

Research Progress on Leaching of Rare Earth Elements in Phosphogypsum

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With the increasing global demand for rare earth elements and the depletion of traditional mineral resources, recycling rare earth elements from industrial solid waste has become an important direction of sustainable resource utilization. Phosphogypsum is a kind of industrial by-product with huge output and trace rare earth elements, its effective treatment and resource utilization are of great significance for environmental protection and economic development. Based on the occurrence state of rare earth elements in phosphogypsum, the research progress of leaching of rare earth elements in phosphogypsum was reviewed in this paper. The leaching mechanism and influencing factors of different leaching agents were summarized and analyzed.

Keywords: phosphogypsum, rare earth element, leaching, solid waste utilization.

1. INTRODUCTION

Rare earth elements comprise 17 elements, including 15 lanthanide elements and scandium and yttrium with similar chemical properties to lanthanide elements [1]. The rare earth element is an important strategic resource. Due to its unique electromagnetic and radioactive shielding properties, it is widely used in the military, new materials, aero-space, and other high-end fields [2–4]. It is an important raw material necessary for the development of high-tech industries.

According to the data released by the United States Geological Survey (USGS), the total global reserves of rare earth resources in 2022 are about 130 million tons. Considering the non-renewable nature of rare earth resources, its source is particularly important. In nature, apart from independent rare earth mineral resources, rare earth is also widely associated with other metallic and non-metallic minerals, such as phosphate rock, bauxite, coal mine, etc., among which the rare earth content in phosphate rock is relatively high [5, 6] and the total amount of phosphate rock containing rare earth is as high as 1×10^{10} t [7], so phosphate rock is a potential source of rare earth elements in industry [8]. In the world, rare earth-containing phosphate ores are mainly distributed in Russia, the United States, and China, especially in Russia's Hibbing phosphate ores with the highest grade (0.5 % ~ 5 %) [9]. China's Zhijin Xinhua in Guizhou Province, Anning in Yunnan Province, Fangshan in Hebei Province, Shangzhuang in Qinghai Province, and other places are rich in apatite-associated rare earth minerals [10]. Among them, Zhijin Xinhua in Guizhou Province has associated rare earth phosphate deposits of about 1.3 billion tons and rare earth oxide reserves of over one million tons, ranking second in China after Inner Mongolia [11]. Because of the low grade of rare earth

elements in phosphate rock, the extraction of rare earth elements often needs to be combined with the preparation of phosphoric acid. At present, the sulfuric acid method is often used to prepare phosphoric acid [12] at home and abroad, so that rare earth elements are initially enriched in phosphogypsum as a by-product, so the extraction and recovery of rare earth elements from phosphogypsum are of great significance.

2. PHOSPHOGYPSUM

2.1. Physicochemical properties of phosphogypsum

Phosphogypsum (PG) is a by-product waste residue in the process of wet-process preparation of phosphoric acid. It is generally gray-black, gray-white fine powder solid, and acidic (pH 2.37 ~ 5.33) [13]. 80 % ~ 90 % of the components are dihydrate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Compared with natural gypsum, its adhesiveness, viscosity, and fluidity are poor. According to the composition and treatment process of phosphate rock, the impurities in PG are different, such as residual phosphoric acid, fluorine, acid insoluble, iron aluminide, organic matter, etc., and there are also a small number of heavy metals and radioactive substances [14]. Therefore, PG should be pre-treated to remove impurities before comprehensive utilization of PG. For example, sulfuric acid should be used to remove harmful impurities, especially soluble phosphorus and fluoride, before PG is used as cement retarder.

2.2. Present situation of comprehensive utilization of PG

At present, the mainstream phosphoric acid preparation process is wet-process phosphoric acid, that is, crude

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phosphoric acid is obtained by adding sulfuric acid to phosphate rock. 4–5 tons of PG can be produced for each phosphoric acid product produced [15]. The annual growth rate of PG is about 1.7×10^8 tons, and only 15 % of the global production of PG is value-added [16]. By the end of 2020, the total amount of global PG solid waste has reached 7×10^9 tons, of which China's inventory is about 8.2×10^8 tons, and is growing at a rate of 7×10^7 tons per year [17, 18].

The large accumulation of PG will encroach on the land, pollute the water body, and cause serious harm to the surrounding environment. At present, the utilization rate of PG in China is less than 50 %. Due to the high content of calcium sulfate, low solubility, and difficult separation, the direct use of PG in the chemical industry, agricultural and forestry production, and building materials has attracted more attention [19]. At present, the utilization of PG is still at the primary and low-value level based on gypsum building materials, cement retarders, road filling materials, and so on [20]. The resource utilization of high-added value is helpful to improve the added value of products and alleviate the environmental problems caused by PG to a greater extent. Therefore, it is imperative to change the idea of PG utilization. There is a certain amount of rare earth elements in PG, and rare earth elements are important non-renewable resources. The comprehensive re-recovery of rare earth in PG has extremely important strategic significance. The extraction and recovery of rare earth elements from PG can not only improve the utilization rate of PG, but also obtain better economic benefits, and provide a new direction for the resource application of PG [21].

3. OCCURRENCE STATE OF RARE EARTH ELEMENTS IN PHOSPHATE ROCK AND PG

3.1. Occurrence state of rare earth in phosphate rock

PG is the by-product of wet-process phosphoric acid from phosphate rock. Studying the occurrence state of rare earth in phosphate rock can clarify the change and trend of rare earth after the wet-process phosphoric acid process. The occurrence forms of rare earth elements in phosphate rock are mainly three categories, which are independent minerals, isomorphism, and adsorption. Because rare earth

elements are similar to Ca^{2+} ion radius, rare earth elements in phosphate rock are mostly present in cellophane and apatite in the form of isomorphism [22, 23], and a small amount exists on the surface of minerals and between particles in the form of independent minerals (such as monazite, bastnaesite, etc.) or ion adsorption (such as clay minerals, mica minerals, etc.) [7, 24].

Most of the rare earth elements in the form of isomorphism are non-ionic rare earths that are difficult to use. It is difficult to separate and purify, and the economic feasibility is poor. To better recycle rare earth elements, the researchers controlled the flow of rare earth elements by adding some additives in the process of sulfuric acid decomposition of phosphate rock. For example, Jeanfavz et al. [25] proposed that 56 % of the rare earth in the concentrate can enter phosphoric acid by introducing aluminum ions, iron ions, silicon ions, or their mixed ions into the slurry when sulfuric acid decomposes phosphate rock; Yang et al. [26] and Wang et al. [27] controlled the crystallization rate and crystal morphology of calcium sulfate in the leaching process by adding calcium sulfate seeds, surfactants and controlling the stoichiometric ratio of sulfuric acid to phosphate rock to reduce the entry of rare earth elements into calcium sulfate precipitation.

3.2. Occurrence state of rare earth in PG

Shivaramaiah et al. [28] proposed that there may be three possible occurrence states of rare earth elements in PG: (1) the occurrence of rare earth elements in PG lattice with isotropic substitution of Ca^{2+} ; (2) Rare earth elements are adsorbed on the surface of PG; (3) The rare earth elements form an amorphous or crystalline independent phase between the PG surface and the PG particles. Current studies have shown that most of the rare earth elements exist mainly in the PG lattice, and a small part of the rare earth elements exist in the other two forms, such as unreacted phosphate rock, monazite, and other minerals containing rare earth, or in the form of insoluble compounds such as sulfate, phosphate, fluoride and calcium sulfate crystals [29–31]. The mechanism of the leaching process of rare earth elements in PG is shown in Figure 1. Under the erosion of sulfuric acid, the PG crystal surface and the rare earth mineral phase dissolve, and the single rare earth phase and the isomorphous REE^{3+} are diffused into the solution through the ash layer.

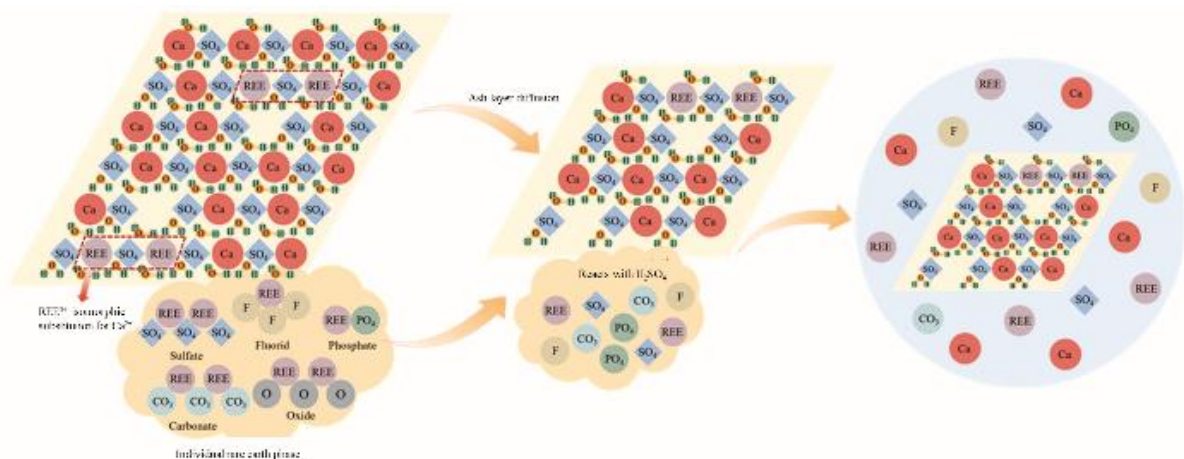


Fig. 1. Mechanism diagram of leaching process of rare earth elements in PG

Yu Weijian et al. used sulfuric acid to study the leaching of rare earth elements in PG and found that with the change of leaching conditions, the leaching of rare earth elements and calcium elements was consistent, and the linear fitting correlation coefficient of the leaching rate of rare earth elements and calcium leaching rate were both greater than 0.9, indicating a strong linear relationship between the two [34]. The results show that rare earth elements in PG samples mainly exist in the PG lattice [32]. Li et al. used time-of-flight secondary ion mass spectrometry to study the occurrence mode of rare earth in PG, and the results showed that rare earth elements were released after the destruction of PG lattice, and rare earth existed in the form of both isomorphous calcium ion substitutes and separated phases such as oxides and sulfates [33]. Therefore, effective methods to achieve high leaching rates are based on the destruction of the PG lattice.

In addition, studies have shown that the production process of phosphate rock has a significant effect on the content of rare earth elements in PG. Sulfuric acid reacts with phosphate rock to form calcium sulfate which is not soluble in the liquid phase. According to the hydration degree of calcium sulfate, it can be divided into a dihydrate process and a semihydrate process. Al-Thyabat and Zhang found that in the process of dihydrate production, light rare earth elements are more likely to enter the gypsum crystal in the form of eutectic and enrich in the PG due to the isomorphic substitution effect with Ca^{2+} . In the process of semi-hydrate production, heavy rare earth elements are more concentrated in the acid solution due to the stronger acidity in the wet production process [34]. In general, about 20%~30% of the rare earth elements in the dihydrate process are enriched in phosphoric acid; about 90% of the rare earth elements in the semi-hydrate process are enriched in PG [35]. The rare earth elements in the PG produced by the semi-hydrated process mainly exist in the form of an independent phase of rare earth phosphate hydrated precipitation [36].

Therefore, some researchers have proposed to control the reasonable phosphoric acid production process to facilitate the comprehensive recovery and utilization of rare earth elements. Due to the influence of process technology and operating conditions, the occurrence state of rare earth elements in PG is complex. The occurrence state of rare earth elements has an important influence on its leaching rate, and it is of great significance to clarify its existence form for recycling.

4. LEACHING METHOD OF RARE EARTH ELEMENTS IN PG

4.1. Acid leaching of rare earth in PG

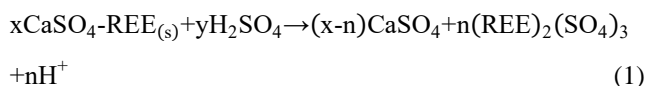
The commonly used leaching agents for acid leaching are strong inorganic acids, such as sulfuric acid, nitric acid, and hydrochloric acid. The use of inorganic acid to leach rare earth elements in PG has created favorable conditions for its migration from a solid phase to a liquid phase, and its leaching efficiency is generally high and the process is simple [37]. The process of pretreatment, acid leaching, solid-liquid separation, and extraction is mainly used to recover rare earth from PG by acid leaching [38].

4.1.1. Leaching pretreatment

Canovas et al. found that water pretreatment of PG can remove a considerable part of impurities without consuming rare earth elements [39]. Masmoudi-Soussi et al. used sodium chloride and sodium carbonate solutions to pretreat PG to ensure better dissolution of impurities and conversion of PG into a calcite matrix that is easy to erode in acidic media, providing better conditions for acid leaching of PG [40]. Rychkov et al. carried out mechanical grinding and ultrasonic impact pretreatment of a PG in Russia. Using sulfuric acid with a mass concentration of 10-20g/L as a leaching agent, after leaching and further concentration and purification, the rare earth leaching rate of PG increased from 15 % to more than 70 % [41]. Lambert et al. developed a new process to improve the leaching rate of rare earth in PG by microwave irradiation. The results showed that the leaching rates of Nd, Y, and Dy reached 80 %, 99 %, and 99 % respectively under the optimum microwave conditions (treated at 1200 W for 15 min). As a processing technology, microwave pre-treatment is a low-cost processing step, which significantly improves the efficiency of rare earth extraction [42].

4.1.2. Leaching of rare earth elements in PG by sulfuric acid

Sulfuric acid is the most widely used inorganic strong acid in the wet-process phosphoric acid process. It has the advantages of low price and no introduction of impurity ions. Therefore, it is applied to the removal of impurities in PG and the leaching of rare earth elements. The rare earth elements in PG are leached by sulfuric acid, and the possible chemical reactions in the leaching process are shown in Eq. 1 [43].



Although sulfuric acid as a leaching agent has the advantage of not introducing impurity ions, due to the isoionic effect of SO_4^{2-} , the solubility of PG in sulfuric acid solution is generally low. In addition, due to the low solubility of rare earth phosphates in solution, rare earth elements may also be reprecipitated by phosphate ions released by PG dissolution during acid leaching, thus hindering the leaching of rare earth elements. Increasing the concentration of sulfuric acid can promote the dissolution of rare earth phosphate, but the higher concentration of sulfate ions may also cause the dissolved rare earth elements to form insoluble sodium/potassium rare earth disulfate ($\left(\frac{\text{Na}}{\text{K}}\right)\text{-REE}(\text{SO}_4)_2$) with sodium ions or potassium ions in the solution. Sodium/potassium rare earth disulfate precipitation will become more stable [44]. Therefore, in the sulfuric acid leaching process of PG, when the sulfuric acid concentration increases to a certain extent, the leaching rate of rare earth elements will not continue to increase, and even decrease [45]. Liang et al. used sulfuric acid to extract rare earth elements from PG produced by Mosaic Company in Florida. When the sulfuric acid concentration was less than 3 %, the rare earth leaching rate increased rapidly with the increase in sulfuric acid concentration, and then showed a slow growth, reaching the maximum leaching value when

the sulfuric acid concentration was about 5 %. After that, the leaching rate of rare earth elements decreased with the increase of sulfuric acid concentration. Experiments show that the best leaching conditions for rare earth elements in PG are 5 % sulfuric acid solution, liquid-solid ratio of 4, leaching temperature of 50 °C, and reaction time of 120 min, under which conditions, the leaching rate of rare earth elements is 43 % [46].

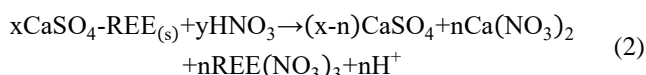
In order to improve the leaching rate of rare earth elements in PG in sulfuric acid solution, researchers have studied various measures such as prolonging the leaching time, increasing the liquid-solid ratio, and mechanical activation. Generally, the leaching rate of rare earth elements in PG by sulfuric acid can be increased from 12 % ~ 40 % to more than 60 %. Lokshin et al. extended the leaching time to several weeks to improve the leaching rate of rare earth elements in PG by sulfuric acid solution. In the experiment, 0.5 % ~ 4 % sulfuric acid solution was used to continuously extract 40 g PG for 3025 h (18 weeks) under the condition of liquid-solid ratio of 2. The leaching rate of rare earth elements increased from 17.2 % to 68.2 % compared with that of leaching for 1 h under the same conditions [44]. Rychkov et al. have shown that the sulfuric acid leaching rate of rare earth elements in PG can be significantly improved by mechanical grinding, adding ion exchange resin, and ultrasonic treatment. The combination of these three methods was used to strengthen the sulfuric acid leaching process of PG. Under the condition that the sulfuric acid concentration was only 10 ~ 20 g/L, the leaching rate of rare earth elements in PG could be increased from 15 %–17 % to more than 70 %. Moreover, after sulfuric acid leaching, the content of PG impurities in the acid-soluble slag decreased significantly, which could be used as raw materials for cement production [41]. Hammas-Nasri et al. washed the PG samples with distilled water, separated them by solid-liquid separation, and then stirred them with 10 % sulfuric acid solution at 60 °C for 1 ~ 2 h two times. The results show that compared with single leaching, two-step leaching can effectively improve the leaching efficiency of rare earth elements and make rare earth elements better leached. XRD and ICP-MS analysis showed that fluoride and phosphate in PG were basically dissolved in the first acid leaching, while the rare earth elements in the residue were dissolved in the sulfuric acid solution in the second acid leaching, and finally about 86 % of the total rare earth leaching rate was obtained [47]. Habashi leached PG with 0.1 ~ 0.5 mol/L sulfuric acid solution at a liquid-solid ratio of 10 at room temperature. The recovery rate of rare earth elements was about 50 %, and it was confirmed that quantitative extraction could not be achieved without destroying the lattice of calcium sulfate [48]. Kijkowska et al. used 10 % ~ 13 % sulfuric acid solution and hydrogen peroxide to leach PG slurry, stirred at 60 °C for 60 ~ 120 min, filtered and washed, and the leaching solution evaporated and crystallized at 100 °C. The recovery rate of rare earth reached 50 %. Through this recovery method, Fe₂O₃ and K₂O in PG are completely removed, and the removal rates of P₂O₅ and F are more than 60 %, which provides favorable conditions for further utilization of PG [49]. Wu Lin et al. took the phosphate ore in Zhijin Xinhua phosphate ore in Guizhou as the research object, and comprehensively compared the effect of adding

surfactants on the leaching rate of rare earth and the leaching rate of PG with organic acids during sulfuric acid leaching. The experimental results show that the addition of surfactant PEG-400 can improve the crystallization properties of calcium sulfate and increase the rare earth leaching rate to 65.89 % [50].

Sulfuric acid as a leaching agent is not only cheap, but also does not introduce impurity ions, which provides convenience for the subsequent reuse of PG. However, the leaching rate of rare earth elements in PG by sulfuric acid solution is low due to the co-ionic effect and the possibility of rare earth disulfate precipitation during leaching. In addition, the strong acidity of sulfuric acid will make the acidity of the leaching solution too high, and the acidity of PG will increase, resulting in the difficulty of comprehensive utilization of PG and the risk of secondary pollution. Therefore, it is one of the future research directions to improve the recovery rate of rare earth elements in PG by using appropriate process strengthening methods at lower concentrations of sulfuric acid.

4.1.3. Leaching of rare earth elements in PG by nitric acid

Nitric acid as a leaching agent has been used in the leaching of trace rare earth elements from phosphate ores. H⁺ of nitric acid is used to decompose phosphate rock, and NO₃⁻ can be retained in the product as a nitrogen fertilizer component, thus realizing the double utilization of nitric acid. Therefore, some researchers have also studied the rare earth elements in PG leaching by nitric acid. The leaching of rare earth elements in PG by nitric acid, and the possible chemical reaction in the leaching process can be expressed by Eq. 2.



Compared with sulfuric acid leaching, nitric acid leaching can generally obtain higher rare earth leaching rate. Walawalkar et al. use hydrochloric acid, nitric acid and sulfuric acid to leach PG from *Agrium* fertilizer plant. The results show that the leaching efficiency of rare earth elements is affected by the degree of dissolution of PG in acid, because the solubility of PG in sulfuric acid is obviously lower than that of hydrochloric acid and nitric acid. Under the optimal leaching conditions, the rare earth leaching rates of hydrochloric acid, nitric acid and sulfuric acid were 51 %, 57 % and 23 %, respectively [51]. Canovas et al. studied the leaching efficiency of rare earth elements in PG under different acid solutions and different working conditions and the release of impurities during the leaching process. The experimental results show that 3 mol/L nitric acid and 0.5 mol/L sulfuric acid are the best leaching concentrations of rare earth elements in PG, and the leaching rates of rare earth elements are 80 % and 46 % ~ 58 %, respectively [39].

Increasing the concentration of nitric acid, extending the reaction time, increasing the reaction temperature and liquid-solid ratio can improve the leaching rate of rare earth elements to a certain extent, but it will also dissolve a large number of fluoride minerals, or promote the hydrolysis of fluorosilicate ions, etc., and the concentration of free

fluoride ions in the solution will increase, so that rare earth elements will be reprecipitated in the form of fluoride. Therefore, after the concentration of nitric acid is too high, the leaching rate of rare earth elements will increase. The leaching rate of rare earth elements may decrease. The precipitation reaction of rare earth fluoride is shown in equation (3) [52].

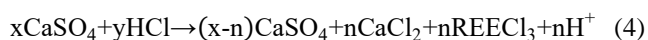


Ismail et al. added calcium salt in the leaching process to reduce free fluorine and increase the leaching rate of rare earth. The results showed that the recovery rate of rare earth was increased from 47.4 % to 59.5 % by leaching PG with a mixture of 3 mol/L nitric acid and 1 mol/L $Ca(NO_3)_2$, compared with that of leaching with only 3 mol/L nitric acid under the same conditions [52]. In the leaching process, calcium salt is added to increase the concentration of calcium ions, which makes calcium ions combine with free fluorine, thus reducing the probability of rare earth fluoride precipitation. Lokshin et al. also studied the effects of $Al(NO_3)_3$, $Ca(NO_3)_2$, $Na_2B_4O_7$, Na_2SO_4 , $H_2B_4O_7$ and other additives on the nitric acid leaching of rare earth in PG, and the results showed that $Na_2B_4O_7$ greatly improved the leaching rate of rare earth from 43.6 % to 96.8 % [53]. They believe that $B_4O_7^{2-}$ may form stable soluble fluorides with fluorine, such as BF_3^- , reducing the probability of rare earth fluoride precipitation formation.

The preparation of phosphate fertilizer by nitric acid decomposition of phosphate ore can not only recover rare earth elements from the leaching solution, but also retain nitrate ions in the product as nitrogen fertilizer, increasing the utilization rate of nitric acid and saving costs. However, for PG leaching, although the leaching rate of rare earth elements is high, the residual nitrate ions as impurities will affect the subsequent reuse of PG, and the leaching solution with high acidity also has a great impact on the environment.

4.1.4. Leaching of rare earth elements in PG by hydrochloric acid

Although relevant studies have shown that the leaching efficiency of using nitric acid is higher than that of sulfuric acid, the economy and practical feasibility are poor for large-scale recovery of rare earth elements, compared with the use of hydrochloric acid leaching is more economical [51]. In the early 1960s, the process of producing phosphoric acid by hydrochloric acid was first industrialized. In the process of phosphoric acid production by hydrochloric acid process, most of the rare earth elements enter the hydrochloric acid decomposition solution. The leaching effect of hydrochloric acid on rare earth elements in PG is similar to that of nitric acid, and with the development of the chlor-alkali industry, the cost advantage of hydrochloric acid is more obvious. The possible chemical reaction of leaching rare earth elements from PG by hydrochloric acid is shown in Eq. 4 [43].



The influence of hydrochloric acid solution concentration, leaching reaction temperature, liquid solid ratio and leaching time on the leaching effect of rare earth in PG is similar to that of nitric acid. Hydrochloric acid can

also react with calcium fluoride in PG to generate free fluorine and react with rare earth elements in the leaching solution to generate rare earth fluoride precipitation, thus reducing the leaching rate, as shown in Eq. 5 and Eq.6 [52].



In recent years, with the development of chlor-alkali industry, the cost of using hydrochloric acid as the leaching agent has gradually decreased, but there are also problems such as calcium chloride in the leaching solution is not easy to remove, and the waste acid wastewater generated by the leaching process is easy to cause secondary environmental pollution.

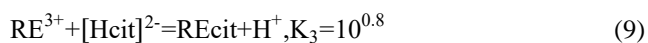
4.1.5. Leaching of rare earth elements in PG by organic weak acid

In general, the extraction of rare earth in PG at home and abroad mainly uses sulfuric acid, nitric acid, hydrochloric acid, and other inorganic strong acids to leach PG, in order to improve the leaching rate, the acid concentration needs to be above 15 %, and the recovery rate of rare earth reaches more than 80 %. However, the use of strong acid to leach rare earth will lead to an increase in the acidity of PG, and the subsequent comprehensive utilization of PG needs to be washed to remove acid or neutralize before use. In recent years, the trend of weak acids as leaching agents is becoming more and more obvious. From the perspective of environmental protection, weak acids are easier to degrade and have little impact on the environment. At the same time, organic acids have a high selectivity for rare earth leaching. Rare earth ions are hard acids and have large ionic radii, so they are more inclined to bond with ligands containing O, N, F, and other hard bases to form complexes with high coordination numbers. Among them, oxygen-containing ligands have the strongest coordination ability with rare earth ions. Therefore, as a common and easily obtained ligand, carboxylic acid ligand can not only be used as a coordination oxygen atom supplier, but also meet the requirements of high coordination number of rare earth complexes with its diversified coordination modes, so it is one of the easiest ligands to coordinate with rare earth ions. At present, citric acid, malic acid, tartaric acid and so on are used in the research, that is, the carboxyl group in organic acids is used to form complexes with rare earth elements [54].

Organic acids can erode rocks and lead to the decomposition and dissolution of minerals. The dissolution of minerals mainly includes the following three mechanisms: (1) produce H^+ , which promotes the dissolution of minerals. H^+ binds with surface oxide ions and weakens key bonds, so that metal substances are released into the solution; (2) Removal of structural metals from the surface of minerals by the formation of surface complexes on the surface of minerals, that is, ligands through exchange with hydroxyl groups on the surface of minerals to form surface complexes, surface complexes polarize key metal-oxygen bonds, thereby promoting the separation of metallic substances on the surface of minerals; (3) Further dissolution of minerals is promoted by reducing the concentration of saturated solution through the

formation of complexes between ligands and metal ions [55–57].

Gasser et al. used different concentrations of boric acid, malic acid, and citric acid to study the leaching of lanthanide Y from PG, and the results showed that citric acid had a better leaching rate of total Ln-Y than boric acid and malic acid. Under the conditions of 1.0 mol/L citric acid, liquid-solid ratio of 5, leaching time of 15 min, and leaching temperature of 85 °C, the maximum leaching rate of total lanthanides from PG was 83.4 % after three cycles of leaching. Er (89.4 %) > Ce (88.2 %) > La (81.8 %) > Pr (71.9 %) > Y (40.7 %) [54]. Citric acid has 3 carboxyl structures and strong coordination with rare earth ions, while malic acid has only two carboxyl structures. The difference in the number of carboxyl groups may lead to the difference in the leaching of rare earth elements between malic acid and citric acid. The coordination reaction between citrate and rare earth ion in the leaching process is shown in Eq. 7, Eq. 8, and Eq. 9 [58].



The existence form of organic weak acid in the solution is also affected by the pH value of the solution. cit^{3-} exists only in pH = 4.5 and is easy to react with trivalent lanthanides and yttrium. In malic acid solution, when pH < 7, there are two ions, $\text{H} - \text{malate}^-$ and malate^{2-} , which form with rare earth elements in 1:1 complexes of 1 or 1:2, such as $\text{LnH}_2\text{Mal}^{2+}$, LnHMal^+ , and LnHmalO_2^- , form multinuclear complexes with malate oxygroups when pH > 7 [58, 59]. Therefore, in the process of organic acid leaching, the concentration and pH value of organic acid can be controlled to achieve the best leaching effect.

Organic weak acid is biodegradable and can be produced by the biological metabolism of organic matter, which is environmentally friendly in the production and application process and avoids the secondary pollution caused by inorganic strong acids. Although the single leaching rate of organic acids to rare earth in PG is low, it is still one of the important research directions in the future because of its green environment and certain selectivity in the leaching process.

4.2. Biological leaching of rare earth in PG

The strong acid leaching method of rare earth leaching from PG, although the rare earth leaching rate is high, but it dissolves toxic substances and acid pollutants, which is unfavorable to the environment. Bioleaching is the focus of research in recent years. Bioleaching is the effective separation of target metals from minerals by utilizing the redox characteristics of microorganisms in the metabolism process, usually using gluconobacter, thiobacillus acid and *Vibrio desulphuricum* [60]. The efficiency of bioleaching depends not only on the oxidation capacity of microorganisms, but also on the types of rare earth minerals and the particle size. Microbial leaching conditions are mild and environmentally friendly. The use of microbial leaching instead of traditional hydrometallurgy can solve the adverse effects of traditional leaching methods on the environment,

so the application of microbial leaching in the field of metallurgical extraction has attracted more and more attention in recent years [61].

Viktorovna et al. used several mixed bacteria of *thiobacillus acidophilus* to bleach rare earth elements and phosphorus in PG. Under the conditions of liquid solid ratio of 5, temperature of 15 ~ 45 °C, ventilation and pH value of 1.5 ~ 1.8, the leaching rate of rare earth was 55 % ~ 70 %. The leaching rate of phosphorus was 93.3 % ~ 94.7 % [62]. Antonick et al. found that gluconobacter oxygens can produce a bioactive substance containing organic acids, the main chemical component of which is gluconic acid, which can be used for the leaching of rare earth elements in PG. The bioactive substance, sulfuric acid, phosphoric acid and industrial gluconic acid were respectively used for the leaching of rare earth elements from PG. The results showed that the bioactive substance leaching agent was more effective than industrial gluconic acid and phosphoric acid for the leaching of rare earth elements at equal molar concentrations [63]. Barmettler et al. cultured a mixed culture of sulfur-oxidizing bacteria for 30 days at a pH value of 1.5 ~ 1.8, and extracted 55 % ~ 70 % rare earth elements from PG [64]. Salo et al. use bioreactors to process PG to recover rare earth elements and remove sulfate from the residual solution. It was found that rare earth leaching began when the concentration of H_2SO_4 was 0.01 mol/L (yield 6 % – 15 %), and the leaching yield showed a steady increase trend when the concentration of H_2SO_4 gradually increased to 0.05 mol/L (yield 34 % – 62 %). Bioreactors require a fairly mild leach solution ($c(\text{H}_2\text{SO}_4) < 0.02 \text{ mol/L}$) for microorganisms to reliably survive and precipitate rare earths from the leach solution [65].

The bioleaching method has the advantages of simple equipment, low energy consumption, and fewer pollutants, but the actual yield and efficiency of rare earth extraction are lower than that of strong acid leaching, and the leaching time is long. Bioleaching is less harmful to the environment than strong acid leaching methods that produce toxic substances and acidic contaminants. The application of biological leaching in the extraction of rare earth from PG also needs to focus on improving the efficiency of rare earth recovery and finding suitable strains for large-scale engineering, especially those that are selective to rare earth minerals or acid resistant.

4.3. Other leaching methods

Compared with acid leaching and bioleaching, other leaching methods such as organic solvent leaching, recrystallization and ion exchange also have certain development prospects.

Organic solvent metallurgy was invented in the early 1960s and is mostly used to recover uranium from low-grade complex ores. In solvent leaching, the leaching process is to use the complexing agent dissolved in the organic solvent for leaching, and metals can be recovered from the organic phase after leaching. As the study progressed, some researchers found that rare earth elements could be recovered from PG while leaching radioactive elements [66].

El-Didamony et al. used tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) to remove radioactive

elements from PG in kerosene, while recovering rare earth elements from the leaching solution. The results showed that the leaching rates of ^{226}Ra , ^{210}Pb , ^{238}U , ^{40}K , and total REE were 65.6 %, 72.8 %, 57.2 %, 70.4 %, and 68.5 %, respectively, when 0.5 mol/LTBP was used at 55 °C and the ratio of liquid to solid was 1 for 2 h. Under the same leaching conditions, the leaching rates of ^{226}Ra , ^{210}Pb , ^{238}U , ^{40}K and total REE were increased to 71.1 %, 76.4 %, 62.4 %, 75.7 %, and 69.8 %, respectively, and the leaching rates were no longer further improved for the third time [67]. Compared with inorganic acid leaching, organic solvent leaching of PG can selectively obtain rare earth elements and reduce solvent consumption and the volume of the leaching solution [68]. Organic solvent leaching has certain selectivity and does not require specific equipment, but the solvent price is high, some of the solvents will be adsorbed in the gypsum to increase the solvent usage and increase the difficulty of the subsequent utilization of PG, thus limiting its utilization in PG recovery and leaching.

Mukaba et al. used a high-pressure reactor to hydrothermal treat PG slurry, and the results showed that the recovery rate of rare earth elements was increased from 5% to 80% by recrystallization of PG [69].

The ion exchange method uses ion exchange resin to exchange rare earth ions from the leaching solution, the rare earth ions are adsorbed to the specific and selective exchanger, and then the rare earth element ions are desorbed to the solution through the re-verse elution process [70]. Virolainen et al. added ion exchange resin to the acid-leaching process, and each 1 kg ion exchange resin could support 20 g rare earth elements, and the recovery efficiency was about 80 %. By adding resin for selective adsorption of rare earth elements, high purity rare earth can be further separated to avoid the influence of other metal elements [71]. Koopman et al. used ion exchange resin to extract and recover the rare earth elements leach during the recrystallization of PG. The study results showed that the extraction rate of Eu was 53 %, that of La was 34 %, and that of Sm was 10 % [72].

5. CONCLUSIONS

As one of the bulk storage solid wastes, PG usually contains a large amount of rare earth elements. It is of great economic and environmental significance to study the recovery of rare earth elements in PG. Most of the rare earth elements in PG are present in the lattice of PG. At present, leaching is mainly used to recycle them. Inorganic strong acids such as sulfuric acid, hydrochloric acid and nitric acid are commonly used leaching agents at home and abroad. They have the advantages of a generally high leaching rate and simple process, but the acidity of the leaching solution is high, which may cause the risk of secondary pollution. The organic solvent leaching effect is good, but the cost of leaching reagents is high, and the organic solvent will increase the difficulty of subsequent utilization of PG and cause environmental problems. The efficiency of the organic weak acid and bioleaching is low, but it has little impact on the environment, and leaching has a certain selectivity. It is an important research direction for the recovery and utilization of rare earth elements in PG in the future.

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REFERENCES

1. Dongyue, X., Caiping, F., Zhongyang, T. Current Status of Rare Earth Resources in China and Progress of Extracting Technology *Conservation and Utilization of Mineral Resources* 41 (1) 2021: pp. 152–160.
<https://doi.org/10.13779/j.cnki.issn1001-0076.2021.01.022>
2. Kumar, D., Sharma, S.K., Verma, S. A Short Review on Rare Earth Doped Nayf4 Upconverted Nanomaterials for Solar Cell Applications *Materials Today: Proceedings* 21 2020: pp. 1868–1874.
<https://doi.org/10.1016/j.matpr.2020.01.243>
3. DaCosta, T.B., DaSilva, M.G.C., Vieira, M.G.A. Recovery of Rare-Earth Metals from Aqueous Solutions by Bio/Adsorption Using Non-Conventional Materials: a Review with Recent Studies and Promising Approaches in Column Applications *Journal of rare earths* 38(4) 2020: pp. 339–355.
<https://doi.org/10.1016/j.jre.2019.06.001>
4. Sharma, V.K., Kumar, V., Joshi, R.S. Investigation of Rare Earth Particulate on Tribological and Mechanical Properties of Al-6061 Alloy Composites for Aerospace *Journal of Materials Research and Technology* 8(4) 2019: pp. 3504–3516.
<https://doi.org/10.1016/j.jmrt.2019.06.025>
5. Bo, T., Yong, F., Keshu, L. Distribution Characteristics and Enrichment Mechanism of Associated Rare Earth Elements Resource in Aluminum-Bearing Rock *Acta Geologica Sinica* 95 (8) 2021: pp. 2284–2305.
<https://doi.org/10.19762/j.cnki.dizhixuebao.2021170>
6. Wei-guo, Z., Wei-feng, X., Xue-jian, C. The Occurrence of Rare Earth Elements in Early Cambrian Stone Coal in Northeast Hunan Province *Chinese Rare Earths* 42 (3) 2021: pp. 34–42.
<https://doi.org/10.16533/J.CNKI.15-1099/TF.202103004>
7. Kai, Z., Yong, X., Xiaoying, W. Development of Concentration and Extraction of Rare Earth from Rare Earth-Containing Phosphorite *Conservation and Utilization of Mineral Resources* 5 2017: pp. 93-98.
<https://doi.org/10.13779/j.cnki.issn1001-0076.2017.05.019>
8. Jingzhong, K., Kunming, X., Junlong, Z. Progress in Research on Rare Earth Recovery from Bauxite, Phosphorite and Nb-Ta Minerals *Chinese Rare Earths* 33 (1) 2012: pp. 81–85.
<https://doi.org/10.3969/j.issn.1004-0277.2012.01.017>
9. Xinhai, Z., Weining, Z. Progress of Flotation Collectors for Phosphorus Ore Bearing Rare Earth *Mineral Resources and Geology* 26 (2) 2012: pp. 168–171.
<https://doi.org/10.3969/j.issn.1001-5663.2012.02.017>
10. Meilong, W., Huixin, J., Song, Y. Study on Occurrence of Rare Earth in Phosphorous Ore of Fanshan, Hebei Province *Industrial Minerals & Processing* 44 (2) 2015: pp. 5–6.
<https://doi.org/10.16283/j.cnki.hgkwyjg.2015.02.003>
11. Qin, Z., Jiang, Y. Chunguang, G. Study on Comprehensive Utilization Technology of Rare Earth Phosphate Ore Associated with Zhijin in Guizhou Province *Phosphate & Compound Fertilizer* 27 (3) 2012: pp. 15–17.
<https://doi.org/10.3969/j.issn.1007-6220.2012.03.005>

12. **Song, Y., Huixin, J., Meilong, W.** Advances in Extraction of Rare Earths from Phosphorite Associated Rare Earths *Hydrometallurgy of China* 34 (2) 2015: pp. 92–95. <https://doi.org/10.13355/j.cnki.sfyj.2015.02.03>
13. **Oubaha, S., ElMachi, A., Mabroum, S.** Recycling of Phosphogypsum and Clay By-Products from Phosphate Mines for Sustainable Alkali-Activated Construction Materials *Construction and Building Materials* 411 2024: pp. 134262. <https://doi.org/10.1016/j.conbuildmat.2023.134262>
14. **Jun, T.** Current Situation and Prospect of Phosphogypsum Treatment and Disposal in the 13Th Five-Year Plan Period *Development Guide to Building Materials* 16 (16) 2018: pp. 45454. <https://doi.org/10.16673/j.cnki.jcfzdx.2018.0087>
15. **Calderón-Morales, B.R., García-Martínez, A., Pineda, P.** Valorization of Phosphogypsum in Cement-Based Materials: Limits and Potential in Eco-Efficient Construction *Journal of building engineering* 44 2021: pp. 102506. <https://doi.org/10.1016/j.jobte.2021.102506>
16. **Hammas-Nasri, I., Horchani-Naifer, K., Férid, M.** Production of a Rare Earths Concentrate after Phosphogypsum Treatment with Dietary NaCl and Na₂CO₃ Solutions *Minerals Engineering* 132 2019: pp. 169–174. <https://doi.org/10.1016/j.mineng.2018.12.013>
17. **Meesschaert, B., Monballiu, A., Ghyselbrecht, K.** Pilot Scale Recovery of Phosphorus as Calcium Phosphate from Nitrified Uasb Effluent of a Potato Processor and Subsequent *Journal of Environmental Chemical Engineering* 8 (6) 2020: pp. 104593. <https://doi.org/10.1016/j.jece.2020.104593>
18. **Chanouri, H., Agayr, K., Mounir, E.M.** Staged Purification of Phosphogypsum Using pH-Dependent Separation Process *Environmental Science and Pollution Research* 31 (7) 2024: pp. 9920–9934. <https://doi.org/10.1007/s11356-023-26199-8>
19. **Ya-fei, G., Ze-yang, Z., Zheng-hu, Z.** Study on Comprehensive Utilization of Phosphogypsum *China Non-Metallic Minerals industry* 4 2021: pp. 4–7. <https://doi.org/10.3969/j.issn.1007-9386.2021.04.002>
20. **Lizhen, Z., Yongxing, Z., Xiufeng, Z.** Research Progress on Resource Utilization of Phosphogypsum in China *Conservation and Utilization of Mineral Resources* 39 (4) 2019: pp. 14–18. <https://doi.org/10.13779/j.cnki.issn1001-0076.2019.04.003>
21. **Jing, Z., Xing, M., Yongbo, T.** Progress in the Treatment and Comprehensive Utilization of Phosphogypsum Impurities *Phosphate & Compound Fertilizer* 36 (9) 2021: pp. 25–28. <https://doi.org/10.3969/j.issn.1007-6220.2021.09.009>
22. **Zhihao, X., Dongsheng, H., Shuang, L.** Study on Process Mineralogy of a Rare Earth-Bearing Phosphate Ore in Zhijin, Guizhou *Multipurpose Utilization of Mineral Resources* 6 2020: pp. 142–147. <https://doi.org/10.3969/j.issn.1000-6532.2020.06.024>
23. **Yang, H.U., Dong-sheng, H.E., Shuang, L.** Occurrence Characteristics of Rare Earth Elements in REE-Bearing Phosphate Ores *Acta Mineralogica Sinica* 40 (1) 2020: pp. 101–105. <https://doi.org/10.16461/j.cnki.1000-4734.2019.39.104>
24. **Bo, Z., Yangkun, N., Fei, C.** Current Situation of Worldwide Rare Earth Resources *Multipurpose Utilization of Mineral Resources* 4 2018: pp. 7–12. <https://doi.org/10.3969/j.issn.1000-6532.2018.04.002>
25. **Fava, J., Lambert, A., Tognet, J.** Process for the Overall Recovery of Uranium, Yttrium, Thorium and Rare Earths Contained in a Phosphate Ore during the Prep *Materials Science and Engineering: A* 1982: pp. 16–25.
26. **Zunliang, Y., Qianlin, C.** Study on Rare Earth Leaching in the Process of Decomposing Phosphate Rock by Sulfuric Acid *Industrial Minerals & Processing* 46 (5) 2017: pp. 4–8. <https://doi.org/10.16283/j.cnki.hgkwyjg.2017.05.002>
27. **Liangshi, W., Zhiqi, L., Xiaowei, H.** Rare Earth Distribution Control During Wet Process of Phosphoric Acid Production *Journal of the Chinese Society of Rare Earths* 26 (3) 2008: pp. 307–312. <https://doi.org/10.3969/j.issn.1008-7524.2008.04.001>
28. **Shivaramaiah, R., Lee, W., Navrotsky, A.** Location and Stability of Europium in Calcium Sulfate and its Relevance to Rare Earth Recovery from Phosphogypsum Waste *American Mineralogist* 101 (8) 2016: pp. 1854–1861. <https://doi.org/10.2138/am-2016-5684>
29. **Borges, R.C., Fávaro, D.I.T., Caldas, V.G.** Instrumental Neutron Activation Analysis, Gamma Spectrometry and Geographic Information System Techniques in the Determination *Environmental Earth Sciences* 75 2016: pp. 1–15. <https://doi.org/10.1007/s12665-016-5468-x>
30. **Santos, A., Mazzilli, B.P., Fávaro, D.** Partitioning of Radionuclides and Trace Elements in Phosphogypsum and Its Source Materials Based on Sequential Extraction *Journal of Environmental Radioactivity* 87 (1) 2006: pp. 52–61. <https://doi.org/10.1016/j.jenvrad.2005.10.008>
31. **Huixin, J., Junqi, L., Fuzhong, W.** Acidolysis Kinetics and RE Leaching Mechanisms of RE-Bearing Phosphorite Ores *Journal of University of Science and Technology Beijing* 33 (9) 2011: pp. 1071–1078.
32. **Weijian, Y., Qingjun, G., Ying, S.** Leaching Kinetics of Rare Earth Elements from Phosphogypsum with Sulfuric Acid *Nonferrous Metals Science and Engineering* 12 (5) 2021: pp. 110–118.
33. **Li, S., Malik, M., Azimi, G.** Extraction of Rare Earth Elements from Phosphogypsum Using Mineral Acids: Process Development and Mechanistic Investigation *Industrial & Engineering Chemistry Research* 61 (1) 2021: pp. 102–114. <https://doi.org/10.1021/acs.iecr.1c03576>
34. **Al-Thyabat, S., Zhang, P.** In-line Extraction of REE from Dihydrate (DH) and Hemidihydrate (HDH) Wet Processes *Hydrometallurgy* 153 2015: pp. 30–37. <https://doi.org/10.1016/j.hydromet.2015.01.010>
35. **Valkov, A.V., Andreev, V.A., Anufrieva, A.V.** Phosphogypsum Technology with the Extraction of Valuable Components *Procedia Chemistry* 11 2014: pp. 176–181. <https://doi.org/10.1016/j.proche.2014.11.031>
36. **Lokshin, E.P., Tareeva, O.A.** Specific Features of Sulfuric Acid Leaching-Out of Lanthanides from Phosphohemihydrate *Russian Journal of Applied Chemistry* 81 2008: pp. 8–13. <https://doi.org/10.1134/S1070427208010023>
37. **Zhuo, Q., Jian-gang, Z., Dong, S.X.** Research Progress on Leaching of Rare Earth Elements in Phosphogypsum *Chinese Rare Earths* 43 (2) 2022: pp. 12–19.
38. **Wei, Z., Deng, Z.** Research Hotspots and Trends of Comprehensive Utilization of Phosphogypsum: Bibliometric Analysis *Journal of Environmental Radioactivity* 242 2022: pp. 106778. <https://doi.org/10.1016/j.jenvrad.2021.106778>
39. **Cánovas, C.R., Chapron, S., Arrachart, G.** Leaching of Rare Earth Elements (REEs) and Impurities from Phosphogypsum: a Preliminary Insight for Further Recovery

- of Critical Raw Materials *Journal of Cleaner Production* 219 2019: pp. 225–235.
<https://doi.org/10.1016/j.jclepro.2019.02.104>
40. **Masmoudi-Soussi, A., Hammam-Nasri, I., Horchani-Naifer, K.** Rare Earths Recovery by Fractional Precipitation from a Sulfuric Leach Liquor Obtained after Phosphogypsum Processing *Hydrometallurgy* 191 2020: pp. 105253.
<https://doi.org/10.1016/j.hydromet.2020.105253>
41. **Rychkov, V.N., Kirillov, E.V., Kirillov, S.V.** Recovery of Rare Earth Elements from Phosphogypsum *Journal of Cleaner Production* 196 2018: pp. 674–681.
<https://doi.org/10.1016/j.jclepro.2018.06.114>
42. **Lambert, A., Anawati, J., Walawalkar, M.** Innovative Application of Microwave Treatment for Recovering of Rare Earth Elements from Phosphogypsum *ACS sustainable chemistry & engineering* 6 (12) 2018: pp. 16471–16481.
<https://doi.org/10.1021/acssuschemeng.8b03588>
43. **Kouraim, M.N., Fawzy, M.M., Helaly, O.S.** Leaching of Lanthanides from Phosphogypsum Waste Using Nonyl Phenol Ethoxylate Associated with HNO₃ and HCl *International Journal of Sciences: Basic and Applied Research* 16 (2) 2014: pp. 31–44.
44. **Lokshin, E.P., Tareeva, O.A., Elizarova, I.P.** A Study of the Sulfuric Acid Leaching of Rare-Earth Elements, Phosphorus, and Alkali Metals from Phosphodihydrate *Russian Journal of Applied Chemistry* 83 2010: pp. 958–964.
<https://doi.org/10.1134/S1070427210060054>
45. **Lokshin, E.P., Vershkova, Y.A., Vershkov, A.V.** Efficiency of Sulfuric Acid Leaching of Lanthanides in Relation to Quality of Phosphosemihydrate Obtained from Khibiny Apatite Concentrate *Russian journal of applied chemistry* 75 2002: pp. 1572–1576.
<https://doi.org/10.1023/A:1022298911751>
46. **Liang, H., Zhang, P., Jin, Z.** Rare Earths Recovery and Gypsum Upgrade from Florida Phosphogypsum *Minerals & Metallurgical Processing* 34 2017: pp. 201–206.
<https://doi.org/10.19150/mmmp.7860>
47. **Hammam-Nasri, I., Horchani-Naifer, K., Férid, M.** Rare Earths Concentration from Phosphogypsum Waste by Two-Step Leaching Method *International Journal of Mineral Processing* 149 2016: pp. 78–83.
<https://doi.org/10.1016/j.minpro.2016.02.011>
48. **Habashi, F.** The Recovery of the Lanthanides from Phosphate Rock *Journal of Chemical Technology and Biotechnology. Chemical Technology* 35 (1) 1985: pp. 5–14.
<https://doi.org/10.1002/jctb.5040350103>
49. **Kijkowska, R., Kowalczyk, J., Mazanek, C.** Rare Earth Elements from Kola Apatite Phosphogypsum *Phosphorus and Potassium* 163 1989: pp. 22–26.
50. **Lin, W., Jie, Z.** Study on RE Leaching from RE-Bearing Phosphate Rock *Chinese Rare Earths* 38 (2) 2017: pp. 56–65.
<https://doi.org/10.16533/J.CNKI.15-1099/TF.201701009>
51. **Walawalkar, M., Nichol, C.K., Azimi, G.** Process Investigation of the Acid Leaching of Rare Earth Elements from Phosphogypsum Using HCl, HNO₃, and H₂SO₄ *Hydrometallurgy* 166 2016: pp. 195–204.
<https://doi.org/10.1016/j.hydromet.2016.06.008>
52. **Ismail, Z., AbuElgoud, E.M., AbdelHai, F.** Leaching of Some Lanthanides from Phosphogypsum Fertilizers by Mineral Acids *Arab Journal of Nuclear Sciences and Applications* 48 (2) 2015: pp. 37–50.
53. **Lokshin, E.P., Vershkova, Y.A., Vershkov, A.V.** Leaching of Lanthanides from Phosphosemihydrate with Nitric Acid *Russian Journal of Applied Chemistry* 75 2002: pp. 1753–1759.
<https://doi.org/10.1023/A:1022285330832>
54. **Gasser, M.S., Ismail, Z.H., Elgoud, E.A.** Process for Lanthanides-Y Leaching from Phosphogypsum Fertilizers Using Weak Acids *Journal of hazardous materials* 378 2019: pp. 120762.
<https://doi.org/10.1016/j.jhazmat.2019.120762>
55. **Goyne, K.W., Brantley, S.L., Chorover, J.** Rare Earth Element Release from Phosphate Minerals in the Presence of Organic Acids *Chemical Geology* 278 (1–2) 2010: pp. 1–14.
<https://doi.org/10.1016/j.chemgeo.2010.03.011>
56. **Furrer, G., Stumm, W.** The Coordination Chemistry of Weathering: I. Dissolution Kinetics of δ -Al₂O₃ and BeO *Geochimica et Cosmochimica Acta* 50 (9) 1986: pp. 1847–1860.
[https://doi.org/10.1016/0016-7037\(86\)90243-7](https://doi.org/10.1016/0016-7037(86)90243-7)
57. **Fuhai, W., Binghui, C., Yanghu, L.** An Experimental Study on Effects of Organic Acids on Dissolution of REE in Weathering Crust of Granite *Chinese Rare Earths* 23 (2) 2002: pp. 1–5.
<https://doi.org/10.3969/j.issn.1004-0277.2002.02.001>
58. **Yanrong, D., Ying, M., Wenjuan, Z.** Leaching Rare Earth Oxides by Hydrochloric Acid and Citric Acid *Journal of the Chinese Society of Rare Earths* 37 (4) 2019: pp. 457–464.
<https://doi.org/10.11785/S1000-4343.20190409>
59. **Ji, B., Li, Q., Zhang, W.** Leaching Recovery of Rare Earth Elements from the Calcination Product of a Coal Coarse Refuse Using Organic Acids *Journal of Rare Earths* 40 (2) 2022: pp. 318–327.
<https://doi.org/10.1016/j.jre.2020.11.021>
60. **Hopfe, S., Konsulke, S., Barthen, R.** Screening and Selection of Technologically Applicable Microorganisms for Recovery of Rare Earth Elements from Fluorescent *Waste Management* 79 2018: pp. 554–563.
<https://doi.org/10.1016/j.wasman.2018.08.030>
61. **Costis, S., Mueller, K.K., Coudert, L.** Recovery Potential of Rare Earth Elements from Mining and Industrial Residues: A Review and Cases Studies *Journal of Geochemical Exploration* 221 2021: pp. 106699.
<https://doi.org/10.1016/j.gexplo.2020.106699>
62. **Viktorovna, B.T., Borisovna, Z.A.** Aleksandrovna, A.E. Method of Processing Phosphogypsum with Extraction of Rare-Earth Elements and Phosphorus: 2012-07-27 *Russian patent* 2012.
63. **Antonick, P.J., Hu, Z., Fujita, Y.** Bio-and Mineral Acid Leaching of Rare Earth Elements from Synthetic Phosphogypsum *The Journal of Chemical Thermodynamics* 132 2019: pp. 491–496.
<https://doi.org/10.1016/j.jct.2018.12.034>
64. **Brandl, H., Barmettler, F., Castelberg, C.** Microbial Mobilization of Rare Earth Elements (REE) from Mineral Solids: A Mini Review *AIMS Microbiology* 3 (2) 2016: pp. 190–204.
<https://doi.org/10.3934/microbiol.2016.2.190>
65. **Salo, M., Knauf, O., Mäkinen, J.** Integrated Acid Leaching and Biological Sulfate Reduction of Phosphogypsum for REE Recovery *Minerals Engineering* 155 2020: pp. 106408.
<https://doi.org/10.1016/j.mineng.2020.106408>
66. **Binnemans, K., Jones, P.T., Blanpain, B.** Towards Zero-Waste Valorisation of Rare-Earth-Containing Industrial

Process Residues: a Critical Review *Journal of Cleaner Production* 99 2015: pp. 17–38.
<https://doi.org/10.1016/j.jclepro.2015.02.089>

67. **El-Didamony, H., Ali, M., Awwad, N.** Treatment of Phosphogypsum Waste Using Suitable Organic Extractants *Journal of radioanalytical and nuclear chemistry* 291 (3) 2012: pp. 907–914.
<https://doi.org/10.1007/s10967-011-1547-3>
68. **Cánovas, C.R., Macías, F., Pérez-López, R.** Valorization of Wastes from the Fertilizer Industry: Current Status and Future Trends *Journal of Cleaner Production* 174 2018: pp. 678–690.
<https://doi.org/10.1016/j.jclepro.2017.10.293>
69. **Mukaba, J., Eze, C.P., Pereao, O.** Rare Earths' Recovery from Phosphogypsum: An Overview on Direct and Indirect Leaching Techniques *Minerals* 11 (10) 2021: pp. 1051.
<https://doi.org/10.3390/min11101051>
70. **Pereao, O., Bode-Aluko, C., Fatoba, O.** Rare Earth Elements Removal Techniques from Water/Wastewater: A Review *Desalination and Water Treatment* 130 2018: pp. 71–86.
<https://doi.org/10.5004/DWT.2018.22844>
71. **Virolainen, S., Repo, E., Sainio, T.** Recovering Rare Earth Elements from Phosphogypsum Using a Resin-In-Leach Process: Selection of Resin, Leaching Agent, and Eluent *Hydrometallurgy* 189 2019: pp. 105125.
<https://doi.org/10.1016/j.hydromet.2019.105125>
72. **Koopman, C., Witkamp, G.J.** Extraction of Lanthanides from the Phosphoric Acid Production Process to Gain a Purified Gypsum and a Valuable Lanthanide *Hydrometallurgy* 58 (1) 2000: pp. 51–60.
[https://doi.org/10.1016/S0304-386X\(00\)00127-4](https://doi.org/10.1016/S0304-386X(00)00127-4)



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