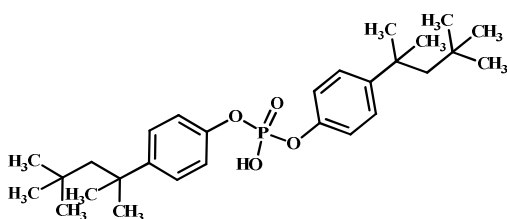
PC-88A



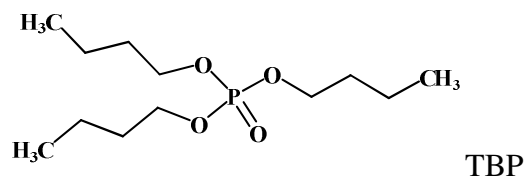
TOPO



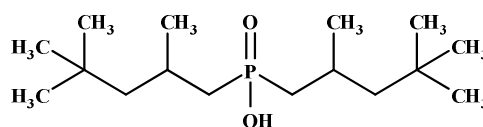
Nacure 1052



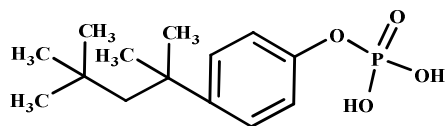
DOPPA



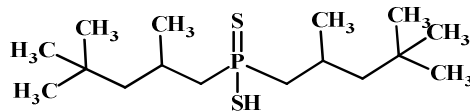
TBP



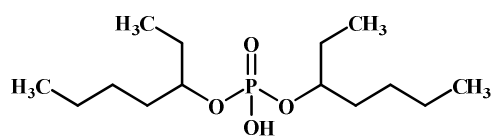
Cyanex 272



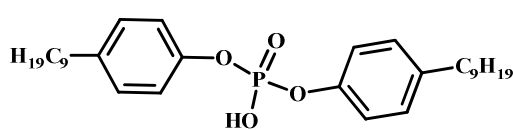
MOPPA



Cyanex 301



D2EPHA



DNPPA

Simultaneous extraction of REEs and U was considered as a promising method because of their similar distribution behavior during the solvent extraction process. Bunus used mixture solvent of D2EHPA+TBP/TOPO diluted in kerosene to extract U and REEs from WPA and achieved remarkable synergistic effect for uranium extraction and



considerable extraction efficiency for REEs. Therefore, an one-cycle extraction process valid for both WPA and phosphonitric acid solutions (leaching solution obtained by decomposing phosphate rocks with nitric acid) was proposed (Fig. 11). In this process, REEs and U were extracted by D2EHPA+TBP and separation of REEs from U was achieved via selective stripping with 7-15% HF solution. However, part of REEs was left in organic phase after REEs stripping and entered in green cake that requires an extra complex process for REEs removal and enrichment (Fig. 12). Furthermore, the one-cycle extraction process is insufficient for the extraction of light rare earth elements (LREEs) from WPA.

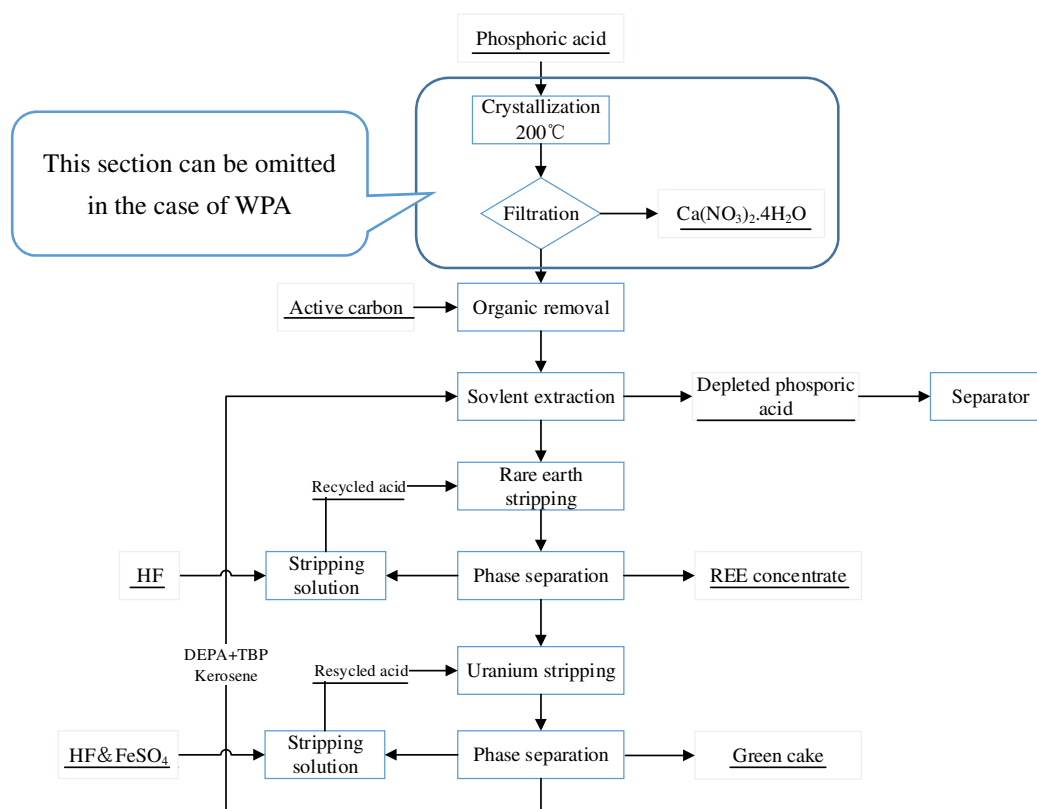


Fig. 11 Flowsheet of the one-cycle extraction-stripping process with D2EHPA+TBP for simultaneous extraction of uranium and REEs[108]

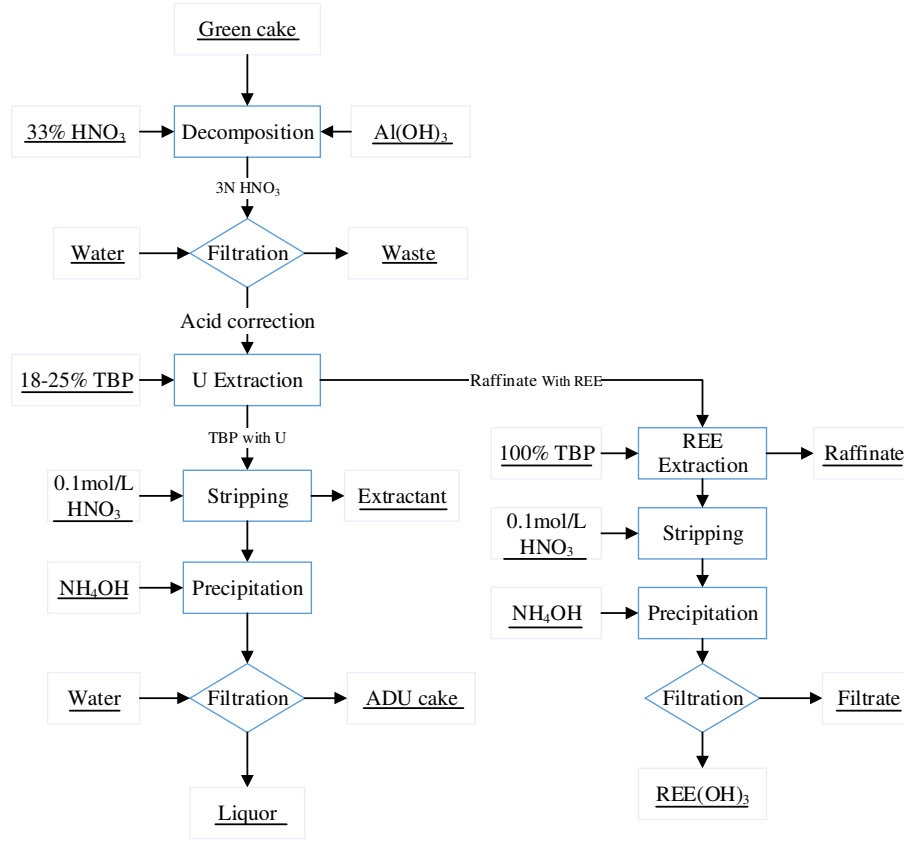
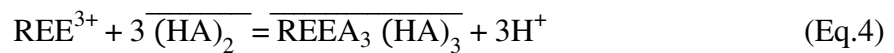


Fig. 12 Process for rare earths separation from green cake[109]

Uranium and REEs can also be extracted simultaneously from phosphoric acid solutions with D2EHPA alone[115]. For example, in 28wt%  $P_2O_5$  WPA, the distribution coefficients of HREEs (Tb-Lu) ranged from 1 to 100 and 3.2 for U (VI)). While efficiencies of LREEs (La-Sm) were less than 0.1. REEs extraction with nonyl phenyl phosphoric acid (NPPA) from WPA shows a similar discipline. Later studies carried by Wang et al.[73, 110] also indicated that only HREEs can be efficiently extracted by D2EHPA under such a of high concentration phosphoric acid (>28wt%  $P_2O_5$ ). Which can be attributed to the high acidity of WPA. Normally, the extraction equation of acidic extractants for rare earth elements can be defined as:



Where HA=acidic extractants. The distribution coefficients of rare earth ions is defined as:

$$D = \frac{[\overline{\text{RE}^{3+}}]}{[\text{RE}^{3+}]} = K_{\text{ex}} \frac{[\text{HA}]^3}{[\text{H}^+]^3} \quad (\text{Eq.5})$$

and the equilibrium constant can be shown as:

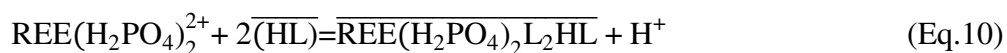
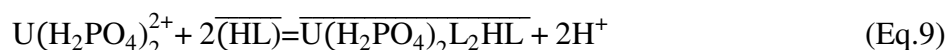
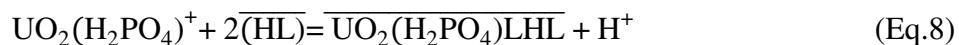
$$K_{\text{ex}} = \frac{[\overline{\text{RE}^{3+}}] \times [\text{H}^+]^3}{[\text{RE}^{3+}] \times [\text{HA}]^3} \quad (\text{Eq.6})$$

$$\text{then,} \quad \log D = \log K_{\text{ex}} + 3 \log [\overline{\text{HA}}] + 3 \text{pH}. \quad (\text{Eq.7})$$

According to equation Eq. 7, distribution coefficients of REEs with acidic extractants increases with increasing value of pH and concentration of extractants. But, a high concentration of extractants increases the viscosity of organic phase, and slow down the speed of mass transfer. In addition,  $\text{Fe}^{3+}$  concentration has significant negative effect on the extraction process of REEs with D2EHPA because of its competitive coordination with D2EHPA[79, 110].

However, industrial scale pilot experiments done by Solvay in the late 1970s to the beginning of the 1980s demonstrated that the mixture of D2EHPA+TOPO cannot efficiently recover REEs under the conditions for effective uranium extraction[63]. while mixture of DOPPA+TOPO is a potential extractant for REEs and U simultaneous recovery from WPA. Extraction Characteristics of REEs and U with DOPPA from phosphoric acid solution (after removing the organic matter) was tested in the presence

and absence of TOPO[106]. High extraction efficiencies of La 71%, Y 93%, U (IV) 100%, U (VI) 86% were achieved with 0.5mol/L DOPPA alone from WPA. REEs and U were extracted in a form of complexes with  $(\text{H}_2\text{PO}_4)^-$  ion according to equations of (Eq. 8), (Eq. 9), and (Eq. 10).



Where HL= DOPPA. Significant synergistic effect of DOPPA +TOPO for rare earth elements and uranium observed only under a low DOPPA concentration ranged from 0.1 to 0.3mol/L. However, no synergistic effect was observed at the optimal concentration of 0.5mol/L DOPPA.

Mixture of DNPPA+TOPO was used for Y and U extraction from merchant grade phosphoric acid solution (MGA) whose concentration is about 54-55% $\text{P}_2\text{O}_5$ [116]. The optimum extraction efficiency was obtained at a mixture of 0.6mol/L DNPPA+ 0.3mol/L TOPO, and the loading capacity for U and Y are 0.65g/L and 1.13g/L respectively. Further study[117] demonstrated that 10%  $\text{Na}_2\text{SO}_4$ +30%  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  (30–40%) were effective for yttrium separation from uranium from the organic phase. High purity yttrium oxide was produced by oxalate precipitation, hot water washing, and calcination (Fig. 13).

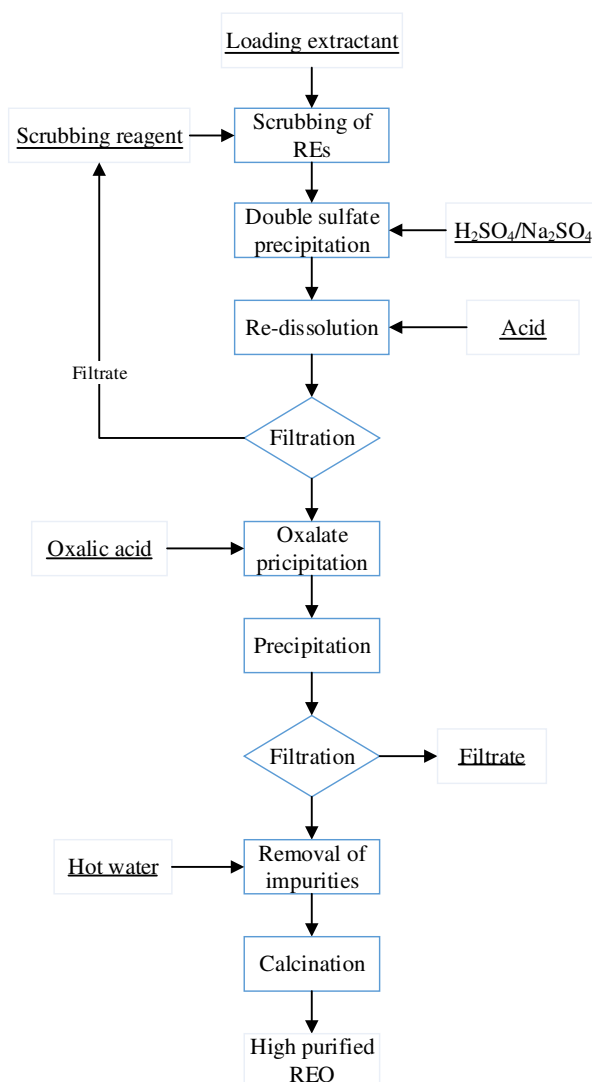


Fig. 13 Conceptual flow-sheet for REEs recovery from MGA and WPA by DNPPA + TOPO and D2EHPA + TBP processes respectively[117].

TOPS-99 (D2EHPA), PC-88A, Cyanex272, and the mixture of PC-88A+Cyanex 301 were used for individual element separation and grouping of REEs from phosphoric acid solutions[111-114]. The extraction efficiencies of these extractants for REEs from phosphoric acid solutions show a decreasing order of TOPS-99 > PC-88A > Cyanex272. The solvent extraction processes of these extractants were considered as the acidic extraction mechanism which was shown as Eq. 4. Therefore, high acidity of WPA reduces the extraction efficiency of the acidic extractants for REEs. PC-88A and

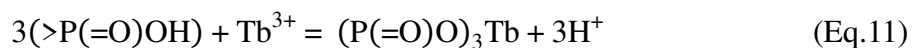
Cyanex272 were studied in individual REEs separation from diluted phosphoric acid solutions. As a matter of fact, TOPS-99 was the only effective extractant for extracting part of REEs from WPA in which concentration of  $\text{H}_3\text{PO}_4$  ranges from 4 to 6mol/L. Considerable extraction efficiencies of HREEs (more than 70%) were achieved in a single stage with 1 mol/L TOPS-99 and no LREEs extraction was observed. For this reason, TOPS-99 was considered as a promising extractant for HREEs or yttrium separation from WPA.

In summary, solvent extraction is a potential effective method for REEs recovery from WPA, moreover, it seems to be promising to simultaneously recover REEs and U, then separated REEs from U via selective stripping in a single process. But challenges still present such as contradiction of the optimal extraction conditions between REEs and U from WPA, inefficiency of LREEs extraction, extra process for REEs separation from U (green cake), and loss of organic phase caused by the large volume of WPA. Hence, further research is needed to seek better extractants for REEs extraction and selective recovery of REEs and U from WPA.

#### **2.2.4 Ion exchange methods**

Ion exchange method using polystyrene resins with phosphinic acid functional ligands has been proposed to recover REEs from phosphoric acid[118, 119]. Research group of Indian Institute of Chemical Technology studied the extraction efficiencies of Tulsion CH-90, Tulsion CH-93[113], Tulsion CH-96, and T-PAR[120] resins for REEs recovery from phosphoric acid. The sorption mechanism of REEs with Tulsion CH-96 depends on the concentration of phosphoric acid. At low phosphoric acid concentrations (0.01-

1mol/L  $\text{H}_3\text{PO}_4$ ), rare earth ions were adsorbed by resin via cation exchange (Eq. 11) and rare earth ions followed the coordination mechanism (Eq. 12) at high phosphoric acid concentration (2-5mol/L  $\text{H}_3\text{PO}_4$ ). Unfortunately, recovery of REEs with these resins from 4-6mol/L  $\text{H}_3\text{PO}_4$  were less than 40%.



Where  $>\text{P}(=\text{O})\text{OH}$  represents the resin.

Al-Thyabat and Zhang[105] recovered REEs from WPA produced by Florida phosphoric acid plant with DOWEX-50WX4 and DOWEX-50WX8 resins. In the study, the increasing dosage of resin increases the extraction efficiencies of rare earth ions and reduces the distribution efficiencies of impurities ( $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ), and the dosage of resin should be more than 5g/kg WPA to guarantee sorption capacity for impurities and REEs. However, the high affinity of resins for iron and aluminum would hinder the sorption of REEs, hence, it was suggested to precipitate these impurities before REEs extraction. Ion exchange method was considered as insufficient for REEs recovery from WPA due to the relative low adsorption efficiency that was less than 60%. While, this method would be promising once a resin with high selectivity and free of high acidity were introduced

For REEs recovery from WPA, methods of crystallization, precipitation may be difficult to develop their applications in industrial scale if no subversive progress were made to avoid the issues of energy consumption and impurities involvement. With regard to ion

exchange was insufficient for the extraction of REEs (REEs recovery < 60%) from WPA currently, while it would be a promising way once a resin with high selectivity and free of high acidity were used. Solvent extraction method was taken as the potential promising method due to its good overall performance.

### 2.3 Recovery of REEs from evaporation sludge

Evaporation sludge is one important byproduct in the dihydrate process. The sludge is generated during the concentration process of phosphoric acid from 28-30wt%  $P_2O_5$  to 54wt%  $P_2O_5$ . In which process most of REEs contained in WPA will be precipitated and enriched into sludge and the REO content is about 0.1-8% depends on the composition of apatite [65, 105]. Preston et al. [65] leached the sludge with 4mol/L  $HNO_3$  and 2mol/L  $H_2SO_4$  at ambient temperature for 48h, the recovery of neodymium were 40% and 20%, respectively. Furthermore, high leaching efficiencies of Nd about 76-78% in one cycle was obtained by 1.1mol/L  $HNO_3$  with the addition of 0.5mol/L  $Ca(NO_3)_2$ . Since  $Ca(NO_3)_2$  reduces the concentration of fluoride ion released by fluorosilicates and prevent it binds with REEs to form of rare earth fluorides precipitate (Eq. 13, Eq. 14). A technical flowsheet was proposed for REEs recovery from sludge (Fig. 14), in this process, sludge went through water washing and  $HNO_3$  leaching and REEs were recovered by solvent extraction with TBP and oxalate precipitation. Further research [64, 66, 67] shown that high purity products of Ce, Nd, Eu were produced via solvent extraction. Al-Thyabat and Zhang [105] recovered 58.1% REEs from evaporation sludge produced by Florida WPA plant via leaching with 7.2 mol/L  $HNO_3$ .





In conclusion, Recovery of REEs from evaporation sludge is of significance because of the high REEs content and environmental issue caused by storage. However, further understanding about the phase of REEs presented in sludge and the leaching mechanism of REEs from sludge with mineral acids are needed for optimizing the recovery of REEs from the sludge.

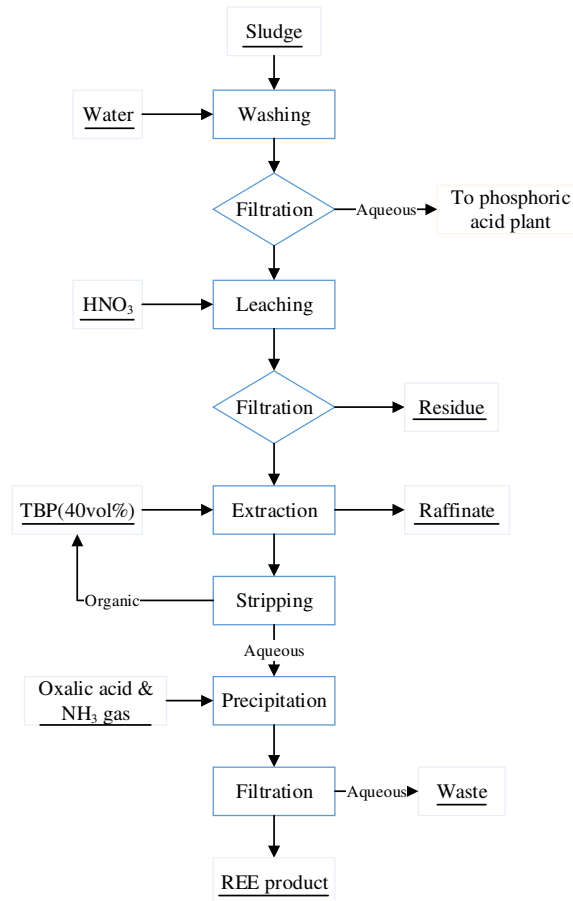


Fig. 14 Technological flowsheet for rare earth elements recovery from evaporation sludge[65]

## 2.4 Recovery of Rare earth elements from phosphogypsum

Phosphogypsum is another important byproduct in  $\text{H}_2\text{SO}_4$  processes. Generally, phosphogypsum presents in two forms: dihydrate phosphogypsum (PDH) and hemihydrate phosphogypsum (PHH) according to the degree of hydration of calcium sulfate. Generally, 4-5 tons of PDH are produced for each ton of phosphoric acid production. So far, more than billion tons of PG has been produced and mostly stockpiled on land all over the world, leading to landfill problems[121]. Furthermore, severe environmental issues were resulted in due to the up-taken impurities such as radioactive elements of  $^{235}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ [122, 123] and heavy metals of Cd, Ni[124]. These elements might percolate into groundwater, soils and cause contaminations during the long-term storage[125, 126]. Even worse, an estimated annually worldwide increase of 200-280 tons PG aggravates these challenges[124, 127-129]. In addition, some phosphoric acid plants in Morocco, Tunisia, South Africa and Mexico directly pour PG into the ocean[130].

In order to utilize the huge amount of PG, plenty of research have focused on transferring PG into building materials (such as cement, concrete, plaster), ammonia sulfate fertilizer, and soil amendments in the past decades[131-135]. And these utilizations require a restriction content of impurities and radioactive elements in products. From another point of view, impurities contained in PG such as rare earth elements and the radioactive elements make PG a secondary resource (Table.6). Therefore, recovery of REEs would be more feasible when combined with the utilization of PG in building materials or other applications.

General processes for REEs recovery from PG include the leaching of REEs from PG with HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and extraction of REEs from leaching solution via precipitation, solvent extraction, ion exchange methods. Recently, some researchers investigated the leaching efficiencies of REEs from PG with organic liquids.

Table. 6 Content of rare earth elements in typical phosphogypsum

Original	Country	Type	REO content	References
Voskresensk Mineral Fertilizers OAO*	Russia	PDH	0.47wt%	Lokshin et al. [136]
Metakhim OAO	Russia	PHH	0.40-0.43wt%	
Ammofos OAO	Russia	PHH	0.585wt%	
Voskresensk Mineral Fertilizers OAO	Russia	PHH	0.59wt%	
Balakovo Mineral Fertilizers OAO	Russia	PHH	0.574wt%	
Kovdor	Russia	PHH	~0.11wt%	Kybartiene et al.[137]
Kirovsk	Russia	PHH	~0.46wt%	
Brazilian WPA plant	Brazil	PDH	0.52-0.54wt%	Santos et al.[138]
Blakovskie	Russia	PDH+PHH	0.3-0.9wt%	Samonov et al.[139]
Abu-Zaabal Company	Egypt	PGF*	0.048wt%	Ismail et al.[140]
Abu-Zaabal Company	Egypt	PDH	0.022wt%	Kouraim et al.[141]
Agrium Fertilizer plant	Canada	PDH	0.02wt%	Walawalkar et al.[127]
Florida WPA plant	America	PDH	0.034wt%	Al-Thyabat et al.[105]
Sfax stockpiles	Tunisia	PDH	0.022wt%	Hammas-Nasri et al.[142]
Wizów	Poland	PDH+PHH	0.11-0.65wt%,	Rzeczycka et al.[143-145]

\*OAO: Open Joint-Stock Company, PGF: phosphogypsum fertilizer, similar to PDH.

### 2.4.1 Recovery of REEs from dihydrate phosphogypsum

In the 1980s, European researchers (including the Soviet Union, Poland, Belgium, German, etc.) have carried on a large number of investigations on REEs extraction from PDH[62, 146]. However, this issue has been laid aside for a period of time since the technical and economic reasons. until recently, due to the increasing REEs demand and environmental issue of PDH, REEs recovery from PDH has received growing attention.

In PDH, REEs content ranges from 0.01-0.40wt%, and they are mainly presented in form of isomorphous substitution by the scheme of Eq.15[147]. Isomorphous substitution of  $\text{Ca}^{2+} + \text{SO}_4^{2-}$  by  $\text{REE}^{3+} + \text{PO}_4^{3-}$  and the presence of Sr-REE sulfates in PDH were also reported[139, 148]. In addition, Shivaramaiah, et al.[149] demonstrated that REEs may be presented as a poorly crystalline nanophase or amorphous form adsorbed on the surface of PDH. It is noted that the deposition form of REEs in PDH has a decisive effect on the leaching efficiency of REEs from PDH.



#### 2.4.1.1 Leaching REEs from PDH with $\text{H}_2\text{SO}_4$

For leaching of REEs from dihydrate phosphogypsum with  $\text{H}_2\text{SO}_4$  under normal lab conditions, low leaching efficiencies range from 12% to 40% were attained (Table. 7). It has been established that it is impossible for REEs be completely liberated and passed into aqueous solution from PDH unless the lattice of PDH was deconstructed[62]. Lokshin et al.[147] pointed out that rare earth presented as independent compounds are easily to be leached with sulfuric acid, while rare earth ions incorporated in the lattice

---

of gypsum are difficult to release. And the key obstacle of leaching REEs from PDH is the inefficient diffusion of proton, sulfate ion, and rare earth ions between layers of calcium sulfate crystals which are tightly bound by calcium ions. Walawalkar et al.[127] attributed that to the low solubility of gypsum in  $\text{H}_2\text{SO}_4$  solution caused by the common-ion effect.

In order to enhance the leaching efficiency of REEs from PDH with  $\text{H}_2\text{SO}_4$ , Kijkowska et al.[150] decomposed PDH with a high liquid/solid ratio (up to 10ml/g) and high REEs leaching efficiency up to 72% was achieved. Al-Thyabat et al.[105] digested the PDH produced by Florida plant with the mixture of concentrated sulfuric acid and phosphoric acid, 49% of REEs leaching efficiency was obtained. On the other hand, Todorovsky et al.[146] introduced the mechanoactivation method to reinforce the leaching process of REEs from PDH. Hammas-Nasri et al.[142] proposed a two-step  $\text{H}_2\text{SO}_4$  leaching process (Fig. 15) to concentrate REEs and purify anhydrate gypsum. Lokshin et al.[147] leached PDH with sulfuric acid for about 3025h under the  $\text{L/S}=2:1$ , leaching efficiency of REEs was increased by 3 times compared with the case of 1h under the same conditions.

Table.7 Leaching efficiency of REEs with various acids from PDH

Origin	Leaching time	L/S ratio	[H <sub>2</sub> SO <sub>4</sub> ]	Efficiency	REO (in PDH)	References.
Private Joint Stock Company 'Ammofos'	-	-	26wt%	12%	0.439wt%	Lokshin et al.[151]
			4wt%	33.5%		
Poland	-	1-2:1	9.2wt%	19.5%	-	Kijkowska et al.[150]
		1-2:1	21.4wt%	39.5%		
		10:1	4.8-30wt%	72.5%		
Agrium Fertilizer plant	2h	8:1	1.5 mol/L <sup>†</sup>	57%	0.020wt%	Walawalkar et al.[127]
			1.5 mol/L <sup>§</sup>	51%		
			1.5 mol/L	23%		
Abu-Zaabal Company	8h	1:1	2 mol/L <sup>†</sup>	46%	0.022wt%	Kouraim et al.[141]
			4 mol/L <sup>§</sup>	30%		
			4 mol/L	30%		
Abu-Zaabal Company	3h	2:1	3 mol/L <sup>†</sup>	43.3%	0.048wt%	Ismail et al.[140]
			2 mol/L <sup>§</sup>	11.9%		
			4 mol/L	12.5%		
Gemol'sk	>0.75h	-	5-20wt%	≤30%	0.60wt%	Lokshin et al.[152]
Private Joint Stock Company 'Metakhim'	1h	2:1	4wt%	17.2%	0.414wt%	Lokshin et al.[147]
	3025h for 19 stages	2:1	4wt%	68.2%		
			3wt%	60.9%		
			2wt%	60.5%		
			1wt%	56.6%		
			0.5wt%	57.1%		

Note: where <sup>†</sup> represents the concentration of HNO<sub>3</sub>, <sup>§</sup> represents the concentration of HCl

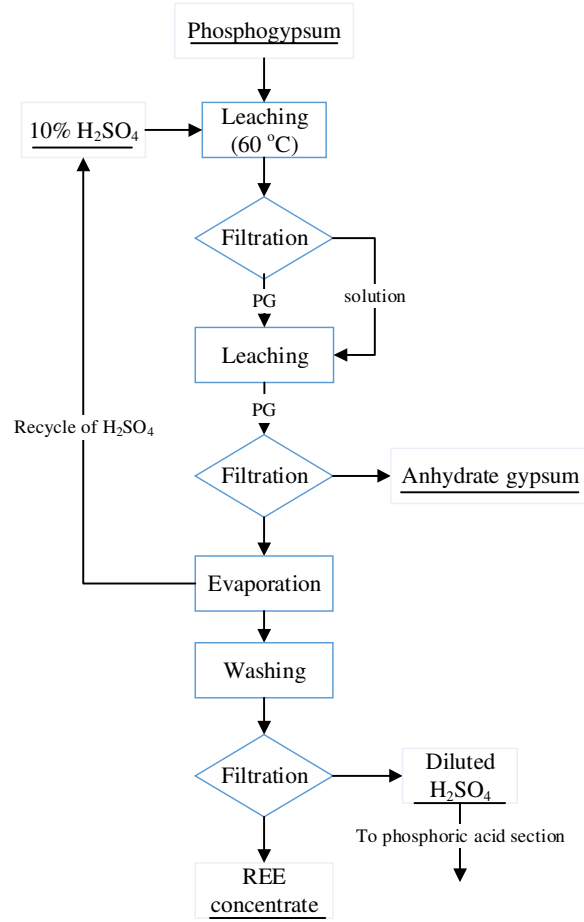


Fig. 15 Process for Tunisian PG purification and REEs recovery[142]

#### 2.4.1.2 Leaching REEs from PDH with HCl and HNO<sub>3</sub>

Similar to the case of leaching process with H<sub>2</sub>SO<sub>4</sub>, the leaching efficiency of REEs from PDH with HCl was lower than that with HNO<sub>3</sub> (Table. 7). One explanation attributes that to the relative low solubility of calcium sulfate in HCl solution due to the salt out effect[127]. On the other hand, Ismail et al.[140] demonstrated that REEs were partially precipitated into residue after being leached in the form of rare earth fluorides (Eq. 16, Eq. 17).



Compared with  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ,  $\text{HNO}_3$  seems to be the most efficient mineral acid for REEs leaching from PDH due to the relative higher solubility of  $\text{CaSO}_4$  in  $\text{HNO}_3$  solution [127, 140]. The leaching efficiency of REEs with  $\text{HNO}_3$  is ranged from 40-50% with low L/S ratio. It is notable that in the case of leaching REEs from Egypt PDH with 2mol/L  $\text{HNO}_3$  for 8h, the leaching efficiency of REEs increased with increasing L/S ratio below  $\text{L/S} < 3$  and decreased with increasing L/S ration after  $\text{L/S} > 3$  [141]. Similar pattern was obtained from the study of temperature effect since the leached REEs were partially precipitated with free fluoride ion in leaching solution (Eq. 14) [140].

High leaching efficiency of REEs up to 93.1% was achieved by 15wt%  $\text{HNO}_3$  with  $\text{L/S}=10:1$  [153]. Under the condition of high L/S ratio, leaching efficiency of REEs increases with increasing concentration of  $\text{HNO}_3$  until the concentration reached 15wt%, then the efficiency goes down gradually with continuous increasing concentration of  $\text{HNO}_3$ . While, in the case of leaching process of PDH produced by Agrium Fertilizer plant, increase of  $\text{HNO}_3$  concentration from 1.5mol/L to 3mol/L only slightly improve the leaching efficiency of REEs about 6%, but the efficiency of calcium was increased significantly about 29% [127]. Effects of additives of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$  shown that only  $\text{Ca}(\text{NO}_3)_2$  has remarkable improvement on leaching efficiency [140, 141].

#### **2.4.1.3 Leaching REEs from PDH with organic liquid**

Recently, a method using organic matters as leaching agent was proposed for REEs recovery from PG treatment. The goal of the process was to remove the radioactive materials and hazardous metals such as  $^{226}\text{Ra}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , Cd, Cr, etc. from PG, while,



REEs contained in PG were recovered at the same time[154-156]. El-Didamony et al.[155, 156] purified PG by removing radioactive elements with organic solution of TBP, TOPO, and mixture of TBP and TOPO in kerosene. Removal efficiencies of 65.6-72.8% for radioactive elements and recovery of 68.5% for total rare earths were achieved by leaching PG with 0.5M TBP with a ratio of organic/solid=1mL/g for 2h at 55°C. And, the removal efficiencies can be enhanced by two successive steps leaching, while, a third step did not bring any further improvement. Moreover, in the case of two successive steps of mixture of 0.7mol/L TBP and 0.9mol/L TOPO, better results can be obtained. Furthermore, the highest removal efficiencies up to 83.4-94.6% and recovery of TREEs of 80.1% were achieved by treating PG with hot solution of Na<sub>2</sub>CO<sub>3</sub> (0.5mol/L) before leaching with TBP–TOPO in kerosene. Reinforcement effect was also observed when leaching REEs from PG with HNO<sub>3</sub> and HCl solutions with the addition of nonyl phenol ethoxylate (NPE)[157]. Even though relative high recovery of REEs was achieved by organic leaching process, the loss of organic reagent that adsorbed and entered into gypsum may lead to significant cost and environmental issues.

#### **2.4.2 Recovery of REEs from PHH**

In Hemihydrate process, over 90% of REEs pass into PHH and the REEs content in PHH is higher than that in PDH, up to 0.3-0.6wt% [158], furthermore, REEs presented in PHH are enriched with yttrium group[153]. Due to the elevated decomposition temperature and phosphorus concentration, REEs in PHH mainly deposited as independent phases which have been proved as REEPO<sub>4</sub>·xH<sub>2</sub>O and REEs-alkali metals double sulfates [9, 10]. The former compound possibly presents as two forms, one is

amorphous precipitate formed by the re-precipitation of rare earth ions from the leaching solution with phosphate ions[149], the other is monazite(or xenotime, allanite) inclusions originated from the undecomposed minerals[137, 138]. It is easy to dissolve the re-precipitate phosphates and double sulfates of REEs by mineral acids, while the monazite phase is difficult to decompose [137, 159]. Leaching REEs from PHH with sulfuric and nitric acid have been systematically studied.

#### **2.4.2.1 Leaching REEs from PHH with H<sub>2</sub>SO<sub>4</sub>**

In the case of recovering REEs from PHH with H<sub>2</sub>SO<sub>4</sub>, there are several challenges need to pay specific attention.

(1) REEs might be reprecipitated by phosphate ions released from PHH and hindered the leaching of REEs during the leaching process. Lokshin et al.[75] leached PHH with 6wt% H<sub>2</sub>SO<sub>4</sub> for 4 cycles, significant phosphorus accumulation in leaching solution and sharp decrease of REEs recovery were observed. Fortunately, the solubility study of REEs in sulfuric-phosphoric acid solution suggests that solubility of REEs decreases with increasing concentration of phosphoric acid and increases with the increasing concentration of sulfuric acid[95]. Hence, it is possible to enhance the leaching efficiency of REEs by increasing the concentration of H<sub>2</sub>SO<sub>4</sub>.

(2) Secondly, REEs might form poorly soluble double sulfates with sodium or potassium dissolved from PHH in sulfuric acid solution. Furthermore, due to the common-ion effect precipitation of double sulfates of REEs get more stable with increasing concentration of sulfuric acid[75]. Significant reduction of REEs recovery

was observed with increasing concentration of  $\text{Na}_2\text{O}$  added into the leaching system of PHH with sulfuric acid[160]. Furthermore, a contradiction between REEs recovery and REEs concentration in leaching solution was presented that once high recovery of REEs (up to 84%) from PHH was obtained, the concentration of REO in leaching solutions did not exceed 1g/L even under optimizing conditions. Higher concentration of REO (more than 3g/L) was achieved, but the leaching efficiency of REEs dropped to 30-40%[161]. Lokshin et al.[160] accounted the contradiction for the transfer process of REEs from PHH to leaching solution which is consisted of two reactions: (1) dissolution of  $\text{REPO}_4 \cdot x\text{H}_2\text{O}$  from PHH into leaching solution, and (2) precipitation of double sulfates of  $(\text{Na/K})\text{REE}(\text{SO}_4)_2$ . The effect of leaching time on recovery of REEs from PHH with  $\text{H}_2\text{SO}_4$  illustrated that the maximum REEs recovery, up to 96.4%, was achieved at 25min.

Therefore, increasing the concentration of sulfuric acid accelerate both the dissolution of REEs from PHH and the re-precipitation of REEs from leaching solution. In fact, the maximum solubility of  $(\text{Na/K})\text{REE}(\text{SO}_4)_2$  was achieved with 10-12wt% sulfuric acid[95]. Hence, in the perspective of preventing double sulfates precipitation of REEs, diluted  $\text{H}_2\text{SO}_4$  is preferred for leaching REEs from PHH.

(3) It is not impossible for REEs precipitated as fluorides during the leaching process because fluoride ions original from fluorosilicates can bind rare earth ions into sparingly soluble fluorides[75]. However, according to the calculation results that free fluorine in leaching solution is far less than the solubility of  $\text{REEF}_3$  in sulfuric acid solution, this problem may arise after several cycles leaching stages.

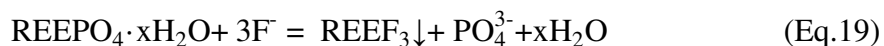
(4) In PHH, REEs mainly present in form of amorphous hydrated phosphates whose solubility depends on the degree of hydration (the value of  $x$  in  $\text{REEPO}_4 \cdot x\text{H}_2\text{O}$ ) [77]. In turn, the degree of hydration of  $\text{REEPO}_4 \cdot x\text{H}_2\text{O}$  is determined by the temperature of apatite decomposition process. For example, solubility of REE hydrated phosphates in sulfuric acid solution decreases remarkably by raising temperature from 75 to 90°C. But the reaction temperature is somewhat different in various hemihydrate phosphoric acid plants.

In order to recover REEs from PHH, a lot of attempts aiming at solving these challenges have been done in the past decades. At the end of 1980s, attention began to be paid on REEs recovery from PHH in Poland. REEs were leached by relatively high concentration sulfuric acid about 50wt%  $\text{H}_2\text{SO}_4$ , and then separated from aqueous solution via precipitation and solvent extraction methods (Fig. 16, Fig. 17) [162, 163]. Kowalski et al. [164] proposed a process which used PHH as raw material for anhydrate cement production while recovered REEs at the same time (Fig. 18). In the process, REEs were leached from PHH with sulfuric acid, then subjected to concentration and enriched into precipitate.

Lokshin et al. [165] put forward a comprehensive flowsheet for REEs recovery from PHH (Fig. 19). In the process, REEs were leached from PHH with 20-24wt%  $\text{H}_2\text{SO}_4$  solution followed by the crystallization of rare earth sulfates under the condition of  $\geq 30\text{wt}\%$   $\text{H}_2\text{SO}_4$ . Then REEs were concentrated in nitrate solution, up to 137g/L REO, by transferring REE sulfates with 105% stoichiometrically  $\text{Ca}(\text{NO}_3)_2$ .

As demonstrated above that REEs presented in form of  $\text{REPO}_4 \cdot x\text{H}_2\text{O}$  in PHH and the

solubility depends on the value of x. For example, REEs in PHH produced by Balakovo Mineral Fertilizers OAO is more easily leached by mineral acid than which is from Ammofos OAO (Russian plants) because of the higher degree of hydration[76]. In addition, Lokshin et al.[77] pointed out that REEs would be more difficult to be leached out after being stored for a long time because the synthesized amorphous rare earth phosphates gradually transferred to crystallization form during the “ageing”. However, during the storage of PHH with the presence of fluorosilicates, rare earth phosphates can be transferred into rare earth fluorides which are more soluble than phosphates in sulfuric acid solution (Eq.18, Eq.19). But, the rare earth fluorides transformation requires keeping PHH under the humid atmosphere for a long period of time.



In order to shorten the leaching time, Lokshin et al.[76] proposed a method that added NaF to activate the leaching of low hydrated rare earth phosphates from PHH produced by Ammofos OAO. A high recovery of REEs up to 69.0% was achieved after 6h leaching with the addition of 1.125 g/L NaF in 8wt% sulfuric acid solution.

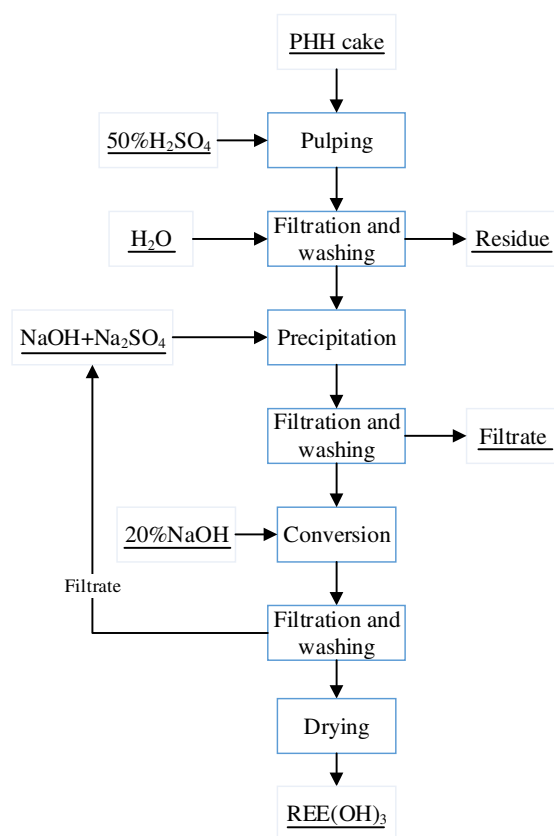


Fig. 16 Flowsheet of precipitation method for REEs recovery from PHH[162]

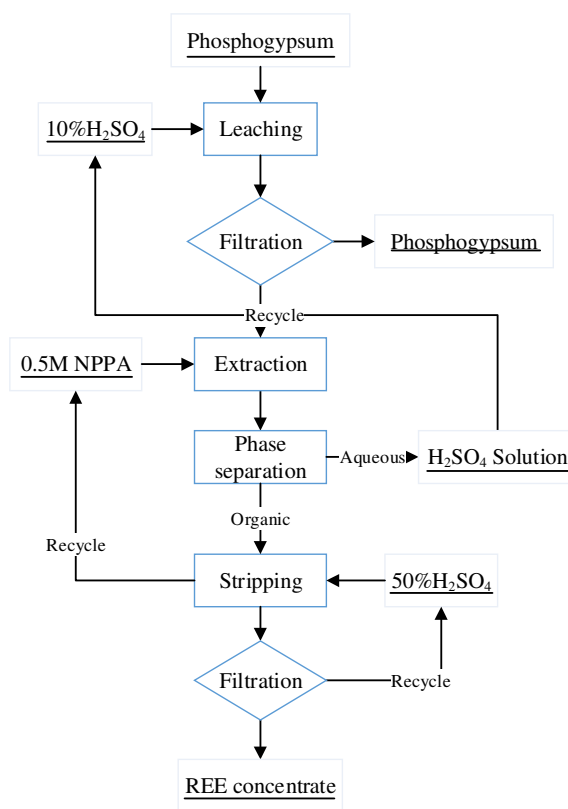


Fig. 17 Flowsheet of solvent extraction method for REEs recovery from PHH[162]

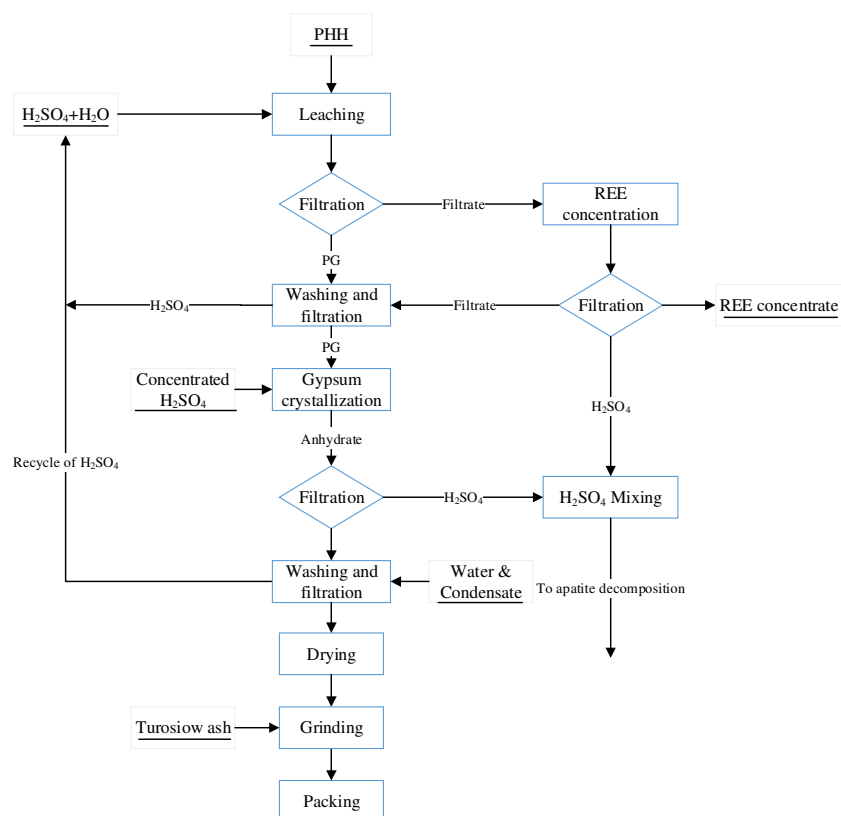


Fig. 18 Flowsheet for waste-free processing of PG from apatite into REE concentrate and anhydrite cement with total  $P_2O_5$  recovery[164]

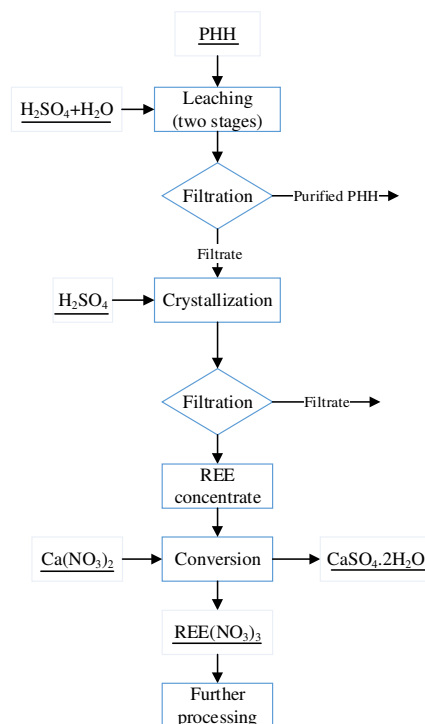
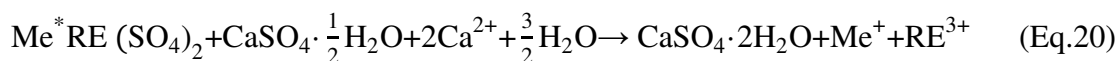


Fig. 19 Technological flowsheet for recovery of rare earth elements from PHH[165].

There was a specific method for REEs recovery from PHH-recrystallization method in which process hemihydrate was transferred into dihydrate and cations impurities including REEs were released and passed into solution at the same time (Eq.20 and Eq.21)[166, 167]. Jarosifiski et al.[166] developed a technology for PHH purification and REEs recovery (Fig. 20). In this process, both the recovery of REEs and the degree of PHH purification depended closely on the hydration level of PHH. Under the optimal leaching conditions of  $T < 20^{\circ}\text{C}$ ,  $L/S=2:1$ , 5-10wt%  $\text{H}_2\text{SO}_4$ , 6h, high leaching efficiency of REEs up to 80% was achieved.



Me\*: elements of alkali metal.

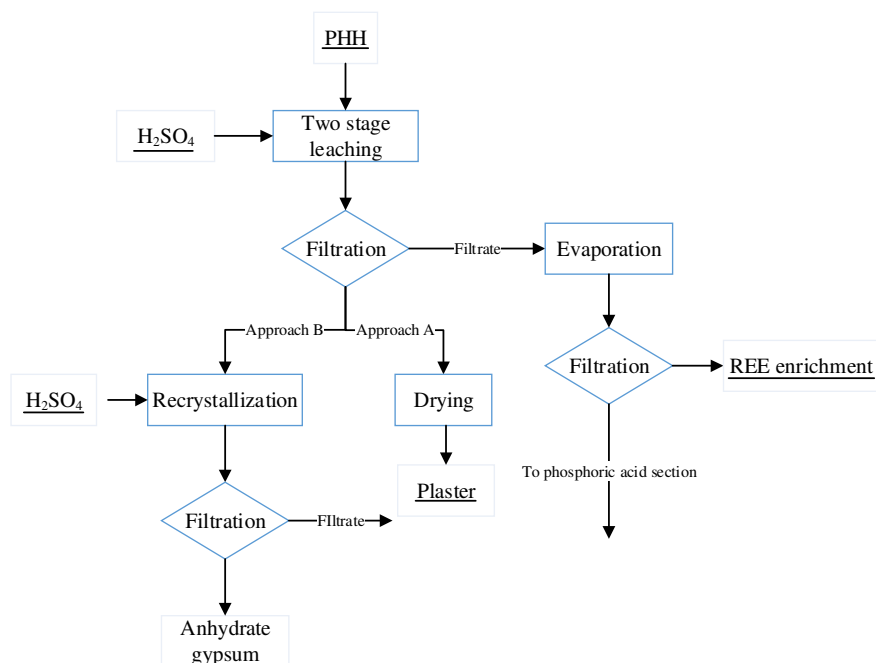


Fig. 20 REEs recovery and purification of PHH produced from Kola apatite[166]



#### 2.4.2.2 Leaching REEs from PHH with HNO<sub>3</sub>

Leaching REEs from PHH with nitric acid seems more efficient than that with H<sub>2</sub>SO<sub>4</sub> due to the higher solubility of REEs in nitric acid solutions[168, 169]. Furthermore, the solubility of CaSO<sub>4</sub> in nitric acid is much higher than in sulfuric acid. Therefore, HNO<sub>3</sub> would facilitate the release of REEs incorporated in the lattice of PHH and REEs enriched in independent phase covered by a PHH crust[153, 170]. Lebedev et al.[171] leached PHH by mixture of 2wt% HNO<sub>3</sub>+5wt% Ca(NO<sub>3</sub>)<sub>2</sub>, the leaching efficiency of REEs increased from 7.5% to 50.7% as the L/S ratio raising from 1 to 10. Lokshin et al.[153] extracted 53.0-83.7% of REEs from PHH by 2-8wt% HNO<sub>3</sub> with only 2.96-6.30% CaSO<sub>4</sub> dissolved into solution which demonstrated that REEs were mainly presented in independent phase. Furthermore, 96.28% REEs recovery from PHH was achieved via two stages leaching with fresh 4wt% HNO<sub>3</sub>. However, CaSO<sub>4</sub> would get saturated in leaching solution after several leaching cycles of PHH with nitric acid and then hindered the dissolution of phosphogypsum and REEs.

In addition, it is noted that leaching efficiency of REEs increases with increasing concentration of nitric acid, while a sharp decrease appeared once nitric acid concentration exceed 25wt% under the elevated temperature (~80-90°C). The most possible reason was that the elevated temperature increases the hydrolysis of fluorosilicate ions and then raises free fluoride ion concentration, which initiates the precipitation of REEs in form of fluorides. In addition, effects of various additives such as Al(NO<sub>3</sub>)<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>B<sub>4</sub>O<sub>7</sub> on the leaching process with 6wt% HNO<sub>3</sub> shown that Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> greatly improves the leaching efficiency of REEs from 43.6%

to 96.8%. The mechanism was attributed to the salting-out effect of sodium and potassium hexafluorosilicates or formation of stable and sparingly soluble fluorides which prevent REEs from precipitating in form of fluorides[172]. And the order of stability of fluorides in nitric acid solution was  $\text{SiF}_6^{2-} < \text{AlF}_6^{3-} < \text{BF}_4^-$ .

In conclusion, recovery of REEs from PG needs to combine with the utilization of PG in building materials or other applications due to the relative low content of REEs. The most promising way is to recover REEs with other valuable elements during the purification of PG. From the view of technology, leaching REEs from PG with diluted  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are recommended because diluted  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  achieved relative high REEs leaching efficiency with minimum deconstruction of  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ .

## 2.5 Recovery of REEs in HDH and HRC processes

HDH and HRC processes are originated from HH process by adding extra recrystallization and filtration procedures on HH process[173]. There are two typical processes-Norsk Hydro HDH process and Nissan-H process which correspond to the flowsheets in Fig. 5 and Fig. 6, respectively[174]. Difference between these two processes is that HDH process has two filtration stages in both hemihydrate section and hemi-dihydrate recrystallization section, while HRC process has only one filtration in hemi-dihydrate recrystallization section. And the acid concentration in recrystallization solution for HDH process is about 0.8mol/kg  $\text{H}_3\text{PO}_4$ , and 3.5-5mol/kg  $\text{H}_3\text{PO}_4$  for HRC process[175].

In HRC processes, more than 95% of REEs transferred in PHH during the

---

decomposition procedure of phosphate rocks, then released into the recrystallization solution, but finally end in PDH[176]. On the other hand, the presence of rare earth ions in recrystallization acid solution may retard the growth of PDH crystals which depends on the supersaturation of  $\text{CaSO}_4$ [175, 177]. Generally, recrystallization processes was conducted with 0.5-3mol/L  $\text{H}_3\text{PO}_4$  at 50-80°C, compared with WPA (4-6mol/L  $\text{H}_3\text{PO}_4$ ), the lower acidity of recrystallization acid makes the REEs recovery more feasible [79].

In order to recover REEs in recrystallization process, solvent extraction and ion exchange methods have been introduced in. Zielinski et al.[41] used alkyl phosphoric acid solvents (M2EHPA, D2EHPA) to extract REEs from the recrystallization solution produced by Kola apatite. Product of Na-REE double sulfates contains 24-25wt% REEs and 80-85% overall REEs recovery were achieved via solvent extraction and precipitation stripping under the optimal conditions (Fig. 21). The investigation also demonstrated that elevated total concentration of sulfuric acid, phosphates, and fluorides leads to the decrease of the extraction efficiency of REEs from recrystallization with alkyl phosphoric acid. In addition, extraction efficiency of REEs with D2EHPA would be significantly reduced once the recrystallization acid solutions has high iron concentration[79]. In this case, extractant of di-dodecyl naphthalene sulfonic acid (Nacure 1052) which has good affinity for both light and heavy rare earth elements was used to avoid the disturbance of iron. However, Nacure 1052 brought another problem - co-extraction of calcium ion which is present in the recrystallization acid solution with relatively high concentration.

DOWEX C-500 ion exchanger with sulfonic acid function groups was used for REEs

extraction from recrystallization acid[176]. With 250g resin/kg recrystallization slurry, individual REEs extraction efficiency ranges from 10% to 50%. The study attributed the low extraction efficiency of REEs to that the extraction ability of resin for REEs was not strong enough to prevent REEs incorporated in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  crystals.

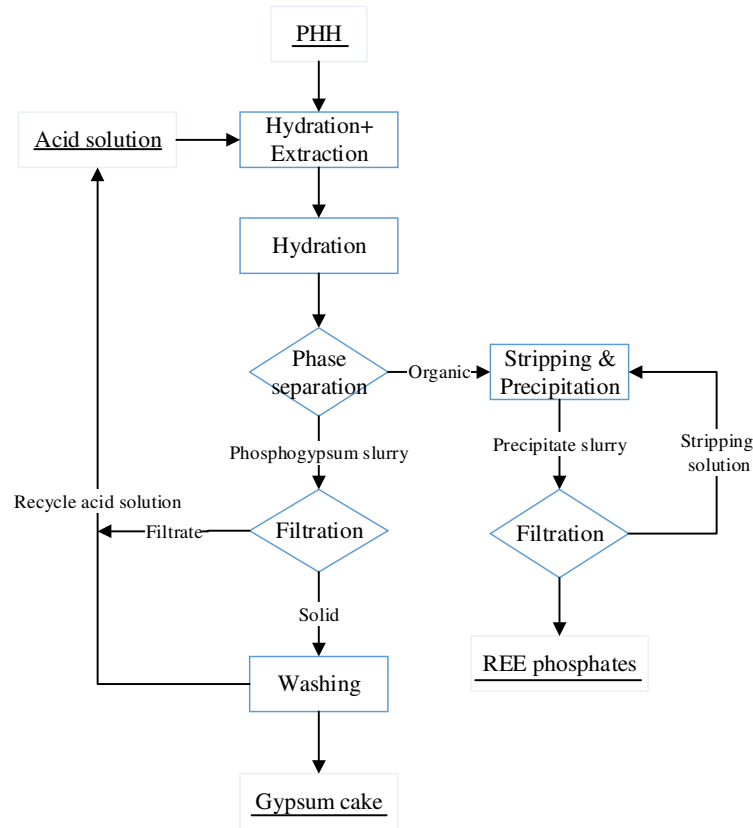
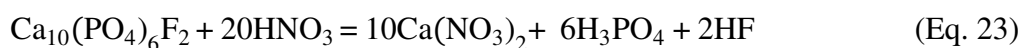


Fig. 21 Process of REEs recovery from recrystallization acid solution

### 3. Recovery of REEs in nitrophosphate processes

Nitrophosphate process is a generally accepted item that involves attacking phosphate rocks with nitric acid to produce a mixture of phosphoric acid and calcium nitrate, which can be represented by Eq.23[178]. The leaching solution was then treated to remove calcium nitrate by various methods including: (1) Odda process[179] that removes calcium by cooling crystallization, (2) sulphonetric process[180, 181] that

converts calcium nitrate into calcium sulfate by adding sulfuric acid, (3) calcium phosphate process[182] that produces calcium phosphate by using phosphoric acid or sulfates, (4) carbonitric process[183, 184] that prepares calcium carbonate by introducing carbon dioxide. And nitrophosphate process is more commonly applied in NP and NPK fertilizer production than in phosphoric acid production.



It is generally considered that the most significant industrial nitrophosphate process was Odda process developed by Erling Johansen in Norway around 1927[179, 185, 186]. This process involves decomposing phosphate rocks with nitric acid, removal of  $\text{Ca}^{2+}$  by cooling to about  $-5^\circ\text{C}$  where calcium forms  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  which can be separated from leaching solution, and neutral precipitation with ammonia to produce nitrophosphate fertilizer. Furthermore, nearly all investigations for REEs recovery in nitric phosphate process are based on the Odda process.

It has been demonstrated that leaching efficiency of REEs from phosphate rocks with nitric acid depends on the properties of concentrate, high efficiency up to 95% was achieved in the case of apatite, while, 80-92% for phosphorite[57, 187]. Therefore, REEs recovery in nitric phosphate process seems superior to that in  $\text{H}_2\text{SO}_4$  processes. While, methods of REEs recovery from nitric-phosphoric acid solution are similar to from WPA. They are crystallization, precipitation, solvent extraction and ion exchange methods.

---

### 3.1 Crystallization and Precipitation methods

Kijkowska et al.[62, 188] crystalized REEs from nitrophosphate process by heating up nitric-phosphoric acid solutions(NPA) to 200°C and kept for 1h, 95.2% of REEs recovery was achieved and REO containing in the crystals is 41.1wt%. In addition, series of pretreatments were required before the heat procedure, including removal of calcium by cooling to -5°C, defluorination by using sodium salts, and partial neutralization to  $\text{HNO}_3 < 2\text{wt}\%$  (Fig. 22(A)). Similar to the case of REEs recovery from WPA by crystallization, the complex process, high-output-capability apparatus and energy expenditure prevent its further application in industry.

Research on REEs recovery from NPA via precipitation method were mainly conducted before 1980s and most of them have been summarized by Habashi[62]. These research precipitated REEs by using ammonium hydroxide to adjust the pH of NPA to 0.3-1.4 at 70-90°C after removal of calcium and fluorine(Fig. 22(B)). Recently, Andropov et al.[189] precipitated REEs from NPA by using gas ammonia to adjust pH to 1.8-2.0, a concentrate contains 24-25wt% REO was obtained. Samarium-neodymium and cerium-praseodymium products were produced via further treatments including dissolution of concentrate with nitric acid, grouping of REEs by solvent extraction with TBP. Lokshin et al.[190] recovered REEs from the precipitate produced by neutralization precipitation from NPA via  $\text{HNO}_3$  dissolution and ion exchange method. To sum up, neutralization precipitation of REEs from NPA consumes large amount of ammonia and introduces  $\text{NH}_4^+$  impurity that hinders its further application in industry.

While, it is not impossible to recover REEs by adjusting pH at 1.8-2.0 during the production of NP fertilizer via stage-wise ammonia hydroxide precipitation.

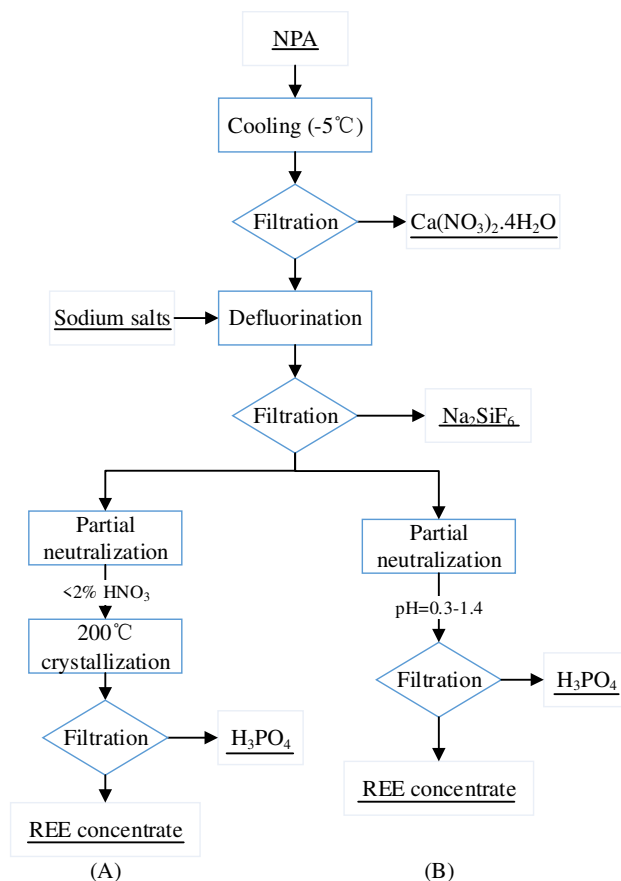
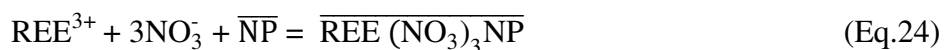


Fig. 22. Recovery of REEs from NPA by crystallization and precipitation[62]

### 3.2 Solvent extraction methods

TBP, D2EHPA, EHEHPA, NPPA, Cyanex272, Cyanex572, DMHMP (Di- (1-methyl heptyl) methyl phosphonate) have been used for the solvent extraction of REEs from nitrophosphate solution. Extraction processes with these extractants in NPA solution are quite similar to the process in pure HNO<sub>3</sub> solution. Their extraction efficiencies for REEs mainly depend on the acidity, concentration of REEs, impurities in NPA, and the functional group of extractants[18].

Neutral phosphorus-based extractants, such as TBP, DMHMP, TOPO are preferable for REEs extraction from NPA than acidic phosphorus extractants, because the elevated acidity of NPA can promote the extraction efficiency of REEs by neutral extractants, and the extraction mechanism can be expressed as Eq.24.



Where  $\overline{\text{NP}}$  represents neutral phosphorus-based extractant. In the 1970s, solvent extraction of REEs from NPA with TBP diluted in kerosene has been extensively studied<sup>[62]</sup>, the general process can be described as Fig. 23. In this process, phosphate rocks were decomposed with nitric acid, the obtained NPA was partial neutralized to pH=0.2 followed by the solvent extraction of REEs with TBP. REEs were stripped from TBP by water, precipitated with  $\text{NH}_3$  and the precipitate was then calcinated to produce REO products. Habashi and Awadalla[58] developed a process to recover REEs by solvent extraction with TBP from NPA after U was extracted by Tertiary amyl alcohol (Fig. 24). Then, REEs were stripped from organic phase with 0.05mol/L  $\text{HNO}_3$  and precipitated by oxalic acid, and subjected calcination concentrate contains 13wt% of REO was obtained.

Thereafter, another similar process was adopt for REEs recovery from Abu Tartur phosphate in the study carried out by Aly et al.[191] (Fig. 25). the process was consist of phosphate rocks decomposition, removal of fluorine from NPA, REEs extraction with TBP and stripping by 0.5mol/L  $\text{HNO}_3$ , oxalic acid precipitation and calcination to produce REO product with a high purity up to 96.4%. Jorjani and Shahbazi[192]



systematically investigated the influence of condition factors on solvent extraction of REEs from NPA with TBP, the optimum results that up to 80-95% of REEs recovery were achieved by contacting 3.65mol/L TBP with NPA after partial neutralization. In addition, 3mol/L  $\text{NH}_4\text{NO}_3$  and deionized hot water were used to scrub the loaded TBP for impurities removal, then more than 89% of REEs were stripped by precipitation with oxalic acid from organic phase. Feng et al.[187] achieved 98.5% HREEs recovery from NPA after recycling for three circles of three stages of countercurrent extraction with 50% TBP diluted in kerosene.

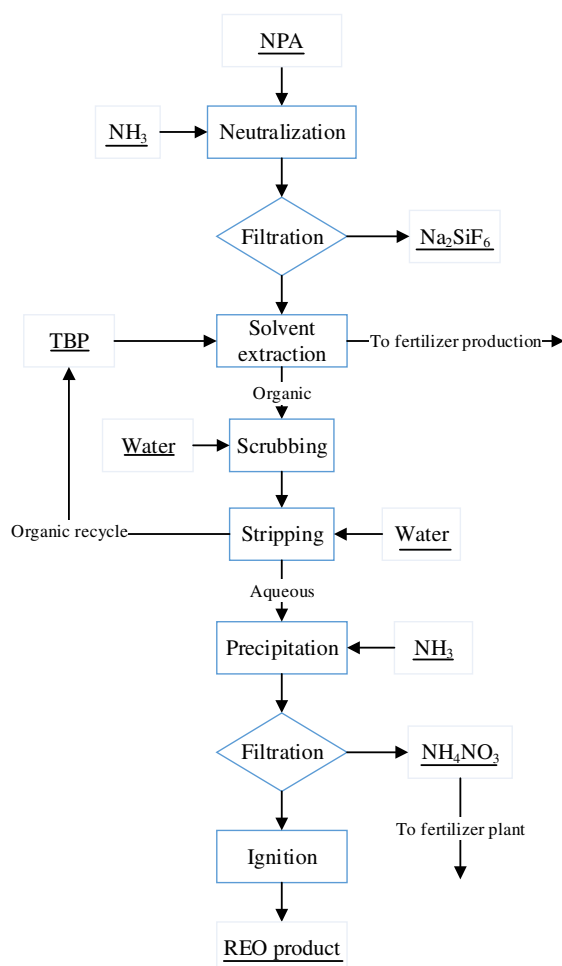


Fig. 23 General process of REEs recovery from phosphate rocks with TBP in nitrophosphate process[62].

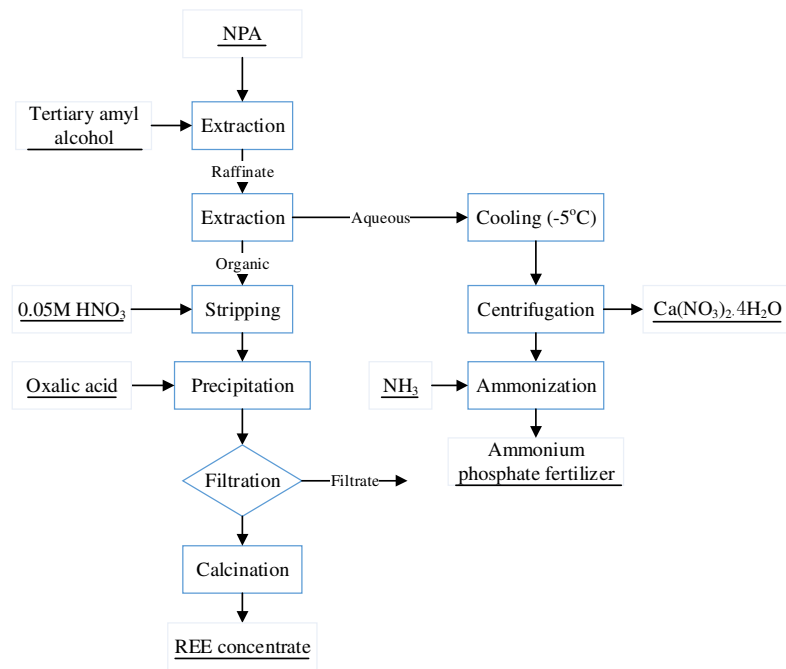


Fig. 24 Process for the recovery of uranium and the lanthanides from NPA[58].

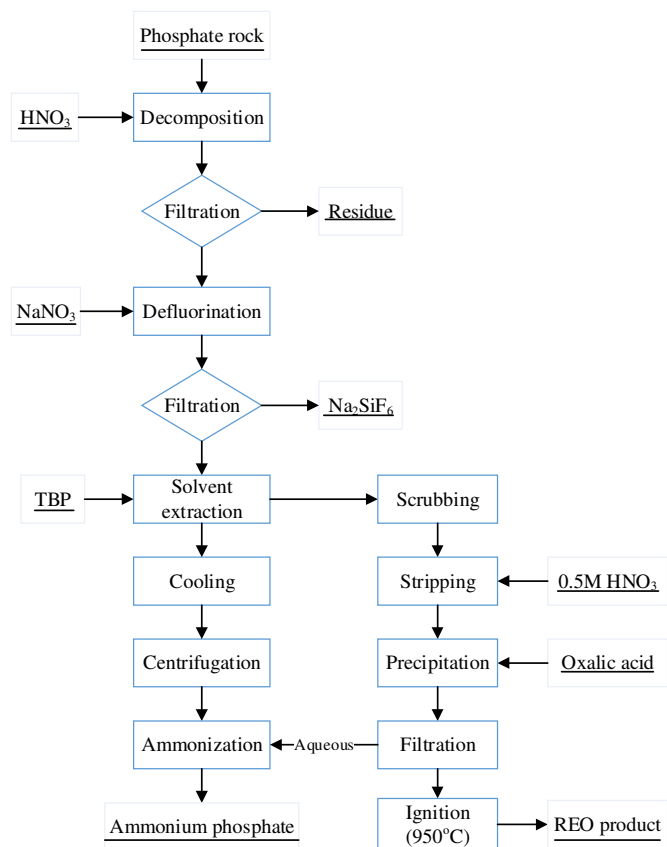


Fig. 25 Flowsheet for REEs recovery from Abu Tartur apatite by nitrophosphate process[191].

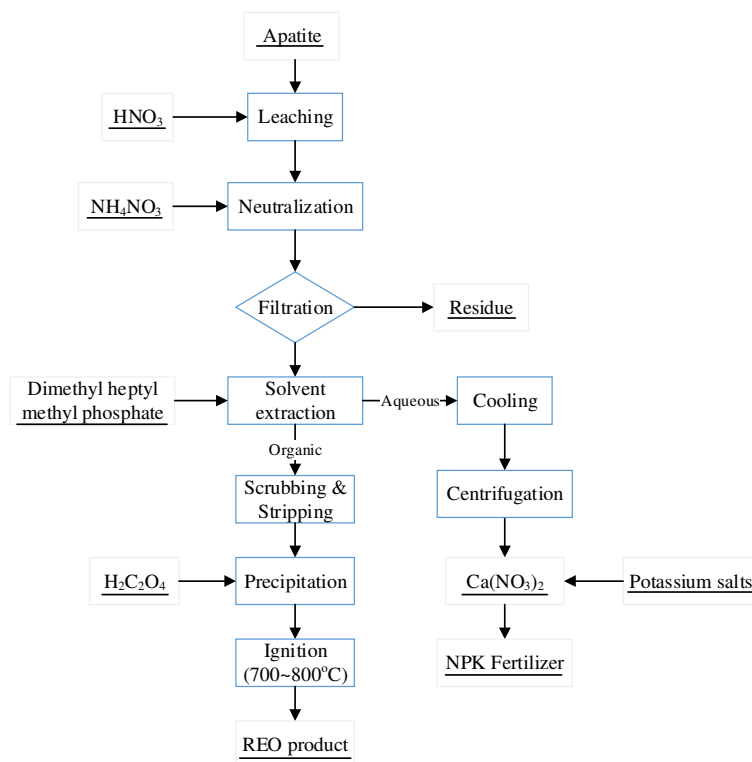


Fig. 26 Flowsheet for recovery of REEs from apatite with DMHMP in nitrophosphate process[193].

REEs extraction with another neutral phosphorus-based extractant DMHMP from NPA was investigated by Li[193]. The study demonstrated that the increase of acidity of NPA decrease the extraction efficiency of DMHMP for REEs due to the formation of hydrogen binding between H and O, while, it is favor for REEs stripping with elevated acidity. Furthermore, addition of salting-out agents such as  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ , etc. significantly enhanced the extraction efficiency of REEs from NPA (Fig. 26).

Acidic phosphorus-based extractants, such as D2EHPA and EHEHPA has been proven to be effective for REEs recovery and grouping in diluted nitric acid solution whose pH value ranges from 2 to 6[194-196]. However, free the  $\text{HNO}_3$  concentration in NPA produced by nitrophosphate process was about 10-12wt%[115, 197]. Bunuş and

Dumitrescu[115] investigated the REEs extraction performance with 1mol/L D2EHPA and 0.1mol/L NPPA from industrial NPA which contains 25wt%  $P_2O_5$  and 10wt%  $HNO_3$ . The distribution coefficients of REEs were all less than 1 except for Lu in the case of D2EHPA, and data for NPPA were even worse. Furthermore, it has been demonstrated that precipitate would form once the concentration of  $H^+$  were less than 0.3mol/L[193]. Therefore, it is difficult to recover REEs from NPA with acidic phosphorus-based extractants due the relative high acidity.

In general, solvent extraction of REEs from NPA with neutral extractant seems promising. But the concentration of  $HNO_3$  in NPA is merely ~10wt%, then salt out reagent of nitrates are needed to enhance the extraction efficiency. Further research is needed for seeking better extractants and optimization methods.

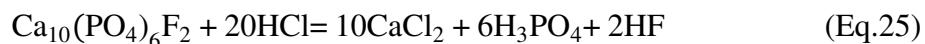
### 3.3 Ion exchange methods

Jie et al.[198] leached phosphorite of Zhijin with  $HNO_3$  at room temperature, and mixed leaching solution with ion exchanger, impurities such as Zr, Nb, Fe, U, etc. were removed by eluting with water and washing liquid. REO product was obtained after being eluted by washing liquid, precipitated by  $NH_4OH$ , and calcinated at 850°C, furthermore, the total recovery of REEs reached as high as 85.44%. According to investigation of Lokshin et al.[190] sulfonic sorbent can adsorb REEs effectively from diluted nitric-phosphoric acid solution in which nitric acid concentration ranges from 2-6wt%  $HNO_3$ . In addition, Brunfelt[199] proposed a method that groups HREEs from LREEs in NPA by using an extraction chromatographic column with TBP as the

stationary phase.

#### 4. Recovery of REEs in hydrochloric acid processes

Hydrochloric acid process (HCl process/route) decomposes phosphate rock with hydrochloric acid and produces a mixture of phosphoric acid and calcium chloride, the main reaction can be displayed as Eq. 25[200]. HCl process decomposes phosphate rock completely and has no specific requirement for the grade of phosphate rock[201-204]. Typical HCl process consists of decomposition of phosphate rock, impurities removal, solvent extraction of phosphoric acid and evaporation of phosphoric acid (Fig. 27(Process A))[202, 205-209]. In addition, HCl process has significant application in feed-grade dicalcium phosphate production (Fig. 27(Process B))[210, 211].



In the decomposition process of phosphate rocks with HCl, more than 90% of REEs would be dissolved into the leaching solution (Table. 8). Generally, leaching efficiency of REEs increases with increasing of concentration of HCl, temperature, and L/S ratio[212, 213]. El-Mottaleb et al.[214] demonstrated that the decomposition process of phosphate rock with HCl was fitted with the shrinking-core model and controlled by the inner diffusion process. Shen et al.[215] put forward a stepwise process that decomposed phosphate rock by 36wt% HCl at room temperature for phosphorus recovery, the obtained residue was redissolved with 36wt% HCl under 65°C for REEs leaching, and then REEs was precipitated by milk of lime (Fig. 28). In this process, 89% of REEs recovery was achieved, but the REE content in product did not exceed 10wt%

and concentration of phosphoric acid is merely 2.68wt%.

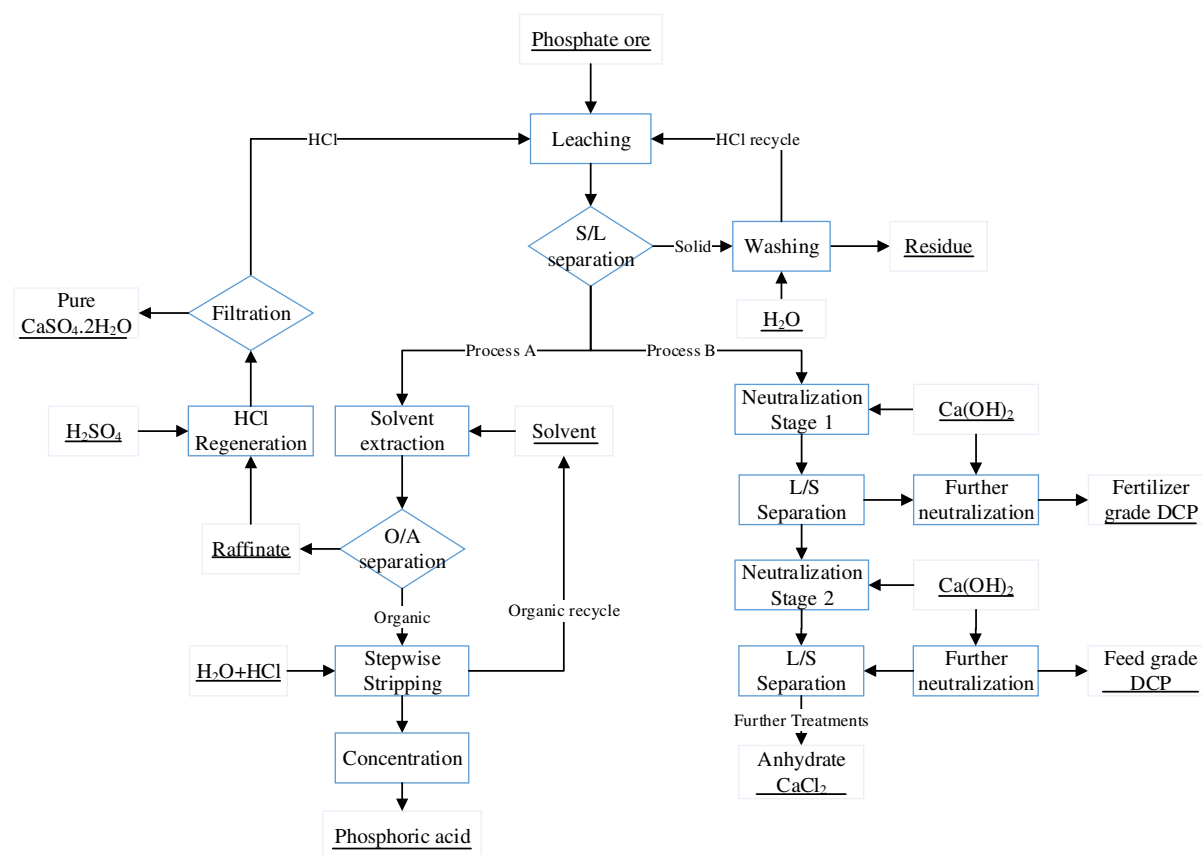


Fig. 27 General process for HCl route of phosphoric acid production[208]

Table. 8 Leaching efficiency of REEs from phosphate rocks with HCl

Origin	Leaching time/h	Temperature	L/S ratio	[HCl]	Efficiency (%)	REO (in ore)	References
China	1.0	RT	6:1	5wt%	96.0*	0.19wt%	Shen et al.[215]
		65°C	6:1	13wt%	89.7		
China	1.33	50°C	3:1	28wt%	97.3	0.08wt%	Nie et al.[216]
China	1.5	RT	2.3:1	30wt%	85.5	2.6wt%	Liu et al.[212]
China	2.0	50°C	2:1	11mol/L	98.0	0.08wt%	Zhao et al.[213]
Syrian	2.0	--	--	10vol%	>85	~0.02wt%	Shlewit[217]
Mongolia	0.17	20°C	9:1	2mol/L	90	~10wt%	Kim et al.[55]
	>1				~100		

Egypt	1	22°C	3:1	1mol/L	85.7	0.21wt%	El-Mottaleb et al.[214]
		90°C			94.1		

96.01%\*: REEs were enriched in the leaching residue. RT: room temperature.

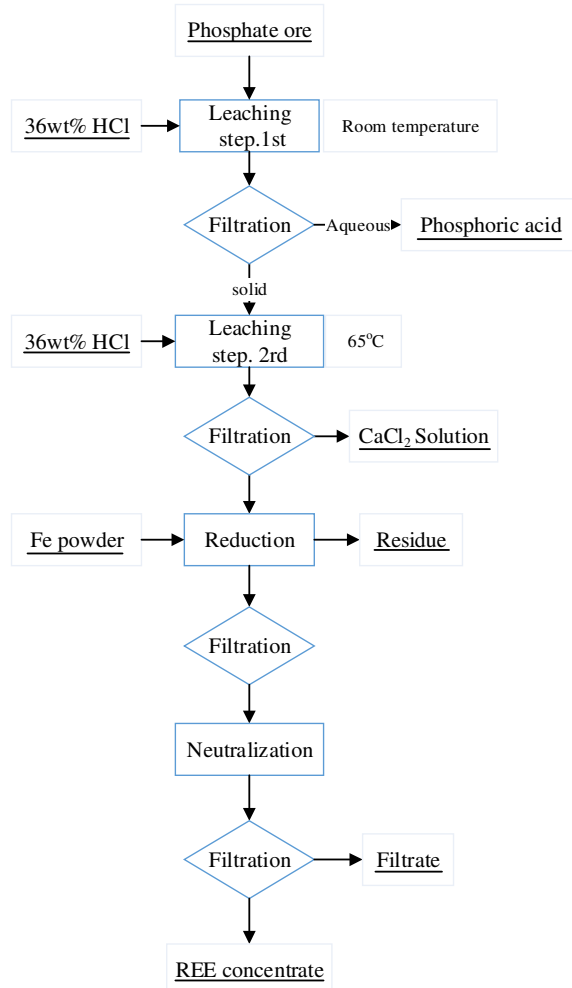


Fig. 28 Two stages leaching process for REEs recovery from phosphate rocks with HCl[215]

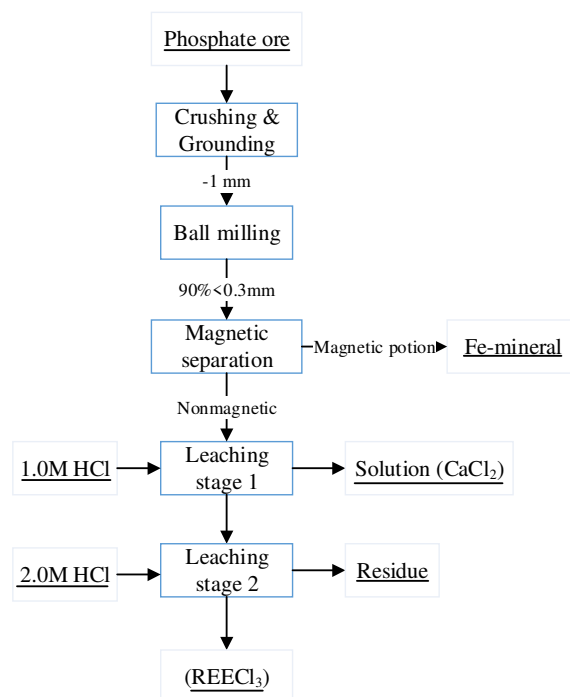


Fig. 29 Optimal processing for REEs recovery from high iron containing phosphate rocks[55]

Recently, Kim et al.[55] proposed a magnet method for REEs separation from high iron containing (23wt% Fe<sub>2</sub>O<sub>3</sub>) phosphate ore produced from Mongolian (Fig. 29). The nonmagnetic portion was then attacked with 1.0mol/L HCl to dissolved and removed Ca from REEs, followed by 2.0mol/L HCl decomposition to recover REEs into leaching solution.

To recover REEs from the leaching solution, methods of neutralization precipitation and solvent extraction have been introduced in. It was reported that REEs can be precipitated from the hydrochloric-phosphoric acid solution (HPA) by neutralization with Ca(OH)<sub>2</sub> to pH=1.5-1.6. REO product with a purity of 87.9% was obtained after acid redissolution, oxalic acid precipitation and calcination, the overall recovery of REEs from phosphate rocks was 84%[62]. Shanxi research institute of chemical industry[61] precipitated REEs from HPA by using milk of lime to adjust pH=2.2-2.3



and kept in a condition of 60°C for 4h followed by standing overnight. Then 94% purity REO was obtained from precipitate via HCl redissolution, oxalic acid precipitation and calcination, the total recovery of REEs exceeded 60% (Fig. 30). Wang et al.[218] achieved 70-79% of total recovery and 94% of REO purity with similar process. Habashi et al.[202] proposed a comprehensive process for simultaneously recovery of uranium, phosphoric acid and REEs from HPA. In this process, uranium and phosphoric acid were recovered from the purified HPA by 5% TBP in hexane and 100% TBP, respectively, finally, REEs were recovered by ammonia precipitation (Fig. 31).

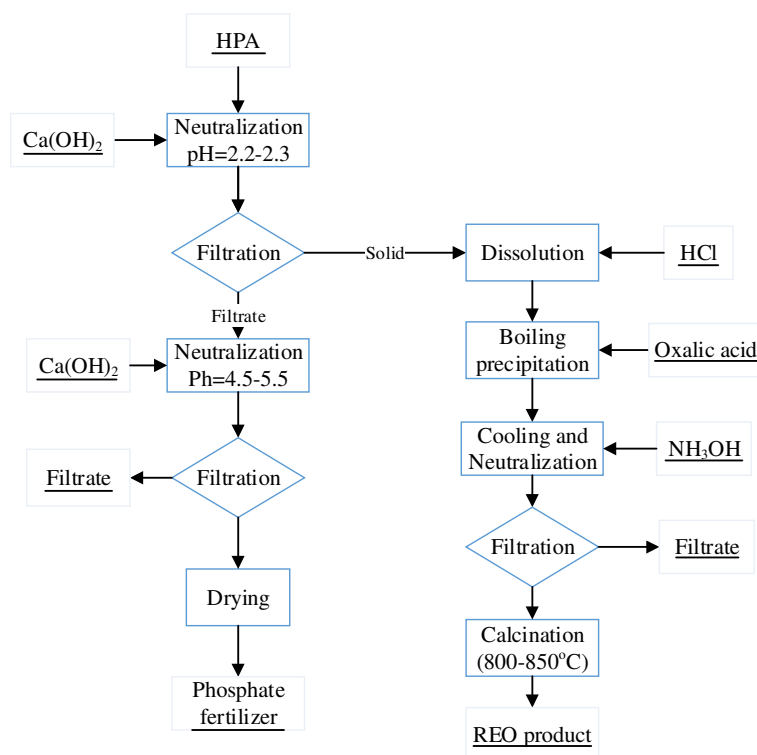


Fig. 30 REEs recovery from phosphate rocks by neutralization precipitation in HCl process[61].

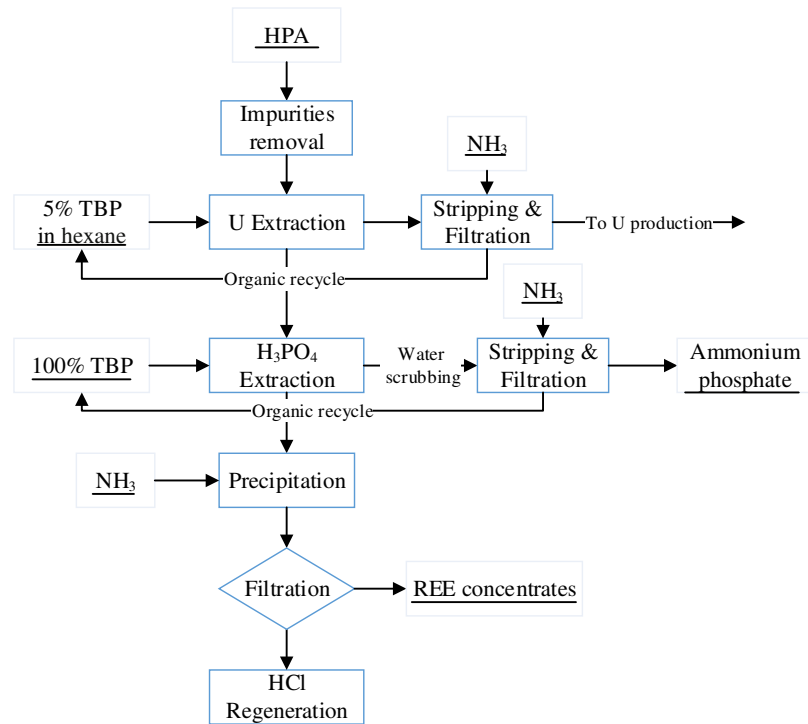


Fig. 31 Process for REEs recovery from phosphate rocks by precipitation in HCl route[202]

Yang et al.[209] demonstrated that TBP extracted 36% of REEs from HPA, while n-butyl alcohol and tri (octyl-decyl) alkyl tertiary amine (N235) have no significant extraction efficiency of REEs from HPA. Shlewit[217] put forward a stepwise solvent extraction process for selective recovery of U, phosphoric acid, and REEs with 0.4mol/L D2EHPA+0.3mol/L TBP in hexane, Iso-amyl alcohol, and 0.2mol/L D2EHPA in toluene, respectively(Fig. 32).

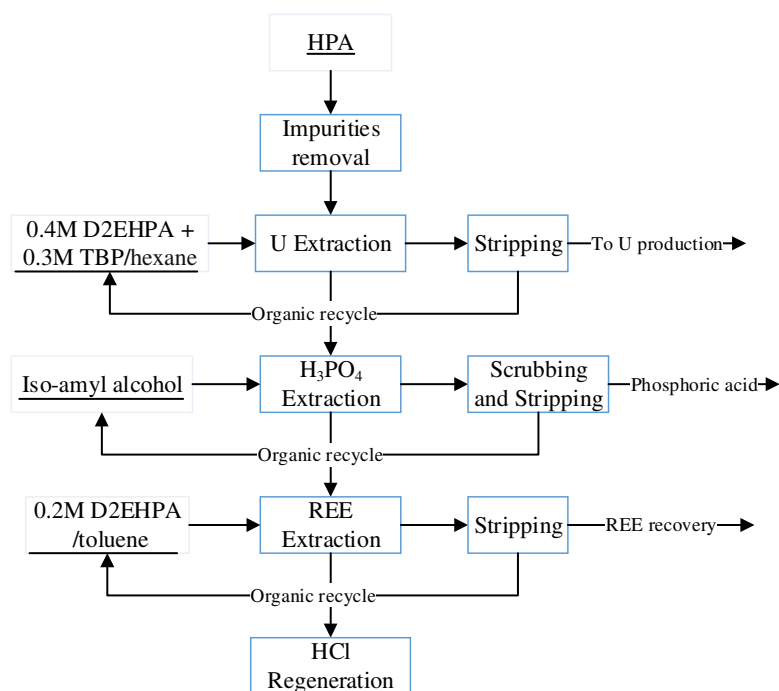


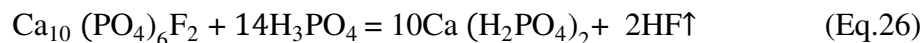
Fig. 32 recovery of REEs from phosphate rocks by solvent extraction with D2EHPA in HCl route[217]

On the whole, the main challenge faced by REEs recovery in HCl processes is the issue of calcium removal. Generally, the  $\text{CaCl}_2$  wastes water was treated by evaporation to produce  $\text{CaCl}_2$  crystals, which leads to a large amount of energy consumption. Luckily, this problem can be avoided by combining REEs recovery with the production of feed-grade calcium hydrogen phosphate. In this process, REEs recovery is possible to achieve via stepwise precipitation with lime milk to adjust pH to 2.0-2.5 before the precipitation of calcium hydrogen phosphate.

## 5. Recovery of REEs in phosphoric acid process

Decomposition of phosphate rock with  $\text{H}_3\text{PO}_4$  did not receive as much concern as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ , but many laboratory research has focused on the kinetics and

thermodynamics of phosphate rock decomposition process with  $\text{H}_3\text{PO}_4$ [219-224]. The process of phosphate rock attacked with  $\text{H}_3\text{PO}_4$  can be described as:



REEs in phosphate rock are mainly presented in the form of isomorphous substitution that can be dissolved along with phosphorus into leaching solution. Wang et al.[225] achieved 90.4% and 98.7% of leaching efficiencies for REEs and phosphorus by attacking phosphate rock with 25%  $\text{P}_2\text{O}_5$  returning acid produced from wet-process phosphoric acid with L/S=10ml/g ore at 65°C for 8h. Jiang et al.[226, 227] demonstrated that >90% REEs entered solid phase and phosphorus went into leaching solution in the case of dissolving phosphate rock by 23%  $\text{P}_2\text{O}_5$  returning acid with L/S=10ml/g ore at room temperature for 2h and a potential process was proposed (Fig. 33) which was also recommended by Stone et al[228]. Another flowsheet proposed by Huang et al.[229] shown as Fig. 34 was aimed at extracting REEs from phosphate rock accompanied with monazite by  $\text{H}_3\text{PO}_4$  decomposition and  $\text{H}_2\text{SO}_4$  calcination-water leaching. Their further research lead to the invention of a precipitation method that extracts >90% REEs in the form of phosphates from  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solution via ageing at 80-120°C for more than 0.5h[230].

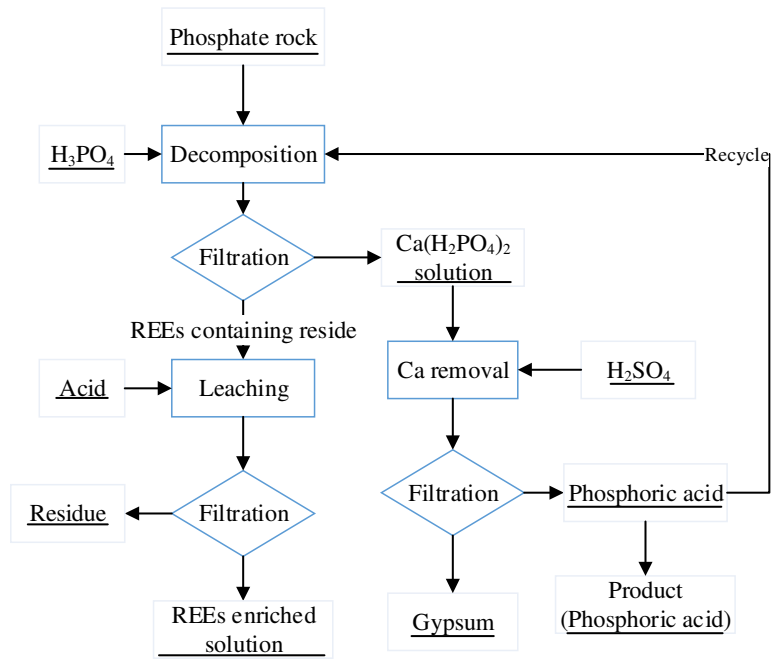


Fig. 34 Process of REEs recovery from phosphate rock with  $\text{H}_3\text{PO}_4$ [227]

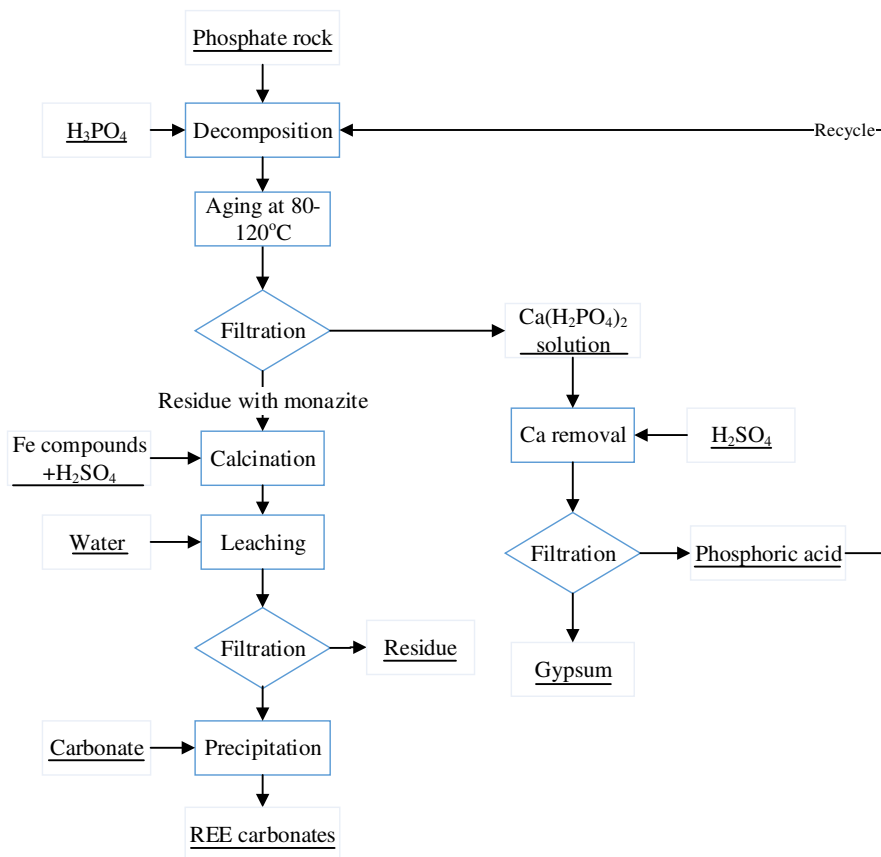


Fig. 35 Process of comprehensive recovery of REEs and phosphorus from phosphate

rock[229]

Leaching phosphate rock with  $\text{H}_3\text{PO}_4$  enable the enrichment of REEs in a single phase either in leaching solution or residue without introducing anion impurities. Another advantage of  $\text{H}_3\text{PO}_4$  process is that the crystallization of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was conducted after extraction of REEs which prevents REEs incorporated in crystals of gypsum. In addition, high quality gypsum can be produced in this process.

## 6. Conclusions and Recommendations

Research on REEs recovery from phosphate rock is essential to fill the coming gap between growing demand and shrinking primary resources, especially for the demand from green energy and new materials.

From the view of practicability, it is urgent to recover REEs in  $\text{H}_2\text{SO}_4$  processes, the main challenge presents in DH is the dispersed distribution and low content of REEs in WPA and PG. With regard to HH, HDH and HRC process all the REEs were transferred into the single phase PHH in these processes. In the case of REEs recovery from WPA, compared with crystallization, precipitation and ions exchange methods, solvent extraction seems more promising. And it has been repeatedly recommended to simultaneously recover REEs and U by solvent extraction. But several challenges are needed to be solved: contradiction of the optimal extraction conditions between REEs and U from WPA, inefficiency for LREEs extraction, extra process for REEs separation from U (green cake), and loss of organic phase caused by the large volume of WPA. Therefore, further research is needed to seek better extractants for REEs extraction and selective recovery of REEs and U from WPA.

---

On the other hand, recovery of REE from PG would be feasible when combined with the utilization of PG in building materials or other applications, diluted  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are preferable for the leaching of REEs from PG. But further investigation about the presented forms of REEs in PG and the leaching mechanisms of REEs are necessarily.

From the perspective of new technology development, REEs recovery in  $\text{HCl}$  and  $\text{HNO}_3$  are of importance. Because the decomposition processes of phosphate rock with  $\text{HNO}_3$ ,  $\text{HCl}$  completely dissolve REEs into a single phase and obtained relative higher concentration of REEs in NPA, HPA than that in WPA. In the case of REEs recovery from NPA, solvent extraction with neutral organic phosphorus extractants such as TBP and DMHMP was considered as the best choice for REEs recovery from NPA owing to the high active proton concentration caused by  $\text{HNO}_3$ . The main challenge presented in these two processes is the issue of removal of calcium from leaching solutions, a deficiency exists in their own. While, it seems to be economic for REEs recovery in  $\text{HNO}_3$  processes for Kola phosphate with  $>1\text{wt}\%$  REEs because this process was reported to run in Russia. In  $\text{HCl}$  processes, combining REEs recovery with the production of feed-grade calcium hydrogen phosphate seems a promising method. In this method, REEs can be selective precipitated by adjusting pH to 2.0-2.5 with lime milk. However, better understanding of the REEs behavior and impurities distribution during the precipitation process of calcium hydrogen phosphate are required.

Another potential promising method is REEs recovery from  $\text{H}_3\text{PO}_4$  process on account of several advantages: (1) no extra anion impurities involved. (2) REEs enrichment in

a single phase with a relative high concentration (3) Good overall recovery of REEs. Especially,  $\text{H}_3\text{PO}_4$  process provides an alternative for the recovery of REEs from high content of monazite, xenotime, allanite inclusions phosphate rocks. While, in order to extent the application of  $\text{H}_3\text{PO}_4$  process for REEs recovery, deeper study on physiochemical properties of REEs in  $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{-H}_3\text{PO}_4$  solutions system is required. Therefore, recovery of REEs from phosphate rock can only be potential feasible when combined with the hydrometallurgical processes without causing much disturbance. The choice of decomposition process should be determined by the characteristics of phosphate rock including the composition, mineralogical properties, etc.. For example, both  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$  processes are suitable for REEs recovery in the case of REEs presented as isomorphous substitution in phosphate rock since REEs in this presented form can easily be decomposed by mineral acids. While, in the case of REEs presented as independent mineral inclusion in phosphate rock, it is better to enrich them in residue,  $\text{H}_3\text{PO}_4$  process would be a good choice. Furthermore, better understanding of the behavior of individual REEs is necessary to improve or develop processes for REEs recovery from phosphate rock. In turn, further research on the physiochemical properties of REEs in acidic phosphate solutions such as the solubility, coordination chemistry are of specific significance.

## Acknowledgements

The authors gratefully acknowledge the financial support from the following projects: the program of the National Natural Science Foundation of China (NSFC: 51674036);



the US Department of Energy under the Critical Materials Institute (CMI project 1.1.2); Beijing Nova program (Z161100004916108); and the China Scholarship Fund (201506460033).

## References

- [1] I. Anastopoulos, A. Bhatnagar, E.C. Lima, Adsorption of rare earth metals: A review of recent literature, *J. Mol. Liq.*, 221 (2016) 954-962.
- [2] N. Krishnamurthy, C.K. Gupta, Extractive metallurgy of rare earths, CRC press, 2004.
- [3] A.N. Belsky, J.C. Krupa, Luminescence excitation mechanisms of rare earth doped phosphors in the VUV range, *Displays*, 19 (1999) 185-196.
- [4] Z. Hu, H. Richter, G. Sparovek, E. Schnug, Physiological and Biochemical Effects of Rare Earth Elements on Plants and Their Agricultural Significance: A Review, *Journal of Plant Nutrition*, 27 (2005) 183-220.
- [5] Y. Xiao, Z. Feng, X. Huang, H. Li, Y. Chen, L. Wang, Z. Long, Recovery of rare earths from weathered crust elution-deposited rare earth ore without ammonia-nitrogen pollution: I. leaching with magnesium sulfate, *Hydrometallurgy*, 153 (2015) 58-65.
- [6] Y. Xiao, Z. Feng, X. Huang, L. Huang, Y. Chen, X. Liu, L. Wang, Z. Long, Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching, *Hydrometallurgy*, 163 (2016) 83-90.
- [7] A. Kumari, R. Panda, M.K. Jha, Y.L. Jin, J.R. Kumar, V. Kumar, Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite, *Journal of Industrial & Engineering Chemistry*, 21 (2015) 696-703.

- 
- [8] R. Vijayalakshmi, S.L. Mishra, H. Singh, C.K. Gupta, Processing of xenotime concentrate by sulphuric acid digestion and selective thorium precipitation for separation of rare earths, *Hydrometallurgy*, 61 (2001) 75-80.
- [9] A.E. Samonov, Commodity priorities speedy recovery and sustainable development of the rare earth industry in Russia, *Gene Expression Patterns*, 6 (2012) 63-68.
- [10] R. Chi, X. Zhang, G. Zhu, Z.A. Zhou, Y. Wu, C. Wang, F. Yu, Recovery of rare earth from bastnasite by ammonium chloride roasting with fluorine deactivation, *Miner. Eng.*, 17 (2004) 1037-1043.
- [11] R. Eggert, C. Wadia, C. Anderson, D. Bauer, F. Fields, L. Meinert, P. Taylor, Rare Earths: Market Disruption, Innovation, and Global Supply Chains, *Annual Review of Environment & Resources*, 41 (2016).
- [12] E. Apergis, N. Apergis, The role of rare earth prices in renewable energy consumption: The actual driver for a renewable energy world, *Energy Economics*, 62 (2017) 33–42.
- [13] J. Nielsen, J. Hjelm, Impedance of SOFC electrodes: A review and a comprehensive case study on the impedance of LSM:YSZ cathodes, *Electrochim. Acta*, 115 (2014) 31-45.
- [14] M.Z. Jacobson, M.A. Delucchi, A path to sustainable energy by 2030, *Scientific American*, 301 (2009) 58-65.
- [15] D.R. Wilburn, Wind energy in the United States and materials required for the land-based wind turbine industry from 2010 through 2030, U.s.geological Survey, (2012).
- [16] F. Habashi, Extractive metallurgy of rare earths, *Can. Metall. Q.*, 52 (2013) 224-233.
- [17] Z.H.I.S. Sebastiaan Peelman, Jilt Sietsma, Yongxiang YANG, Leaching of rare earth elements: past and present in: ERES2014: 1st European Rare Earth Resources Conference,

---

Milos Greece, 2014, pp. 446-456.

[18] F. Xie, T.A. Zhang, D. Dreisinger, F. Doyle, A critical review on solvent extraction of rare earths from aqueous solutions, *Miner. Eng.*, 56 (2014) 10-28.

[19] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review, *Journal of Cleaner Production*, 51 (2013) 1-22.

[20] E. Machacek, J.L. Richter, K. Habib, P. Klossek, Recycling of rare earths from fluorescent lamps: Value analysis of closing-the-loop under demand and supply uncertainties, *Resources Conservation & Recycling*, 104 (2015) 76-93.

[21] H.M.D. Bandara, K.D. Field, M.H. Emmert, Rare Earth Recovery from End-of-Life Motors employing Green Chemistry Design Principles, *Green Chemistry*, 18 (2015) 753-759.

[22] L. Pietrelli, B. Bellomo, D. Fontana, M.R. Monteverdi, Rare earths recovery from NiMH spent batteries, *Hydrometallurgy*, 66 (2002) 135-139.

[23] P. Davris, E. Balomenos, D. Panias, I. Paspaliaris, Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid, *Hydrometallurgy*, 164 (2016) 125-135.

[24] S. Al-Thyabat, P. Zhang, Extraction of rare earth elements from upgraded phosphate flotation tailings, *Minerals & Metallurgical Processing*, 33 (2016) 23-30.

[25] C.R. Borra, Y. Pontikes, K. Binnemans, T. Van Gerven, Leaching of rare earths from bauxite residue (red mud), *Miner. Eng.*, 76 (2015) 20-27.

[26] Z. Liu, H. Li, Metallurgical process for valuable elements recovery from red mud—A review, *Hydrometallurgy*, 155 (2015) 29-43.

[27] K. Binnemans, Y. Pontikes, P.T. Jones, T.V. Gerven, B. Blanpain, Recovery of rare earths

---

from industrial waste residues: a concise review, Proceedings of the 3rd International Slag Valorisation Symposium: the Transition to Sustainable Materials Management pages:191-205, (2013) 191-205.

[28] Y.M. Khawassek, A.A. Eliwa, E.A. Gawad, S.M. Abdo, Recovery of rare earth elements from El-Sela effluent solutions, Journal of Radiation Research & Applied Sciences, 8 (2015) 583-589.

[29] T. Graupner, C. Mühlbach, U. Schwarz-Schampera, F. Henjes-Kunst, F. Melcher, H. Terblanche, Mineralogy of high-field-strength elements (Y, Nb, REE) in the world-class Vergenoeg fluorite deposit, South Africa, Ore Geology Reviews, 64 (2015) 583-601.

[30] B.G. N, Geochemistry of rare earth elements in phosphorites from the namibian shelf, Geochemistry International C/C of GEOKHMIIA, 43 (2005) 937.

[31] J. Hein, A. Koschinsky, M. Mikesell, K. Mizell, C. Glenn, R. Wood, Marine Phosphorites as Potential Resources for Heavy Rare Earth Elements and Yttrium, 6 (2016) 88.

[32] M. Chen, T.E. Graedel, The potential for mining trace elements from phosphate rock, Journal of Cleaner Production, 91 (2015) 337-346.

[33] P. Christmann, A Forward Look into Rare Earth Supply and Demand: A Role for Sedimentary Phosphate Deposits?, Procedia Engineering, 83 (2014) 19-26.

[34] Phosphate rock may be new rare-earth source, Chem.eng.news, Oct. (24) (1966) 52-53.

[35] S.M. Jasinski, Mineral Commodity Summaries 2017, Phosphate Rock, US Geological Survey, Department of the Interior, (2017) 124-125.

[36] A.E. Grosz, A.L. Meier, B.F. Clardy, J.M. Howard, Rare earth elements in the Cason Shale of Northern Arkansas: a geochemical reconnaissance, Arkansas Geological Commission, 1995.

- 
- [37] D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud, B.A. Moyer, A. Chagnes, Recovery of uranium from wet phosphoric acid by solvent extraction processes, *Chem. Rev.*, 114 (2014) 12002-12023.
- [38] A.J.G. Notholt, Phosphate rock: factors in economic and technical evaluation, *Geological Society of London Special Publications*, 79 (1994) 53-65.
- [39] Y. Pan, M.E. Fleet, N.D. Macrae, Oriented monazite inclusions in apatite porphyroblasts from the Hemlo gold deposit, Ontario, Canada, *Mineralogical Magazine*, 57 (1993) 697-708.
- [40] L. Schoneveld, C. Spandler, K. Hussey, Genesis of the central zone of the Nolans Bore rare earth element deposit, Northern Territory, Australia, *Contrib. Mineral. Petrol.*, 170 (2015) 11.
- [41] A.S. Stefan Zielinski, Marek Buca, Recovery of Lanthanides from Kola Apatite in Phosphoric Acid Manufacture, *J. Chem. Tech. Biotechnol.*, 56 (1993) 355-360.
- [42] A.N. Zaitsev, C. Terry Williams, T.E. Jeffries, S. Strekopytov, J. Moutte, O.V. Ivashchenkova, J. Spratt, S.V. Petrov, F. Wall, R. Seltsmann, A.P. Borozdin, Rare earth elements in phoscorites and carbonatites of the Devonian Kola Alkaline Province, Russia: Examples from Kovdor, Khibina, Vuorijarvi and Turiy Mys complexes, *Ore Geology Reviews*, 61 (2014) 204-225.
- [43] G. Nie, T.C. Sun, S. Li, H.L. Li, Containing Rare Earth Phosphate Rock Processing and Rare Earth Enrichment in those Processes, *Advanced Materials Research*, 734-737 (2013) 1022-1028.
- [44] P. Zhang, Comprehensive Recovery and Sustainable Development of Phosphate Resources, *Procedia Engineering*, 83 (2014) 37-51.

- 
- [45] D. Soudry, S. Ehrlich, O. Yoffe, Y. Nathan, Uranium oxidation state and related variations in geochemistry of phosphorites from the Negev (southern Israel), *Chem. Geol.*, 189 (2002) 213-230.
- [46] R.E. Harald Puchelt Bearing of rare earth patterns of apatites from igneous and metamorphic rocks, *Earth. Planet. Sci. Lett.*, 31 (1975) 279-286.
- [47] G.S. Awadalla, Geochemistry and microprobe investigations of Abu Tartur REE-bearing phosphorite, Western Desert, Egypt, *Journal of African Earth Sciences*, 57 (2010) 431-443.
- [48] F.R. Simandl G J., Ferri F, Rare Earth Element Concentrations in Phosphate Deposits, Fernie Formation, Southeastern British Columbia, Canada, British Columbia Ministry of Energy and Mines, BCGS-Geofile 08 (2011).
- [49] G. Simandl, R. Fajber, D. Grieve, Rare Earth Element Concentrations in Phosphate Deposits, Fernie Formation, Southeastern British, Canada, British Columbia, Ministry of Energy and Mines-BCGS-Geofile, 9 (2011).
- [50] S. Jaireth, D.M. Hoatson, Y. Mieizitis, Geological setting and resources of the major rare-earth-element deposits in Australia, *Ore Geology Reviews*, 62 (2014) 72-128.
- [51] M. Jami, Geology, geochemistry and evolution of the Esfordi phosphate-iron deposit, Bafq area, Central Iran, in, 2005, pp. 201-241.
- [52] Z.G.H. Mokhtari M A A, Emami M H, Genesis of iron-apatite ores in Posht-e-Badam Block (Central Iran) using REE geochemistry, *Journal of Earth System Science*, 122 (2013) 795-807.
- [53] P. Emsbo, P.I. McLaughlin, G.N. Breit, E.A. du Bray, A.E. Koenig, Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?, *Gondwana Research*, 27

---

(2015) 776-785.

[54] D.E. Harlov, U.B. Andersson, H.J. Förster, J.O. Nyström, P. Dulski, C. Broman, Apatite–monazite relations in the Kiirunavaara magnetite–apatite ore, northern Sweden, *Chem. Geol.*, 191 (2002) 47-72.

[55] R. Kim, H. Cho, K.N. Han, K. Kim, M. Mun, Optimization of Acid Leaching of Rare-Earth Elements from Mongolian Apatite-Based Ore, *Minerals*, 6 (2016) 63.

[56] R. Amli, Mineralogy and Rare Earth Geochemistry of Apatite and Xenotime from the Gloserheia Granite Pegmatite, Froland, Southern Norway, *Am. Mineral.*, 60 (1975) 607-620.

[57] Y. Wu, Review of comprehensive utilization of phosphate rock-rare earth recovery, *Journal of Wuhan institute of chemical industry*, 1 (1983) 1-13(in Chinese).

[58] F. Habashi, F.T. Awadalla, The recovery of uranium and lanthanides during the production of nitrophosphate fertilisers using tertiary amyl alcohol, *J. Chem. Technol. Biotechnol.*, 36 (1986) 1-6.

[59] L. Wang, Z. Long, X. Huang, X. Peng, Y. Han, D. Cui, Rare Earth Distribution Control During Wet Process of Phosphoric Acid Production, *Journal of the Chinese Rare Earth Society*, 26 (2008) 307-312.

[60] I.J. Goldstein, Preparation of the precipitate and of rare earth oxides from Kola apatites, *Rev. chem*, 16 (1965) 359-360.

[61] S.r.i.o.c. industry, Lab-scale report for REs recovery from Tangdu phosphate rock and precipitating calcium hydrogen phosphate(in Chinese), *Applied Chemical Industry*, (1977) 16-26.

[62] F. Habashi, The recovery of the lanthanides from phosphate rock, *Journal of Chemical*

---

Technology and Biotechnology. Chemical Technology, 35 (1985) 5-14.

[63] A. Rollat, Recovery of Rare Earths from Wet-Process Phosphoric Acid, the Solvay Experience, Procedia Engineering, 138 (2016) 273-280.

[64] J. Preston, The recovery of rare earth oxides from a phosphoric acid byproduct. Part 4. The preparation of magnet-grade neodymium oxide from the light rare earth fraction, Hydrometallurgy, 42 (1996) 151-167.

[65] J. Preston, P. Cole, W. Craig, A. Feather, The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction, Hydrometallurgy, 41 (1996) 1-19.

[66] J. Preston, P. Cole, A. Du Preez, M. Fox, A. Fleming, The recovery of rare earth oxides from a phosphoric acid by-product. Part 2: The preparation of high-purity cerium dioxide and recovery of a heavy rare earth oxide concentrate, Hydrometallurgy, 41 (1996) 21-44.

[67] J. Preston, A. Du Preez, P. Cole, M. Fox, The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide, Hydrometallurgy, 42 (1996) 131-149.

[68] M. Mashkovtsev, M. Botalov, D. Smyshlyaev, R. Pajarre, P. Kangas, V. Rychkov, P. Koukkari, Pilot-scale recovery of rare earths and scandium from phosphogypsum and uranium leachates, 8 (2016) 01026.

[69] Russian scientists develop rare-earth metal recovery technology, in, [online] June 21, 2016.

[70] P. Becker, Phosphates and phosphoric acid, Marcel Dekker, Inc., 1983.

[71] S. Al-Thyabat, P. Zhang, In-line extraction of REE from Dihydrate (DH) and HemiDihydrate (HDH) wet processes, Hydrometallurgy, 153 (2015) 30-37.



- 
- [72] C. De Vreugd, G. Witkamp, G. Van Rosmalen, Growth of gypsum III. Influence and incorporation of lanthanide and chromium ions, *J. Cryst. Growth*, 144 (1994) 70-78.
- [73] L. Wang, Y. Yu, Y. Liu, Z. Long, Centrifugal extraction of rare earths from wet-process phosphoric acid, *Rare Metals*, 30 (2011) 211-215.
- [74] E.F.M. Association, Booklet No. 4 of 8 Production of phosphoric acid, in: Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry, 2000.
- [75] E. Lokshin, Y.A. Vershkova, A. Vershkov, O. Tareeva, Efficiency of sulfuric acid leaching of lanthanides in relation to quality of phosphosemihydrate obtained from khibiny apatite concentrate, *Russ. J. Appl. Chem.*, 75 (2002) 1572-1576.
- [76] E. Lokshin, O. Tareeva, Activation of leaching of rare earth elements from phosphohemihydrate, *Russ. J. Appl. Chem.*, 86 (2013) 1638-1642.
- [77] E. Lokshin, O. Tareeva, Specific features of sulfuric acid leaching-out of lanthanides from phosphohemihydrate, *Russ. J. Appl. Chem.*, 81 (2008) 8-13.
- [78] E.P. Lokshin, O. Tareeva, Solubility of  $\text{YF}_3$ ,  $\text{CeF}_3$ ,  $\text{PrF}_3$ ,  $\text{NdF}_3$ , and  $\text{DyF}_3$  in solutions containing sulfuric and phosphoric acids, *Russian Journal of Inorganic Chemistry*, 52 (2007) 1830-1834.
- [79] C. Koopman, G. Witkamp, G. Van Rosmalen, Removal of heavy metals and lanthanides from industrial phosphoric acid process liquors, *Sep. Sci. Technol.*, 34 (1999) 2997-3008.
- [80] J.A. Ober, Mineral commodity summaries 2017, in, US Geological Survey, 2017.
- [81] R. Kijkowska, Preparation of lanthanide orthophosphates by crystallisation from phosphoric acid solution, *Journal of materials science*, 38 (2003) 229-233.
- [82] Z.S. Cetiner, S.A. Wood, C.H. Gammons, The aqueous geochemistry of the rare earth

---

elements. Part XIV. The solubility of rare earth element phosphates from 23 to 150 °C, *Chem. Geol.*, 217 (2005) 147-169.

[83] E. Lokshin, O. Tareeva, Recovery of lanthanides from extraction phosphoric acid produced by the dihydrate process, *Russ. J. Appl. Chem.*, 83 (2010) 951-957.

[84] P. Puszkiwicz. A, M, Kimek, M, Solubility of phosphates of rare earth elements in phosphoric acid *Prem Chem*, 47 (1968) 195-196.

[85] I. Melikhov, Y. Trofimov, D. Chirkst, K. Chalian, Y. Dibrov, Isolation of Rare Earth Element's Radionuclides from Phosphoric Acid Solutions on Cerium (III) Phosphate, Phosphorus, Sulfur, and Silicon and the Related Elements, 51 (1990) 449-449.

[86] I.A. Dibrov, D.E. CHIRKST, K. Chaliyan, Recovery of Lanthanides in the Sulphuric Acid Leaching Process of Kola Apatites, *Miner. Process. Extr. Metall. Rev.*, 15 (1995) 142-142.

[87] I. Dibrov, D. Chirkst, O. Cheremisina, K. Chaliyan, Inorganic Synthesis and Industrial Inorganic Chemistry-Crystallization of Lanthanide Phosphates and Fluorides from Wet-Process Orthophosphoric Acid, *Russ. J. Appl. Chem.*, 72 (1999) 183-188.

[88] B. Zakharova, L. Komissarova, V. Traskin, S. Naumov, P. Melnikov, Precipitation of rare earth phosphates from H<sub>3</sub>PO<sub>4</sub> solutions, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 111 (1996) 2-2.

[89] M. Kul, Y. Topkaya, I. Karakaya, Rare earth double sulfates from pre-concentrated bastnasite, *Hydrometallurgy*, 93 (2008) 129-135.

[90] L. Pietrelli, B. Bellomo, D. Fontana, M. Montereali, Rare earths recovery from NiMH spent batteries, *Hydrometallurgy*, 66 (2002) 135-139.

[91] G.A. Moldoveanu, V.G. Papangelakis, Recovery of rare earth elements adsorbed on clay

---

minerals: I. Desorption mechanism, *Hydrometallurgy*, 117 (2012) 71-78.

[92] K.A. Gschneidner, L. Eyring, G.H. Lander, *Handbook on the physics and chemistry of rare earths* Elsevier, 1987.

[93] R.D. Abreu, C.A. Morais, Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide, *Miner. Eng.*, 23 (2010) 536-540.

[94] L.T. Peiró, G.V. Méndez, Material and energy requirement for rare earth production, *JOM*, 65 (2013) 1327-1340.

[95] E.P. Lokshin, O. Tareeva, T. Kashulina, Effect of sulfuric acid and sodium cations on the solubility of lanthanides in phosphoric acid, *Russian Journal of Applied Chemistry*, 81 (2008) 1-7.

[96] E. Lokshin, O. Tareeva, Treatment of rare-earth concentrate to remove phosphorus and fluorine compounds, *Russ. J. Appl. Chem.*, 83 (2010) 1919-1924.

[97] J.F. Da Silva, M.M. Queimado, Solubility products of lanthanide fluorides, *Revist. Portug. Quím.*, 15 (1973) 29-34.

[98] E. Lokshin, Y.A. Vershkova, K. Ivlev, O. Tareeva,  $\text{LaF}_3$  and  $\text{YbF}_3$  solubilities in solutions containing sulfuric and phosphoric acids, *Russian journal of inorganic chemistry*, 49 (2004) 645-648.

[99] E.P. Lokshin, O.A. Tareeva, I.R. Elizarova, Recovery of rare earth elements from wet process extraction phosphoric acid, *Russ. J. Appl. Chem.*, 86 (2013) 623-628.

[100] E.P. Lokshin, O.A. Tareeva, I.R. Elizarova, Deposition of rare earth elements from a wet-process phosphoric acid by fluorine compounds, *Russ. J. Appl. Chem.*, 84 (2011) 773-781.

[101] E. Lokshin, O. Tareeva, I. Elizarova, V. Kalinnikov, Recovery of rare earth elements from

---

the wet process phosphoric acid, *Russ. J. Appl. Chem.*, 88 (2015) 1-12.

[102] E. Lokshin, O. Tareeva, I. Elizarova, Treatment of fluorophosphate rare earth concentrate, *Russ. J. Appl. Chem.*, 85 (2012) 1800-1806.

[103] K. Weterings, J. Janssen, Recovery of uranium, vanadium, yttrium and rare earths from phosphoric acid by a precipitation method, *Hydrometallurgy*, 15 (1985) 173-190.

[104] G. Xu, Rare Earth, Metallurgical Industry, Bei Jing, (1995) 521-522.

[105] S. Al-Thyabat, P. Zhang, REE extraction from phosphoric acid, phosphoric acid sludge, and phosphogypsum, *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min Metall. C)*, 124 (2015) 143-150.

[106] M. Krea, H. Khalaf, Liquid–liquid extraction of uranium and lanthanides from phosphoric acid using a synergistic DOPPA–TOPO mixture, *Hydrometallurgy*, 58 (2000) 215-225.

[107] R.S. Long, D.A. Ellis, R.H. Bailes, Recovery of uranium from phosphates by solvent extraction, in: Geneva Conference Paper, No. P/524, 1956.

[108] F. Bunus, I. Miu, R. Dumitrescu, Simultaneous recovery and separation of uranium and rare earths from phosphoric acid in a one-cycle extraction-stripping process, *Hydrometallurgy*, 35 (1994) 375-389.

[109] F.T. Bunus, Uranium and rare earth recovery from phosphate fertilizer industry by solvent extraction, *Mineral Processing and Extractive Metallurgy Review*, 21 (2000) 381-478.

[110] L. Wang, Z. Long, X. Huang, Y. Yu, D. Cui, G. Zhang, Recovery of rare earths from wet-process phosphoric acid, *Hydrometallurgy*, 101 (2010) 41-47.

[111] S. Radhika, B.N. Kumar, M.L. Kantam, B.R. Reddy, Liquid–liquid extraction and separation possibilities of heavy and light rare-earths from phosphoric acid solutions with acidic

---

organophosphorus reagents, *Sep. Purif. Technol.*, 75 (2010) 295-302.

[112] S. Radhika, B. Nagaphani Kumar, M. Lakshmi Kantam, B. Ramachandra Reddy, Solvent extraction and separation of rare-earths from phosphoric acid solutions with TOPS 99, *Hydrometallurgy*, 110 (2011) 50-55.

[113] S. Radhika, V. Nagaraju, B. Nagaphani Kumar, M.L. Kantam, B.R. Reddy, Solid-liquid extraction of Gd(III) and separation possibilities of rare earths from phosphoric acid solutions using Tulsion CH-93 and Tulsion CH-90 resins, *Journal of Rare Earths*, 30 (2012) 1270-1275.

[114] B.R. Reddy, S. Radhika, B.N. Kumar, Liquid-liquid extraction studies of trivalent yttrium from phosphoric acid solutions using TOPS 99 as an extractant, *Sep. Sci. Technol.*, 45 (2010) 1426-1432.

[115] R.D. F. Bunu, Simultaneous extraction of rare earth elements and uranium from phosphoric acid, *Hydrometallurgy*, 28 (1992) 331-338.

[116] D. Singh, K. Yadav, R. Vijayalakshmi, H. Singh, Extraction studies using Di-nonyl Phenyl Phosphoric Acid (dnppa) and Tri-n-octyl Phosphine Oxide (TOPO) for uranium and yttrium from Merchant Grade Phosphoric Acid (MGA), in: *Proceedings of international conference on peaceful uses of atomic energy-2009*. V. 1, 2009.

[117] D.K. Singh, M. Anitha, K.K. Yadav, M.K. Kotekar, R. Vijayalakshmi, H. Singh, Simultaneous recovery of yttrium and uranium using D2EHPA–TBP and DNPPA–TOPO from phosphoric acid, *Desalination and Water Treatment*, 38 (2012) 292-300.

[118] B.R. Reddy, B.N. Kumar, S. Radhika, Solid - Liquid Extraction of Terbium from Phosphoric Acid Medium using Bifunctional Phosphinic Acid Resin, Tulsion CH - 96, *Solvent Extr. Ion Exch.*, 27 (2009) 695-711.

- 
- [119] B.R. Reddy, J.R. Kumar, Rare Earths Extraction, Separation, and Recovery from Phosphoric Acid Media, *Solvent Extr. Ion Exch.*, 34 (2016) 226-240.
- [120] B. Nagaphani Kumar, S. Radhika, B. Ramachandra Reddy, Solid–liquid extraction of heavy rare-earths from phosphoric acid solutions using Tulsion CH-96 and T-PAR resins, *Chem. Eng. J.*, 160 (2010) 138-144.
- [121] X. Li, Z. Zhou, G. Zhao, Z. Liu, Utilization of phosphogypsum for backfilling, way to relieve its environmental impact, *Gospodarka Surowcami Mineralnymi*, 24 (2008) 226–232.
- [122] M. Azouazi, Y. Ouahidi, S. Fakhi, Y. Andres, J.C. Abbe, M. Benmansour, Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco, *Journal of environmental radioactivity*, 54 (2001) 231-242.
- [123] R.A. Zielinski, M.S. Al-Hwaiti, J.R. Budahn, J.F. Ranville, Radionuclides, trace elements, and radium residence in phosphogypsum of Jordan, *Environ. Geochem. Health*, 33 (2011) 149-165.
- [124] H. Tayibi, M. Choura, F.A. López, F.J. Alguacil, A. López-Delgado, Environmental impact and management of phosphogypsum, *Journal of Environmental Management*, 90 (2009) 2377-2386.
- [125] P. Rutherford, M. Dudas, R. Samek, Environmental impacts of phosphogypsum, *Sci. Total Environ.*, 149 (1994) 1-38.
- [126] S.M.B. de Oliveira, P.S.C. da Silva, B.P. Mazzilli, D.I.T. Favaro, C.H. Saueia, Rare earth elements as tracers of sediment contamination by phosphogypsum in the Santos estuary, southern Brazil, *Appl. Geochem.*, 22 (2007) 837-850.
- [127] M. Walawalkar, C.K. Nichol, G. Azimi, Process investigation of the acid leaching of rare

---

earth elements from phosphogypsum using HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, *Hydrometallurgy*, 166 (2016) 195-204.

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

[129] J. Yang, W. Liu, L. Zhang, B. Xiao, Preparation of load-bearing building materials from autoclaved phosphogypsum, *Construction and Building Materials*, 23 (2009) 687-693.

[130] N.F. Fuleihan, Phosphogypsum Disposal-The Pros & Cons of Wet Versus Dry Stacking, *Procedia Engineering*, 46 (2012) 195-205.

[131] N. Değirmenci, Utilization of phosphogypsum as raw and calcined material in manufacturing of building products, *Construction and Building Materials*, 22 (2008) 1857-1862.

[132] K. Oliveira, M. Menezes, E. Von Sperling, V. Jacomino, Transfer factor of rare earth elements from phosphogypsum amended Brazilian tropical soils to lettuce, corn and soybean, *The Journal of Solid Waste Technology and Management*, 38 (2012) 202-210.

[133] X. Li, Z. Zhou, G. Zhao, Z. Liu, Utilization of phosphogypsum for backfilling, way to relieve its environmental impact, *Gospodarka Surowcami Mineralnymi*, 24 (2008) 226-232.

[134] I.S. Alcordo, J.E. Rechcigl, Phosphogypsum in agriculture: a review, *Advances in Agronomy*, 49 (1993) 55-118.

[135] M.M. Smadi, R.H. Haddad, A.M. Akour, Potential use of phosphogypsum in concrete, *Cem. Concr. Res.*, 29 (1999) 1419-1425.

[136] E. Lokshin, O. Tareeva, I. Elizarova, On integrated processing of phosphogypsum, *Russ. J. Appl. Chem.*, 86 (2013) 463-468.

- 
- [137] N. Kybartiene, Z. Valancius, V. Leskeviciene, L. Urbonas, Influence of the composition of phosphate rock on the amount of water-insoluble phosphate impurities in semi-hydrate phosphogypsum, *Ceramics–Silikáty*, 59 (2015) 29-36.
- [138] A. Santos, B. Mazzilli, D. Fávaro, P. Silva, Partitioning of radionuclides and trace elements in phosphogypsum and its source materials based on sequential extraction methods, *Journal of Environmental Radioactivity*, 87 (2006) 52-61.
- [139] A. Samonov, New data on mineral forms of rare metals in phosphogypsum wastes, in: *Doklady Earth Sciences*, Springer, 2011, pp. 1312-1315.
- [140] Z. Ismail, E. Abu Elgoud, M. Gasser, H. Aly, F. Abdel Hai, I. Ali, Leaching of Some Lanthanides from Phosphogypsum Fertilizers by Mineral Acids, *Arab Journal of Nuclear Sciences and Applications*, 48 (2015) 37-50.
- [141] S. El-Reefy, A. Nayl, H. Aly, Leaching and Group Separation of Lanthanides from Phosphogypsum.
- [142] I. Hammas-Nasri, K. Horchani-Naifer, M. Férid, D. Barca, Rare earths concentration from phosphogypsum waste by two-step leaching method, *Int. J. Miner. Process.*, 149 (2016) 78-83.
- [143] J. Kulczycka, Z. Kowalski, M. Smol, H. Wirth, Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste—case study of the WIZÓW Chemical Plant (Poland), *Journal of Cleaner Production*, 113 (2016) 345-354.
- [144] M. Rzeczycka, A. Miernik, Z. Markiewicz, Simultaneous degradation of waste phosphogypsum and liquid manure from industrial pig farm by a mixed community of sulfate-reducing bacteria, *Polish Journal of Microbiology*, 59 (2010) 241-247.



- 
- [145] K. Grabas, A. PAWEŁCZYK, C. MORA, A. DYONIZY, P. NOWAK, A. OSTROWSKI, S. STREK, W. STREK, Recovery of lanthanides from apatite phosphogypsum, in: COM 2014-Conference of Metallurgists Proceedings, 2014.
- [146] D. Todorovsky, A. Terziev, M. Milanova, Influence of mechanoactivation on rare earths leaching from phosphogypsum, *Hydrometallurgy*, 45 (1997) 13-19.
- [147] E. Lokshin, O. Tareeva, I. Elizarova, A study of the sulfuric acid leaching of rare-earth elements, phosphorus, and alkali metals from phosphodihydrate, *Russ. J. Appl. Chem.*, 83 (2010) 958-964.
- [148] D. Freyer, W. Voigt, Crystallization and phase stability of  $\text{CaSO}_4$  and  $\text{CaSO}_4$ -based salts, *Monatshefte für Chemie/Chemical Monthly*, 134 (2003) 693-719.
- [149] R. Shivaramaiah, W. Lee, A. Navrotsky, D. Yu, P. Kim, H. Wu, Z. Hu, R. Riman, A. Anderko, Location and stability of europium in calcium sulfate and its relevance to rare earth recovery from phosphogypsum waste, *Am. Mineral.*, 101 (2016) 1854-1861.
- [150] R. Kijkowska, and Pawłowska-Kozicska, D., , *Pr.Nauk. Institute Technologii Neorganicznej i Nawosow Mineralnych Politechniki Wroclawskiej*, no. 30 (1986) pp. 17-26.
- [151] K.V.T. Lokshin E. P., Ivlev K. G. et al, *The Method of the Extraction of Rare-Earth Elements from Phosphogypsum*, (2007).
- [152] N. Vorob'ev, A. Teterevko, V. Zyk, Extraction of rare earth elements from phosphogypsum with sulphuric acid, *VESTSI-NATSYIANAL'NAIA AKADEMIIA NAVUK BELARUSI SERIYA KHIMICHNYKH NAVUK*, (1998) 103-106.
- [153] E. Lokshin, Y.A. Vershkova, A. Vershkov, O. Tareeva, Leaching of lanthanides from phosphohemihydrate with nitric acid, *Russ. J. Appl. Chem.*, 75 (2002) 1753-1759.

- 
- [154] M. Al-Hwaiti, K.A. Ibrahim, M. Harrara, Removal of heavy metals from waste phosphogypsum materials using polyethylene glycol and polyvinyl alcohol polymers, *Arabian Journal of Chemistry*, (2015).
- [155] H. El-Didamony, M. Ali, N. Awwad, M. Fawzy, M. Attallah, Treatment of phosphogypsum waste using suitable organic extractants, *J. Radioanal. Nucl. Chem.*, 291 (2012) 907-914.
- [156] H. El-Didamony, H. Gado, N. Awwad, M. Fawzy, M. Attallah, Treatment of phosphogypsum waste produced from phosphate ore processing, *J. Hazard. Mater.*, 244 (2013) 596-602.
- [157] M. Kouraim, M. Fawzy, O. Helaly, Leaching of Lanthanides from Phosphogypsum Waste using Nonyl Phenol Ethoxylate Associated with  $\text{HNO}_3$  and  $\text{HCl}$ , *International Journal of Sciences: Basic and Applied Research*, 16 (2014) 31-44.
- [158] A. Valkov, V. Andreev, A. Anufrieva, Y. Makaseev, S. Bezrukova, N. Demyanenko, Phosphogypsum Technology with the Extraction of Valuable Components, *Procedia Chemistry*, 11 (2014) 176-181.
- [159] S.A. Wood, A.E. Williams-Jones, The aqueous geochemistry of the rare-earth elements and yttrium 4. Monazite solubility and REE mobility in exhalative massive sulfide-depositing environments, *Chem. Geol.*, 115 (1994) 47-60.
- [160] E.P. Lokshin, K. Ivlev, O. Tareeva, Leaching-out of lanthanides from waste phosphosemihydrate with sulfuric acid solutions of increased concentration, *Russ. J. Appl. Chem.*, 78 (2005) 1761-1766.
- [161] E.P. Lokshin, A. Vershkov, Y.A. Vershkova, Problems of rare-earth metals extraction on

---

the sulfur-acid processing of Hybin apatite concentrate, *Metally* (Moscow), (2001) 42-50.

[162] R. Kijkowska, Kowalczyk, J., Mazanek, C. & Mikołajczyk, T., Fundamentals of non-waste processing of apatite phosphogypsum, *Scientific Works of Wrocław University of Technology* 59, (1989).

[163] K. Podbiera-Matysik, K. Gorazda, Z. Wzorek, Potential management of waste phosphogypsum with particular focus on recovery of rare earth metals, *Polish Journal of Chemical Technology*, 17 (2015) 55-61.

[164] Z. Kowalski, J. Kulczycka, H. Wirth, The concept of using the phosphogypsum dumps 'Wizów' as a source of secondary raw material, *Czasopismo Techniczne*, 128 (2006) 39-45 (in Polish) .

[165] E. Lokshin, K. Ivlev, O. Tareeva, Synthesis of lanthanide nitrates from phosphosemihydrate, *Russ. J. Appl. Chem.*, 78 (2005) 1903-1912.

[166] A. Jarosiński, J. Kowalczyk, C. Mazanek, Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare earths, *J. Alloys Compd.*, 200 (1993) 147-150.

[167] M.V. Genkin, A.V. Evtushenko, A.A. Komkov, A.M. Safiulina, V.S. Spiridonov, S.V. Shvetsov, A method for extracting rare-earth metals, in, *Google Patents*, 2013.

[168] F. Spedding, S. Jaffe, Conductances, solubilities and ionization constants of some rare earth sulfates in aqueous solutions at 25°C, *J. Am. Chem. Soc.*, 76 (1954) 882-884.

[169] J. Rard, F. Spedding, Electrical conductances of some aqueous rare earth electrolyte solutions at 25. deg.. III. Rare earth nitrates, *The Journal of Physical Chemistry*, 79 (1975) 257-262.

- 
- [170] Y.A. Vershkova, O. Tareeva, K. Ivlev, E. Lokshin, Solubility of Calcium Sulfate Dihydrate in Nitric Acid at 20°C, *Russ. J. Appl. Chem.*, 76 (2003) 156-157.
- [171] V.N. Lebedev, Smirnova, I.P., Masloboev, V.A., and Mikhlin, E.B., *Physicochemical and Technological Problems of Processing of Resources of the Kola Peninsula*, St. Petersburg: Nauka,, (1993) pp. 56 - 60.
- [172] O. Amano, A. Sasahira, Y. Kani, K. Hoshino, M. Aoi, F. Kawamura, Solubility of lanthanide fluorides in nitric acid solution in the dissolution process of FLUOREX reprocessing system, *J. Nucl. Sci. Technol.*, 41 (2004) 55-60.
- [173] J. Wing, The Hemi Era In Phosphoric Acid, in: American Institute of Chemical Engineers Clearwater Convention, Clearwater Beach, Florida, USA, 2006.
- [174] E.R. Riegel, Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology, Vol. 1, in, New York: Springer, 2007.
- [175] G. Witkamp, M. Seckler, O. Bruinsma, G. Van Rosmalen, Recrystallization of calcium sulfate in phosphoric acid solutions; batchwise operation, *J. Cryst. Growth*, 99 (1990) 1117-1123.
- [176] C. Koopman, G. Witkamp, Extraction of lanthanides from the phosphoric acid production process to gain a purified gypsum and a valuable lanthanide by-product, *Hydrometallurgy*, 58 (2000) 51-60.
- [177] C. Koopman, G. Witkamp, Ion exchange extraction during continuous recrystallization of  $\text{CaSO}_4$  in the phosphoric acid production process: lanthanide extraction efficiency and  $\text{CaSO}_4$  particle shape, *Hydrometallurgy*, 63 (2002) 137-147.
- [178] E.F.M.A. (EFMA), Production of phosphoric acid. Booklet 7 of 8. Best available

---

techniques for pollution and control in the European Fertilizer Industry, (2000).

[179] E. Johnson, Process of producing calcium nitrate and ammonium salts from phosphate rock and like phosphate material, in, Google Patents, 1932.

[180] J.D. Logemann, W. Slot, Process for the continuous preparation of nitrophosphate fertilizers, in, Google Patents, 1971.

[181] J. Tinge, Cadmium and chromium present in calcium sulfate dihydrate produced by the nitrophosphate process, *Sep. Purif. Technol.*, 38 (2004) 75-83.

[182] F. Nielsson, L. Yates, Nitric Phosphates, Manufacture from Phosphate Rock, Nitric Acid Ammonia, and Potassium or Other Soluble Sulfates, *J. Agric. Food. Chem.*, 1 (1953) 672-677.

[183] T.P. Hignett, Nitrophosphates, in: *Fertilizer Manual*, Springer, 1985, pp. 203-210.

[184] W. Fuller, W. Riley, D. Seamands, Phosphorus Availability, Solubility Characteristics of Nitric Phosphate Fertilizers in Calcareous Soils, and Comparative Effectiveness in Greenhouse Pot Cultures, *J. Agric. Food. Chem.*, 5 (1957) 935-941.

[185] J. Steen, E.H. Aasum, T. Heggeboe, F. Nielsson, The Norsk Hydro nitrophosphate process, *Manual of Fertilizer Processing, Fertilizer Science and Technology Series*, 5., (1987) 393-419.

[186] I. Hussain, The operating experience of nitrophosphate plant, *Procedia Engineering*, 46 (2012) 172-177.

[187] Y. Feng, X. Jiang, S. Wang, Y. Fang, W.Z. Jiang, W. Denggao Liu, Recovery of heavy rare earth elements from phosphorite, *Non-ferrous metal (smelting part)*, 2 (2012) 34-36.

[188] R. Kijkowska, M. Sarnowski, K. Baran, Studies on extraction of rare earth elements from apatite Kola, (1976).

[189] M. Andropov, A. Anufrieva, A. Buynovskiy, Y. Makaseev, I. Mazov, R. Nefedov, V.

---

Sachkov, O. Stepanova, A. Valkov, Extraction of rare earth elements from hydrate-phosphate precipitates of apatite processing, in: IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2016, pp. 012001.

[190] E. Lokshin, O. Tareeva, I. Elizarova, Sorption conversion of phosphate concentrates of rare-earth metals, *Russ. J. Appl. Chem.*, 87 (2014) 1038-1043.

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

[192] E. Jorjani, M. Shahbazi, The production of rare earth elements group via tributyl phosphate extraction and precipitation stripping using oxalic acid, *Arabian Journal of Chemistry*, (2012).

[193] H. Li, F. Guo, Z. Zhang, D. Li, Z. Wang, A new hydrometallurgical process for extracting rare earths from apatite using solvent extraction with P350, *J. Alloys Compd.*, 408 (2006) 995-998.

[194] K. Chitra, A. Gaikwad, G. Surender, A. Damodaran, Studies on kinetics of forward and backward extraction of neodymium by using phosphonic acid monoester as an acidic extractant, *The Chemical Engineering Journal and The Biochemical Engineering Journal*, 60 (1995) 63-73.

[195] H.-C. Kao, P.-S. Yen, R.-S. Juang, Solvent extraction of La (III) and Nd (III) from nitrate solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, *Chem. Eng. J.*, 119 (2006) 167-174.

[196] A. Geist, W. Nitsch, J.-I. Kim, On the kinetics of rare-earth extraction into D2EHPA, *Chem. Eng. Sci.*, 54 (1999) 1903-1907.

- 
- [197] E. Lokshin, V. Ivanenko, O. Tareeva, R. Korneikov, Sorption extraction of lanthanides from phosphoric acid solutions, *Russ. J. Appl. Chem.*, 82 (2009) 537-544.
- [198] Z. Jie, S. Chuanmin, Y. Guofeng, X. Fei, Separation and enrichment of rare earth elements in phosphorite in Xinhua, Zhijin, Guizhou, *Journal of rare earths*, 24 (2006) 413-414.
- [199] A. Brunfelt, Separation of rare-earth elements from apatite, *Separation Science*, 8 (1973) 623-625.
- [200] F.T. Awadalla, F. Habashi, Recovery of uranium and lanthanides from calcium hydrogen phosphate  $[\text{Ca}(\text{H}_2\text{PO}_4)_2]$ -calcium nitrate-water and  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -calcium chloride-water systems, *Industrial & Engineering Chemistry Research*, 28 (1989) 1101-1103.
- [201] B. Zhong, D. Wu, H. Yang, X. Yang, M. Huang, Study on the way to use low grade phosphate rock in China, *Inorganic chemicals industry*, 41 (2009) 1-5.
- [202] F. Habashi, Y. Xinbao, The hydrochloric acid route for phosphate rock, *J. Chem. Technol. Biotechnol.*, 38 (1987) 115-126.
- [203] F. Habashi, In-situ and dump leaching technology: application to phosphate rock, *Nutrient Cycling in Agroecosystems*, 18 (1988) 275-279.
- [204] J. Jiang, Way for the development and utilization of Low-grade phosphate rock, *Multipurpose utilization of mineral resources*, (2014) 16-19.
- [205] C. Wang, D. Yao, Study of the cycle process for phosphate rock decomposition with HCl(in Chinese) *Chemical fertilizer industry*, 5 (1988) 002.
- [206] Y. Jin, Y. Ma, Y. Weng, X. Jia, J. Li, Solvent extraction of  $\text{Fe}^{3+}$  from the hydrochloric acid route phosphoric acid by D2EHPA in kerosene, *Journal of Industrial and Engineering Chemistry*, 20 (2014) 3446-3452.

- 
- [207] B. Abraham, B. Ruth, Process for the preparation of phosphoric acid, in, Google Patents, 1959.
- [208] S. Van Der Sluis, Y. Meszaros, J. Wesselingh, G. Van Rosmalen, A clean technology phosphoric acid process, in, Delft University Press, 1987.
- [209] Y. Yang, f. Xie, L. Huang, H. Nie, Experimental study on extraction of acid from HCl decomposing solution of phosphate concentrate, Hydrometallurgy of China, (2012) 303-305.
- [210] D. Loewy, C. Fink, Processes for the manufacture of feed-grade dicalcium phosphate and phosphoric acid, in, Google Patents, 1976.
- [211] Q. Song, D. Xia, A. Tang, Review of feed grade calcium hydrogen phosphate production technology, Guizhou chemical industry, (1991) 27-32.
- [212] Z. Liu, Y. Liu, M. Liu, Study on acid leaching of rare earth-containing apatite concentrates, Non-ferrous metal (Smelting part), 5 (2013) 37-39.
- [213] L. Zhao, D. Nie, H. He, Z. Wang, A. Xue, S. Wu, Study on leaching of rare earth from middle-low grade collophanite with hydrochloric acid, Non-ferrous metal (Smelting part), 4 (2014) 45-47.
- [214] M.A. El-Mottaleb, M. Cheira, G.A. Gouda, A.A. Saiyd, Leaching of Rare Earth Elements from Egyptian Western Desert Phosphate Rocks using HCl, Chemistry of Advanced Materials, 1 (2016).
- [215] J. Shen, X. Zhang, G. Gu, F. He, W. Zhang, J. Guo, Test of leaching rare- earth elements from phosphate rock containing rare- earth elements, Industrial mineral & processing, 35 (2006) 11-13.
- [216] D. Nie, A. Liu, Z. Wang, Z. Wang, J. Cao, M. Zhu, Study on dissolution of rare earth



---

bearing middle-low grade phosphate ore by hydrochloric acid hydrolysis process, *Industrial mineral & processing*, 44 (2015) 7-9.

[217] H. Shlewit, Treatment of phosphate rocks with hydrochloric acid, *J. Radioanal. Nucl. Chem.*, 287 (2011) 49-54.

[218] G. Wang, X. Niu, C. Zhao, Y. Zhang, J. wANG, Study of rare earths enrichment from Yunan phosphate rock and production of feed-grade calcium phosphate, *Inorganic chemicals industry*, (1997) 6-9.

[219] H. Marshall, L. Rader Jr, K. Jacob, Factors affecting the phosphoric acid-phosphate rock reaction, *Industrial & Engineering Chemistry*, 25 (1933) 1253-1259.

[220] K. Antar, M. Jemal, Kinetics and thermodynamics of the attack of a phosphate ore by acid solutions at different temperatures, *Thermochim. Acta*, 474 (2008) 32-35.

[221] S.V. Dorozhkin, Fundamentals of the Wet-Process Phosphoric Acid Production. 1. Kinetics and Mechanism of the Phosphate Rock Dissolution, *Industrial & Engineering Chemistry Research*, 35 (1996) 4328-4335.

[222] H. Lefires, H. Medini, A. Megriche, A. Mgaidi, Dissolution of Calcareous Phosphate Rock from Gafsa (Tunisia) Using Dilute Phosphoric Acid Solution, *International Journal of Nonferrous Metallurgy*, 03 (2014) 1-7.

[223] K. Brahim, K. Antar, I. Khattech, M. Jemal, Effect of temperature on the attack of fluorapatite by a phosphoric acid solution, *Scientific Research & Essays*, 3 (2007) 35-39.

[224] F.B. Brahim, A. Mgaidi, M. Elmaaoui, Kinetics of leaching of tunisian phosphate ore particles in dilute phosphoric acid solutions, *Can. J. Chem. Eng.*, 77 (1999) 136-142.

[225] S.D. Wang, K.X. Jiang, X.X. Jiang, L.Y. Feng, Y.Q. Fan, W. Jiang, Leaching REEs from

---

Phosphorite with Returning Acid(in Chinese), *Nonferrous Metals*, (2012) 33-36.

[226] X. Jiang, L. Feng, S. Wang, D. Zhang, W. Liu, Y. Fan, Study on Comprehensive Recovery of REEs from Phosphorite(in Chinese), in: Chinese rare earth resources comprehensive utilization and environmental protection conference, 2012, pp. 21-25.

[227] K. Jiang, L. Feng, X. Jiang, S. Wang, Y. Fan, A method for rare earths separation from phosphate rock. CN 102312089A, in, China, Jan 12, 2012.

[228] K. Stone, A.M.T.S. Bandara, G. Senanayake, S. Jayasekera, Processing of rare earth phosphate concentrates: A comparative study of pre-leaching with perchloric, hydrochloric, nitric and phosphoric acids and deportment of minor/major elements, *Hydrometallurgy*, 163 (2016) 137-147.

[229] H. Xiaowei, W. Liangshi, W. Shengxi, L. Zhiqi, F. Zongyu, C. Dali, D. Jinshi, H. Li, Method for comprehensive recovery of rare earths and phosphorus from phosphate rock associated with monazite. CN105331812A, (Feb 17, 2016).

[230] W. Liangshi, H. Xiaowei, W. Shengxi, Y. Ying, W. Chunmei, C. Dali, F. Zongyu, D. Jinshi, L. Zhiqi, Method for comprehensive recovery of rare earths and phosphorus from phosphate rock. CN106319247A, (Jan 11, 2017).