



Review

Recovery of rare earth elements from phosphate rock by hydrometallurgical processes – A critical review



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ABSTRACT

Generally, phosphate rock contains about 0.05 wt% rare earth elements (REEs) on average. And the world commercial phosphate rock production is estimated to be 250 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 H₂SO₄, HNO₃, HCl, H₃PO₄, various REEs recovery processes via crystallization, precipitation, solvent extraction and ion exchange methods are systematically reviewed.

In H₂SO₄ 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 HCl, HNO₃ and H₃PO₄ processes, REEs entirely transfers 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.

1. Introduction

1.1. Rare earths resource

The rare earth elements (REEs) are a series of elements with similar physicochemical 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 history of rare earths industry (Fig. 1), at present, REEs are mainly

produced from bastnasite, monazite, ion-absorbed clay, xenotime and loparite [5–11]. However, the increasing demand, especially from green energy and new materials [11–15] exacerbated its contradiction with the shrinking easy-processing REEs resources. Which 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

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-tri-methyl 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

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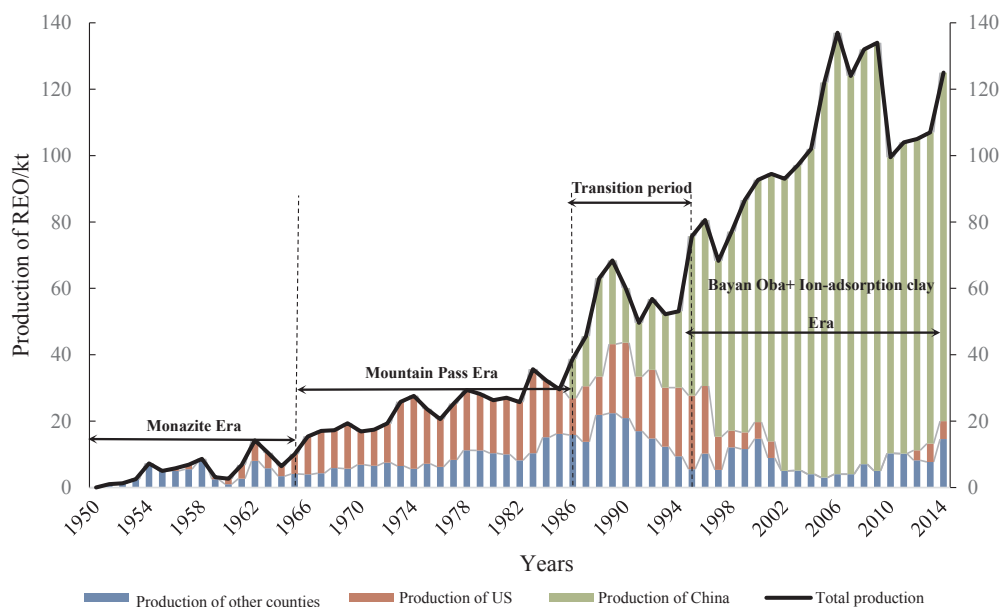


Fig. 1. World production of REO from 1950 to 2014, source-USGS (Monazite era (1800s-1964), Mountain Pass era (1965-1984), Bayan Obo and ion adsorbed clay era (1991-present)).

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 rock is considered as one of the most promising potential new recourses of REEs in terms of the following advantages [33,34]:

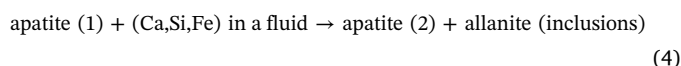
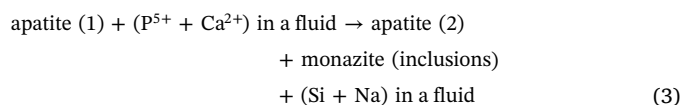
- i. The mature phosphoric acid and phosphate fertilizer industries consume about 250 million tons of phosphate rocks per year [35]. Generally, phosphate rocks contains 0.046 wt% REEs on average [36], which means about 125kt of REEs potential yearly production and the value is relative high due to the 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.

1.2. Phosphorous resource and REEs distribution

Phosphate rock, formulated as $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$, are classified as igneous apatite and sedimentary phosphorite according to their mineralization mechanism [38]. In phosphate rock, REEs present majorly in the form of isomorphous substitution for Ca and deposit as the REE-francolite that can be easily released into leaching solution by mineral acids. Generally substitution of Si^{4+} for P^{5+} or Na^+ for Ca^{2+} was accompanied to maintain the electrostatic neutrality. The overall substitutions can be expressed as the reactions below:



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 hydrothermal 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, especially for the high REEs content ores. Which leads to difficulty in REEs dissolution during the leaching process. The typical phosphate rock with relative high REEs content (> 0.046 wt%) were listed in Table.1.

Various mineral acids are used in the decomposition process of phosphate rock, with the corresponding hydrometallurgical processes of phosphate rock are H_2SO_4 processes, HNO_3 processes, HCl processes, H_3PO_4 processes. Based on these processes, REEs recovery technologies have been extensively investigated in the past century (Fig. 2).

The history of REEs recovery from phosphate rock dates back to the 1930s, USSR firstly began the investigation of recovery of REEs by-product 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_3 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 produced 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 carried out extensive experimental work on U and REEs extraction from WPA with mixture of

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