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Review

Development Review on Leaching Technology and Leaching Agents of Weathered Crust Elution-Deposited Rare Earth Ores

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Abstract: Weathered crust elution-deposited rare earth ores are key strategic resources and the main source of medium and heavy rare earths. This paper summarizes the development of leaching technology of rare earth ores, compares the advantages and disadvantages of the three generations of leaching technology, and introduces the improved heap leaching technology and the new technology of the leaching–extraction integration and enhanced leaching, focusing on the leaching of weathered crust elution-deposited rare earth ores. In this paper, the development of the leaching agents is expounded, and the research status and the development trend of the composite ammonium salt leaching agent, impurity inhibition leaching agent, swelling inhibition leaching agent, and seepage-promotion leaching agent are also introduced. And this paper summarizes the leaching mechanism and the development direction of leaching agents. Moreover, the future key research direction of weathered crust elution-deposited rare earth ores is proposed, which is green, efficient, safe development and utilization.

Keywords: weathered crust elution-deposited rare earth ore; leaching technology; leaching agent; research progress

1. Introduction

Due to the unique physical and chemical properties of rare earth, it plays a key role in multiple fields of industry. It is an indispensable key substance for high-tech industries and is known as a key strategic resource in the 21st century. Rare earth ores are mainly divided into mineral-type rare earth ores and weathered-type rare earth ores (also known as ion adsorption rare earth ores). Mineral-type rare earth ores are the main source of light rare earths and are mainly represented by fluorocarbon ores, which can be recovered and enriched by gravity separation, magnetic separation, and flotation [1,2], while the weathered crust elution-deposited rare earth ores are adsorbed on clay minerals in the form of hydrated ions or hydroxyl hydrated ions, which are the main source of medium and heavy rare earths and can only be recovered and enriched by ion exchange. Chemically active cations (Na^+, Ka^+, H^+, NH_4^+, etc.) can exchange and resolve rare earth ions in rare earth ores.

For the mining of weathered crust elution-deposited rare earth ores, China has successively developed three generations of rare earth leaching technologies, such as pool leaching, heap leaching, and in situ leaching [3]. The heap leaching and in situ leaching technologies are developed on the basis of the pool leaching technology, which are suitable for large-scale rare earth mining. Rare earth ores with different ore body structures are suitable for different leaching technologies. For rare earth ores with false floors and few ore body fractures, the in situ leaching technology is favored; otherwise, the heap leaching technology is a better option. Aiming at the shortcomings of traditional heap leaching and in situ leaching technologies, scientific researchers have developed modified heap

leaching technology, leaching–extraction integration and enhanced leaching–extraction integration technology, enhanced leaching technology, etc., to provide technical support for the development and utilization of weathered crust elution-deposited rare earth ores.

NaCl was initially used as the rare earth leaching agent, but the rare earth leaching efficiency was low, and the use of high-concentration NaCl also generated the high-salt wastewater that would cause soil salinization and environmental pollution [4]. In order to solve the shortcomings of the NaCl leaching agent, researchers developed an ammonium sulfate leaching agent, which solved the pollution problem of high-salt waste residue and wastewater; however, the ammonium sulfate leaching agent also produced problems such as ammonia and nitrogen pollution and a high impurity content in the leachate. Thus, researchers developed ammonia-free or low-ammonia leaching agents and impurity inhibition leaching agents. Some research results have been applied to rare earth ores and have provided theoretical basis and technical support for the green development of weathered crust elution-deposited rare earth ores.

The weathered crust elution-deposited rare earth ores are rich in a large number of clay minerals. Clay minerals have the characteristics of swelling by water absorption and shrinking by water loss, which directly affects the permeability of rare earth leaching, especially in situ leaching, in which the penetration rate of the leaching agent and the recovery efficiency of rare earth are greatly affected by the properties of rare earth ores. For rare earth ores with high clay mineral content and fine particle size, the leaching agent will penetrate slowly into the ore body; thus, much more leaching agent is consumed and the leaching cycle is increased. If such rare earth ores are improperly injected during in situ leaching, there is a high possibility of causing geological disasters, such as landslides, which result in loss of personnel and property and seriously affect the economic benefits of rare earth ores. To this end, scholars have carried out a lot of research on inhibiting the swelling of clay minerals and have promoted the seepage of leaching agents and developed a series of swelling inhibition leaching agents and seepage promotion leaching agents, which provide a new method for the safe and efficient exploitation of weathered crust elution-deposited rare earth ores.

2. The Development of Leaching Technology for Rare Earth Ores

The rare earth of weathered crust elution-deposited rare earth ores are adsorbed on clay minerals in the form of hydrated ions or hydroxyl hydrated ions [5], and can only be recovered and enriched by ion exchange. China has successively developed three generations of leaching technologies. The first-generation leaching technology was pool leaching. On this basis, in order to expand the scale of leaching, the second-generation heap leaching technology and the third-generation in situ leaching technology were developed. The in situ leaching process of rare earth ores is shown in Figure 1. Traditional heap leaching refers to transporting the excavated rare earth ores to the heap leaching site. There is a diversion layer at the bottom of the heap leaching site, and the rare earth ores are piled on it. The heap can be built at one time or on the heap after the heap leaching is completed. Or, accumulating layer by layer after heap leaching with plastic film in each layer, the leachate of the top layer is collected into the transfer tank through the diversion layer, and the rare earth enrichment is obtained after impurity removal and precipitation, and the leachate of the other layers is sent to the tail water recycling system. In situ leaching is to inject the leaching agent into the ore body through the liquid injection well on the surface of the rare earth ores [6], The leaching agent diffuses and penetrates in the ore body, then collects the leachate through the diversion hole at the bottom of the ore body, and finally removes impurities and precipitates to obtain rare earth enrichment. Since the in situ leaching technology does not require "moving mountains", the labor intensity is small, and the damage to the surface vegetation is small, so it is a leaching technology with more development prospects.
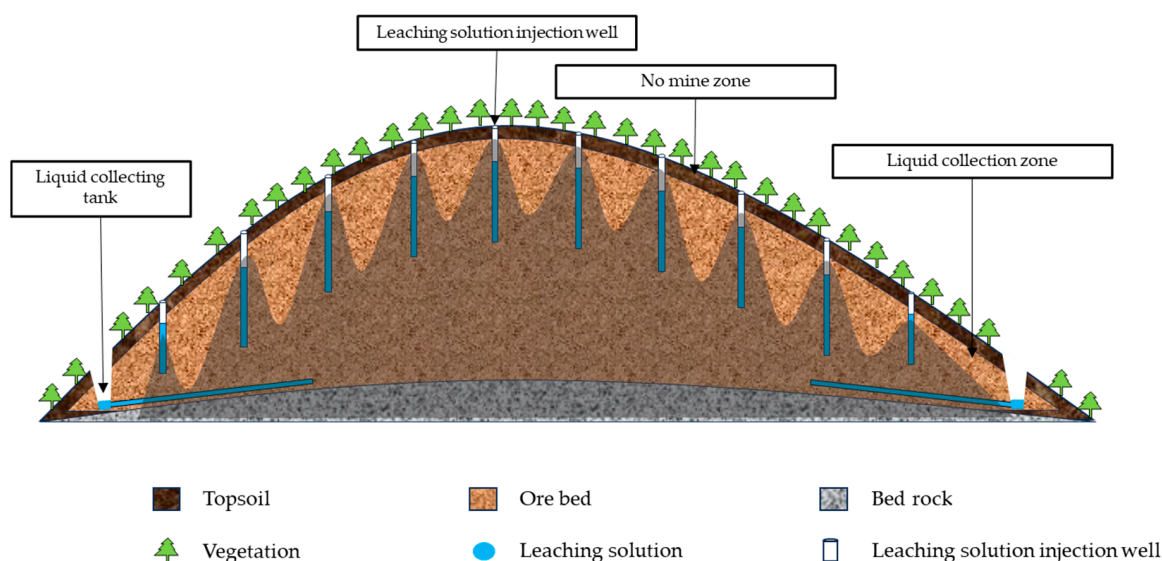
Figure 1. In situ leaching process of rare earth ores.

Rare earth ores with different ore body structures should choose the appropriate leaching technology. In situ leaching is more suitable for rare earth ores with false floors and few ore body cracks; for rare earth deposits without false floors or cracks, leachate will leak and pollute groundwater, and the recovery rate of rare earth is low, so heap leaching is a more suitable craft.

In order to reduce the pollution of the leaching technology of weathered crust elution-deposited rare earth ores and recover rare earths efficiently, safely, and greenly, scientific researchers have continuously improved the traditional leaching technology to develop improved heap leaching technology, integrated leaching and extraction methods, and enhanced leaching technology, etc., to provide technical support for the efficient development and utilization of weathered crust elution-deposited rare earth ores.

2.1. Improvement of Heap Leaching Technology

In the traditional heap leaching process, the top of the rare earth pile is covered with the leaching solution. This creates trouble for vegetation restoration carried out promptly on the top of the pile. Wei Ju et al. [7,8] proposed a horizontal liquid injection so that vegetation restoration can be carried out quickly on the top of the pile. The formation and distribution of preferred flow paths of the rare earth pile under indoor horizontal injection conditions were studied. It was found that under horizontal injection conditions, the fine particles of the rare earth moved away from the liquid injection end and also toward the lower part of the pile, and the migration of the fine particles resulted in the formation of the preferential flow paths. The permeability of rare earth with different particle compositions for a novel heap leaching technology was also discussed. The permeability of the rare earth piles is governed by the migration of fine particles. In the rare earth with a combination of coarse and fine particles, preferential flow paths are easy to develop, as in this soil, the fine particles easily migrate, and they cannot block the pore channels.

2.2. Leaching-Extraction Integration Technology

The rare earth oxides (REO) in the leachate obtained by the traditional in situ leaching technology are only 0.3–2.0 g/L, and ammonium bicarbonate is usually used as a pre-cipitating agent to obtain rare earth carbonates, which are then calcined to obtain rare earth oxides (REO > 90%), and then dissolved in hydrochloric acid [9], extracted, and separated to produce a single rare earth or high-purity rare earth product. In order to solve the problems of long enrichment and recovery process of low-concentration rare earth leachate and low recovery rate of rare earth in the exploitation process of weathered crust

elution-deposited rare earth ore, Huang Xiaowei et al. [10] invented the leaching–extraction integration technology (Figure 2) and used P507/P204 to carry out step-by-step coupled extraction of low-concentration rare earth leachate to achieve high-efficiency centrifugal extraction enrichment of light and heavy rare earth and effective separation of impurities, such as aluminum and iron. Compared with traditional in situ leaching and the precipitation enrichment and extraction methods, it can greatly shorten the production process, improve resource utilization, and reduce raw material consumption and production costs. The leaching–extraction integration technology can effectively solve the pollution problems of ammonia–nitrogen wastewater and radioactive waste residue in the exploitation process of weathered crust elution-deposited rare earth ores in southern China.
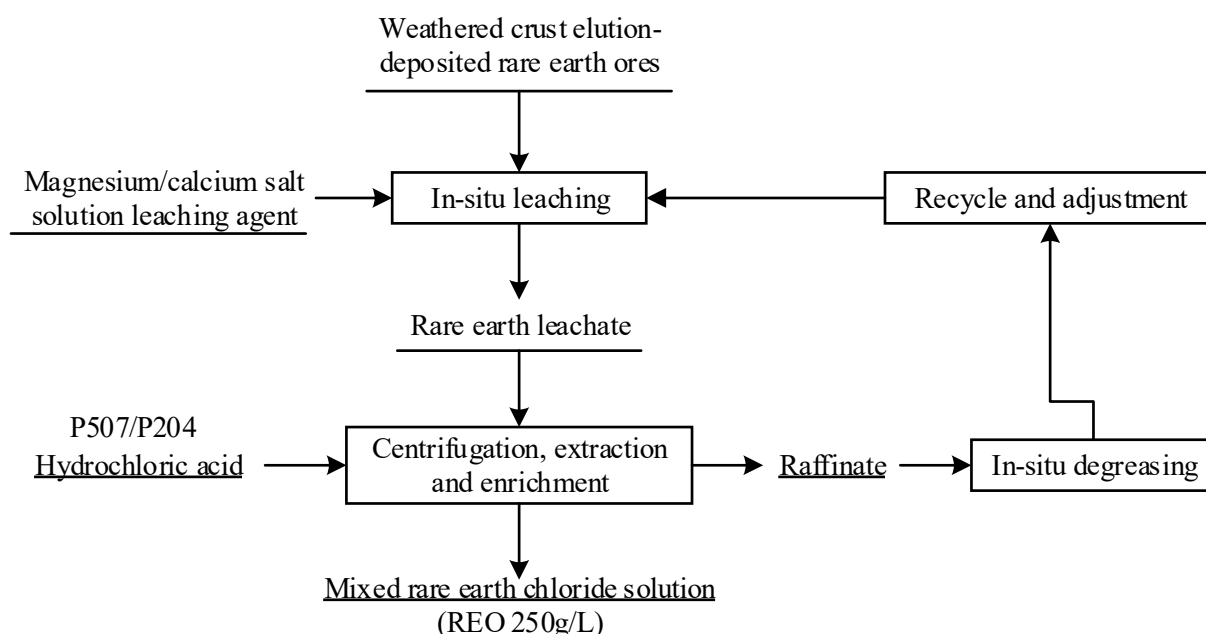

Figure 2. Process flow chart of green and efficient leaching–extraction integration technology for rare earth raw ores [10].

2.3. Enhanced Leaching Technology

In view of the weak penetration of the leaching agent in the in situ leaching technology of weathered crust elution-deposited rare earth ores, Qiu Tingsheng et al. [11] used $(NH_4)_2SO_4$ as a leaching agent, and the leaching rate of IATRE ores increases with the magnetization time increasing under the optima leaching conditions of rare earth, and the optima magnetization time was about 30 min. The magnetic field not only can enhance the leaching rate of rare earth but also can reduce the usage of leaching agent by 10–20%. Zhou Lingbo et al. [12] conducted an indoor simulated column leaching experiment on rare earth samples with 2 wt% $MgSO_4$ as a leaching agent and an electric field applied at both ends of the samples. Compared with a single $MgSO_4$ solution leaching, applying an electric field with a strength of 6 V/cm can save the leaching time of 30 min and increase the flow velocity of the rare earth leachate by 26.98%. Under the optimal conditions of applying an electric field with a strength of 6 V/cm for 20 min to the leaching system after 10 min of rare earth leachate flowing out, the leaching efficiency of samples increases from 81.20% to 86.05% with the increase in 4.85%. Yin Shaohua et al. [13] found that an ultrasonic-assisted leaching process with $MgSO_4$ is not only effective but also environmentally friendly, and it is beneficial to leach rare earth at laboratory scale. In addition, Wang Gaofeng et al. [14] reported an innovative REE mining technique, electrokinetic mining (EKM), which can enhance the migration of REEs with the applied electric field. Compared to the conventional techniques, EKM achieves about 2.6 times higher recovery efficiency, a nearly 80% decrease in leaching agent usage and a 70% reduction in metallic impurities in the obtained REEs.

Although the leaching–extraction integration technology and the enhanced leaching technology have obvious effects on the exploitation of weathered crust elution-deposited rare earth ores, there are corresponding engineering problems to be solved in actual production, and further research is needed. With the leaching technology, it is difficult to carry out large-scale industrial applications.

3. Development of a Leaching Agent for Rare Earth Ores

Initially, NaCl was used as the leaching agent to leach rare earth from weathered crust elution-deposited rare earth ores. Due to the low leaching efficiency of rare earth and serious soil salinization, NaCl was replaced by ammonium sulfate later. Moldoveanu Georgiana A. et al. [15] used 0.5 mol/L of ammonium sulfate to recovery rare earth, and the leaching efficiency of yttrium-rich and yttrium-medium rare earth both could achieve about 80%.

3.1. Composite Ammonium Salt Leaching Agents

In order to improve the leaching rate and leaching efficiency of rare earth in weathered crust elution-deposited rare earth ores, researchers focused on the influence of a composite ammonium salt leaching agent composed of a variety of ammonium salts on the leaching of rare earths. He Zhengyan et al. [16,17] studied the effect of a compound leaching agent composed of NH_4Cl and $(NH_4)_2SO_4$ on the leaching process of weathered crust elution-deposited rare earth ores. Compared with $(NH_4)_2SO_4$, the rare earth leaching rate reached up to 91%. Chai Xiuwei et al. [18] explored the effect of compound ammonium carboxylate composed of ammonium acetate and ammonium citrate on the leaching of weathered crust elution-deposited rare earth ores and found that the leaching rate of rare earth can reach 80% at a molar ratio of ammonium acetate to ammonium citrate of 7:3; the ammonium concentration was 0.15 mol/L, pH 4.0, and the temperature was 313 K.

Since the weathered crust elution-deposited rare earth ores mainly use ammonium salt as the leaching agent, the composite leaching agent composed of a variety of ammonium salts is a current research hotspot, which has a good effect on improving the leaching rate of rare earth. Therefore, it has important significance to develop ammonium salts and reagents with the effects of an impurity inhibitor, swelling inhibitor, and permeation promoter.

3.2. Ammonia-Free or Low-Ammonia Leaching Agents

As researchers pay more and more attention to environmental protection, the problem of ammonia–nitrogen pollution in traditional ammonium salt leaching agents cannot meet the actual production requirements. The research and development of new leaching agents without or with low ammonia has become a research hotspot. In order to reduce or eliminate the problem of ammonia–nitrogen pollution from the original source, Xiao Yanfei et al. [19] proposed to use magnesium sulfate ($MgSO_4$) instead of $(NH_4)_2SO_4$ as the leaching agent and found that above 92% of the rare earth leaching rate was obtained when the pH value was around 5.7, and 0.02 mol/L $MgSO_4$ solution was used to leach weathered crust elution-deposited rare earth ores. Xiao Yanfei et al. [20] innovatively proposed the use of ferrous sulfate ($FeSO_4$) as $(NH_4)_2SO_4$ alternative can leach out the rare earth in both the ion exchange phase and the colloidal phase during in situ leaching. It was found that the leaching rate of rare earth by $FeSO_4$ is higher than that of $(NH_4)_2SO_4$, reaching 102%. The leaching efficiency is defined as the ratio of the mass of RE_2O_3 in the leachate to the total mass of exchangeable RE_2O_3 in rare earth ore. Not only exchangeable phase rare earth can be exchanged by $FeSO_4$, but also the colloidal phase rare earth can be dissolved. Therefore, the leaching efficiency exceeds 100%. Lai Fuguo et al. [21] studied the leaching effect of a composite leaching agent composed of magnesium sulfate and ascorbic acid on rare earth. The rare earth in the colloidal phase was leached out using the strong reductive properties of ascorbic acid, and the rare earth leaching rate reached 107.5%. Yang Lifen et al. [22] compared the leaching efficiency of rare earth with ammonium sulfate, magnesium sulfate, aluminum sulfate, ammonium chloride, magnesium chloride, and

aluminum chloride. A novel leaching method was proposed, which was firstly leaching with ammonium sulfate and then with aluminum sulfate, followed by water washing and lime neutralizing. With the ratio of ammonium sulfate to aluminum sulfate varying from 1:0 to 0.5:0.5, the residual ammonium in tailing decreases from 11.2% to 0.6%. The LE of IARE can be increased, and the danger caused by tailings landslides, and pollutant emissions can be reduced by replacing ammonium sulfate with aluminum sulfate as a leaching agent. Bioleaching is a novel technology. Compared with traditional leaching methods, bioleaching is a low-cost and environmentally friendly process. Meng Xiaoyu et al. [23] simulated bioleaching of IRE-ore by biosynthetic citrate/($(NH_4)_3$Cit) and found that more than 90% of the total REE leaching efficiency can be obtained at extremely low citrate concentrations (about 3.3 mmol/L), which were only 10% of the commonly used ammonium sulfate concentration. Analytical results showed that Cit species directly transferred REEs from the IRE-ore surface to solution via a complexation reaction, which was synchronized and synergistic with the ion-exchange reaction of NH_4^+. This work provides a new idea for the clean and efficient utilization of IRE-ore and is expected to overcome the common disadvantages and bottlenecks of traditional technology of inorganic salt leaching and the principle of cation exchange. However, bioleaching needs harsh chemical treatments and further studies are needed to elucidate the mechanism of microbe–REE interactions. Shi Qiyuan et al. [24] changed the molecular structure of ammonium salts and used ammonium citrate as a leaching agent to substitute ammonium sulfate. The column leaching results showed that a high leaching efficiency of REE could be obtained at a relatively low concentration of ammonium. Both the cation and anion of ammonium citrate were benefit to the leaching of REEs. A liquid/solid ratio of 4:1, pH of 6, and NH_4^+ of 30 mmol/L were the optima conditions for ammonium citrate leaching, and the leaching efficiency of rare earth was nearly 100%. This work provided a new approach to solve the problems of traditional leaching technology with ammonium salts. Xia Houbin [25] used sugarcane leaves, rice straw, weeds, mulberry trees, etc. as raw materials, and the filtrate obtained after slicing, crushing, stacking, soaking, cooking, and filtering was used as a medium, and then fermented and transformed by microorganisms, fungi, and strains to obtain plant extracts. The permeability and leaching performance of plant extract and $(NH_4)_2SO_4$ for rare earth leaching were comparatively studied, and it was found that the horizontal average penetration velocity, vertical average penetration velocity and leaching rate of rare earth by plant extract were 0.141 cm/min, 0.213 cm/min, 94.45%, respectively, and were better than $(NH_4)_2SO_4$ leaching agent.

From the above studies, it can be found that in order to reduce or eliminate the problem of ammonia–nitrogen pollution from the original source, the research and development of an ammonium-free leaching agent mainly focuses on magnesium salts, iron salts, and plant fermentation broths. The research on the magnesium salt leaching agent is relatively mature, but plant fermentation liquid extracts would be a better development direction. The development of efficient plant extracts can not only overcome the environmental pollution problems of traditional leaching agent but also improve the utilization rate of plants and open up opportunities for the green development of rare earth.

3.3. Impurity Inhibition Leaching Agent

In weathered crust elution-deposited rare earth ores, rare earth elements are adsorbed on clay minerals in the form of hydrated or hydroxyl hydrated cations [26]. At the same time, impurity ions, such as Al^{3+}, Fe^{3+}, Ca^{2+}, and Mg^{2+}, are also absorbed. When rare earth is leached by ion exchange, these impurity ions are also exchanged into the leachate at the same time. Although the impurity content can be reduced after impurity removal, the rare earth will also enter the impurity removal residue, resulting in the loss of rare earth, and these impurities will also increase the subsequent difficulty and cost of separation. With the continuous development of exploitation technology of weathered crust elution-deposited rare earth ores, impurity inhibition leaching has also become the focus of scientific and technological workers.

At present, impurity inhibition leaching occurs mainly through inorganic salt or the addition of an inhibitor to reduce the leaching of impurities. Chen Zhuo et al. [27] used magnesium sulfate, magnesium chloride, and magnesium nitrate as leaching agents. It was found that high temperature contributes to improving the mass transfer efficiency of rare earth and aluminum, and 0.2 mol/L of magnesium nitrate as the leaching agent can obtain the highest leaching mass transfer efficiency of rare earth, and 0.2 mol/L of magnesium sulfate as the leaching agent can make the leaching and mass transfer efficiency of Al the lowest. Qiu Tingsheng et al. [28] developed an environmentally friendly impurity inhibitor, LG-01. LG-01 can react with impurity ions, such as aluminum and iron, to form complexes, thereby reducing the concentration of impurity ions in the leachate, yielding a rare earth leaching efficiency of 95.6%, and the removal rate of impurity ions is 92%. Yang Xiuli et al. [29] used ammonium nitrate and ammonium sulfate as a compound leaching agent and ammonium acetate as an inhibitor. The leaching rate of rare earth was exceeded 80% with 2.0% compound leaching agent (4:1 of molar ratio of ammonium nitrate/ammonium sulfate) and 0.05% ammonium acetate at 0.5 mL/min flow-rate at room temperature. Feng Jian et al. [30] developed a composite leaching agent composed of $(NH_4)_2SO_4$ and ammonium formate. The leaching rates of rare earth and aluminum were 92.97% and 37.79%, respectively, which significantly inhibited the leaching of aluminum. Zhu Dongmei et al. [31] used molecular dynamics to simulate the interaction of sulfosalicylic acid with aluminum, lanthanum, and yttrium, and found that when the concentration of sulfosalicylic acid was 0.15 wt%, the concentration of aluminum ions in the leachate was 47.19 mg/L. Sulfosalicylic acid can undergo complexation reaction with free aluminum ions to form a complex, which can inhibit the leaching of aluminum, while there is only weak adsorption between sulfosalicylic acid and rare earth ions. Chen Zhuo et al. [32] studied the leaching process of rare earth with formate (ammonium formate, potassium formate, and sodium formate) and found that when the concentration of ammonium formate was 1% at room temperature, the leaching rates of rare earth and aluminum are 87% and 37%, respectively. Ammonium formate could effectively recover rare earth elements from weathered crust elution-deposited rare earth ores and inhibit the leaching of impurity aluminum. Yan Huashan et al. [33] carried out a leaching kinetic experiment with a combined leaching agent for an ionic RE ore. When a combined leaching agent composed of QZX-02 and ammonium sulfate (mass ratio of 7:3) was used, the leaching rate of RE^{3+} was 97.58%, and the concentration of Al^{3+} in the leachate was 0.016 g/L. Compared with single ammonium sulfate, the leaching rate of RE increased by 8.96%, and the concentration of Al^{3+} decreased by 0.069 g/L. The combined leaching agent and impurity ions could produce carboxylic acid organic compounds on the surface of clay minerals, which inhibit the leaching of impurity ions and improve the leaching of RE ions. Guo qi et al. [34] used magnesium sulfate as a leaching agent and investigated the effects of pH and the concentration of magnesium sulfate on the leaching of aluminum and rare earth. At a pH of 2, a liquid-to-ore ratio of 1.4 and 0.5 wt% $MgSO_4$, the leaching rate of rare earth was 91.0%, while that of aluminum was 7.7%.

The current research on impurity inhibition leaching agents mainly focuses on adding impurity inhibitors to the traditional ammonium salt leaching agent, but the effect of impurity inhibition leaching needs to be further improved, and there are few studies on the impurity inhibition leaching mechanism, so it is necessary to screen and develop efficient impurity inhibition leaching agents.

3.4. Swelling Inhibition Leaching Agent
3.4.1. Hydration Expansion Mechanism of Clay Minerals

The weathered crust elution-deposited rare earth ores contain a large amount of clay minerals, and the clay minerals are mainly silicate minerals with a layered structure, which are composed of negatively charged silicon–oxygen tetrahedrons and aluminum–oxygen octahedrons, a phenomenon in which low-valent cations replace high-valent cations, thereby making the clay sheets negatively charged [35]. The clay minerals in weathered crust

elution-deposited rare earth deposits are mainly composed of kaolinite, halloysite, illite, montmorillonite, etc., among which kaolinite and halloysite are composed of silica tetrahedrons and alumina octahedrons at a ratio of 1:1. The layered crystal minerals, illite, and montmorillonite are layered crystal minerals with a 2:1 composition [36]. Crystal minerals exist in the form of wafers, and there are interlayer substances such as water molecules, cations, hydroxyl groups, and water complexes between the wafers, and the wafers are united by the positive charge of the cations. If the balance of interlayer substances is broken by external factors, the distance between wafers will change, which is the most important manifestation of hydration expansion.

The hydration expansion mechanism of clay minerals mainly includes [37]: (1) surface hydration: the action of charged atoms, exchangeable cations, and hydrogen bonds in clay minerals makes water molecules enter the intercrystalline layers of clay minerals and adsorb water successively on the surface and form a hydration film and push the clay mineral crystal layers apart, causing the layers to swell. (2) Osmotic hydration: It is caused by the repulsion between the diffusion double layer and the osmotic pressure. After the surface of the clay mineral is hydrated, the osmotic pressure generated by the cation concentration between the mineral layers is higher than the cation concentration on the mineral surface, which makes the water molecules enter the mineral. Between the layers, the interlayer cations diffuse outward to form a diffused electric double layer. The repulsive force of the electric double layer causes the interlayer spacing to increase, and the clay minerals expand. Zhang Zhenyue et al. [38] found that the zeta potential on the surface of clay minerals increases with the valence state of cations and the pH of the solution, reducing the thickness of the electric double layer between clay mineral layers, and reducing the negative charge on the surface of the clay minerals can inhibit expansion of the clay minerals.

Therefore, there are many factors that affect the expansion of clay minerals, such as the type of clay minerals, the concentration and properties of cations between mineral layers, etc. By adding swelling inhibitors to clay minerals, the surface charge of clay can be reduced, the hydrophilicity of the clay surface can be changed, and the expansion of clay minerals can be inhibited.

3.4.2. Current Research on Swelling Inhibitors

Clay minerals have the characteristics of swelling by absorbing water and shrinking by losing water. The expansion of clay minerals by water absorption leads to changes in the pore structure of rare earth ores, thereby reducing their permeability and prolonging the in situ leaching cycle. If rare earth ores are improperly injected during in situ leaching, it is very easy to cause geological disasters, such as landslides, resulting in loss of personnel and property and seriously affecting the economic benefits of rare earth ores. Therefore, it is of great significance to study the swelling inhibition mechanism in the in situ leaching process and develop suitable swelling inhibition leaching agents for the safe exploitation of weathered crust elution-deposited rare earth ores.

There are three types of swelling inhibition mechanisms for clay minerals: (1) reducing the negative charge on the surface of clay minerals and inhibit their expansion; (2) interaction with hydroxyl groups on the surface of clay minerals to form groups that are weakly hydrophilic or tightly connected between crystal planes; (3) transforming expansive clay minerals into non-expandable clay minerals by ion exchange. But, at present, the purpose of inhibiting the hydration expansion of clay minerals is mainly achieved through the first two ways, including inorganic swelling inhibitors and organic swelling inhibitors [39].

(1)   Inorganic swelling inhibitors

Inorganic swelling inhibitors are mainly salts, such as potassium salts, ammonium salts, magnesium salts, calcium salts, and sodium salts. Salt can dissociate cations in water and diffuse into the clay mineral wafers, reduce the electric double-layer repulsion between layers, and inhibit the expansion of clay minerals. Although the swelling inhibition effect of the inorganic salt swelling agent is good and the price is relatively low, the action time is

short, and it is not resistant to erosion, so it is not suitable for long-term swelling inhibition, and it is only used for short-term clay mineral swelling inhibition. Since the K^+ diameter of KCl is close to the distance between clay mineral layers, it is easy to enter the interlayer, neutralize the negative charge between layers [40], and have the best effect on inhibiting the expansion of clay minerals. Usually, 4% of KCl aqueous solution is selected as the standard for swelling inhibitors. Chen Zhuo et al. [41] also evaluated the effect of magnesium salt leaching agent on the swelling of clay minerals and found that $Mg(NO_3)_2$ could inhibit the hydration swelling of clay minerals at room temperature. In order to alleviate the swelling of clay minerals in weathered crust elution-deposited rare earth ores during in situ leaching, Zhang Zhenyue et al. [42] found that urea had a better swelling inhibitory effect.

In addition to inorganic salt swelling inhibitors, there are also inorganic cationic polymers, such as aluminum hydroxy and zirconium hydroxy. Inorganic cationic polymers can dissociate polynuclear hydroxyl bridging ions in aqueous solution and adsorb the negatively charged surface of clay, reducing the negative charge on the surface of clay minerals and inhibiting the expansion of clay minerals. The swelling inhibition time effect of inorganic cationic polymers is longer than that of inorganic salt swelling inhibition agents. Since organic cations can be firmly adsorbed on the surface of clay particles and are not easily replaced by other ions, the organic swelling inhibition agent is resistant to erosion and has a longer timeliness. He Zhengyan et al. [43] used diallyl dimethyl ammonium chloride (DMDACC) to inhibit the expansion of clay minerals in weathered crust elution-deposited rare earth ores and found that the leaching rate of the combination of 2 wt% $(NH_4)_2SO_4$ and 1.2 wt% DMDACC as leaching agent is as high as 97.14%. Compared with the use of 2 wt% $(NH_4)_2SO_4$ only, the linear expansion height of the rare earth ore is reduced from 2.44 mm to 2.00 mm. The expansion inhibition effect of rare earth ore is significant.

(2) Organic swelling inhibitors

In recent years, with the in-depth study on swelling inhibition agents of clay minerals, the development of organic swelling inhibition agents has gradually become a research hotspot, mainly including polyetheramines, polymeric alcohols, polyquaternary ammoniums, ultra-multi-branched polymers, and biological swelling inhibitors. Polyetheramine swelling inhibition agents are mainly polyetheramines, polyetheramine derivatives, and organic swelling inhibition agents synthesized from polyetheramines [44]. Polyetheramine is environmentally friendly and has good thermal stability and biodegradability. The aqueous solution of polyether amine is weakly alkaline, and the positively charged amino group is adsorbed on the surface of clay minerals to neutralize the negative charge on the surface and inhibit hydration expansion [45].

Shu Xiaobo et al. [46] investigated the swelling inhibition performance of polyether amine (PEA) as clay inhibitors. It was found that the PEA could enter into the clay interlayer to expel water molecules. Mao Hui et al. [47] used polyether amines (PEA) as clay inhibitors and applied molecular dynamics to investigate the arrangement and dynamic properties of neutral PEA (N-PEA) and protonated PEA (P-PEA) in the MMT interlayer. It was found that N-PEA prefers to adsorb on the surface of MMT using $-NH_2$ groups, which reduced the ability of MMT clay to capture the water molecules.

Polymer alcohol is a good swelling inhibitor since it is soluble in water, has low toxicity, and can be degraded by microorganisms. The swelling inhibition mechanism of polyalcohol mainly includes a turbidity point mechanism, a reduction in filtrate water activity, and an adsorption mechanism. The turbidity point mechanism means that when the polymeric alcohol is higher than the turbidity point temperature, the precipitated small droplets will form a hydrophobic film on the surface of the clay mineral. Reducing the water activity of the filtrate means that after adding polyol, the water activity of the filtrate is lower than the pore water activity, which can prevent water molecules from penetrating into the clay layer. The adsorption mechanism refers to the ether bond in the polymer alcohol molecule and the oxygen atom on the hydroxyl group forming a hydrogen bond

with the clay mineral, which is tightly adsorbed on the surface of the clay minerals to prevent the hydration expansion of the clay minerals.

De Souza Carlos Eduardo et al. [48] investigated the mechanisms of shale stabilization by hydrophobically modified poly(ethylene glycol) (PEG). The hydrophobic modification of PEG400 with long alkyl chains (lauric acid) significantly enhanced its affinity for the clay surface. The modified PEG was able to intercalate in the basal spacing of the clay, keeping the alkyl chains outside the interlayers of the clay, blocking and preventing the water uptake by the clay.

The swelling inhibition mechanism of polyquaternary ammonium salt mainly contains a large number of quaternary ammonium ions and hydroxyl groups. Positively charged quaternary ammonium ions can enhance the force between clay mineral layers, while hydroxyl groups form hydrogen bonds between layers, reducing the adsorption of water molecules and effectively inhibiting the hydration expansion of clay minerals. Ye Zhengqin et al. [49] created a series of polyquaternary ammonium as swelling inhibitors prepared from dimethylamine, epichlorohydrin, and melamine (DEM). The swelling inhibition rate of DEM-8 reached up to 92.3% when its concentration reached 0.8%. It might adsorb on the surface of clay through hydrogen bonds and electrostatic interaction by an anchoring effect and a hydrophobic effect. Thus, DEM-8 has a strong inhibition capability for the hydration swelling of bentonite.

Hyperbranched polymers are a class of highly branched three-dimensional macro-molecules with good solubility, unique three-dimensional spherical structure, asymmetric random branches and a large number of modifiable terminal functional groups, which are easy to modify [50]. Xie, Gang et al. [51] investigated the inhibition mechanism of low-molecular-weight branched polyethyleneimine (BPEI) and 1,6-hexamethylenediamine (HMDA) on sodium bentonite (Na$^+$ Bent). The results indicated that as the number of primary amine groups in the inhibitor increased, the saturated adsorption amount decreased, and the adsorption rate increased. Low-molecular-weight BPEI molecules enter the interlayer of Na$^+$ Bent and replaced the sodium ions. The BPEI molecules became firmly embedded in the interlayer of Na$^+$ Bent, resulting in the removal of water molecules and significant reduction in interlayer space. The swelling inhibition capacity of BPEI is better than HMDA and other inhibitors. And as the number of primary amines increases, the inhibitive performance increases.

Biological swelling inhibition agents contain functional groups such as cations, hydroxyl groups, and hydrophobic groups [52]. They have good environmental friendly advantages, biodegradability, and swelling inhibition ability and can effectively inhibit the hydration swelling of clay minerals. Bio-inhibitors can be divided into sugars and their derivatives as well as nitrogen-based compounds. Chitosan is chitin extracted from shells. It is a natural macromolecule with positive charge in nature after deacetylation. However, the poor water solubility of chitosan limits its application. Chitosan reacts with cationic etherification agent to prepare chitosan ammonium salt with good water solubility. This is because the molecular weight of chitosan ammonium salt is too large to enter the interlayer of clay minerals and can only be adsorbed on the surface of clay minerals, but it prevents water molecules from entering the interlayer, thereby effectively inhibiting the hydration expansion of the clay minerals. An, Yuxiu et al. [53] studied the inhibition of chitosan quaternary ammonium salt (HTCC) in MMT. The results indicated that the inhibition of HTCC was better than polyether amine. The positive ions in the HTCC could adsorb onto the surface and interlayer of MMT and neutralize the negative charge. That led to the inhibition of clay hydration. HTCC reduced the hydrolyzation of ether and showed better bond inhibition and resistance temperature. In order to comprehensively evaluate the above-mentioned swelling inhibition agents, their advantages and disadvantages are illustrated in Table 1.

Table 1. Advantages and disadvantages of above-mentioned swelling inhibition agent.

Swelling Inhibition Agent	Advantages	Disadvantages
Inorganic swelling inhibitors	Effective, cheap	Undurable
Inorganic cationic polymers	Effective	No acid resistance, expensive
Polyetheramines	Effective, eco-friendly	Poor thermal stability
Polymeric alcohols	Soluble in water, low toxicity	Poor solubility
Polyquaternary ammoniums	Effective, durable	Vulnerable
Ultra-multi-branched polymers	Soluble in water, effective	Expensive
Biological swelling inhibitors	Effective, eco-friendly	Poor solubility

The swelling inhibition agents developed above have good swelling inhibition properties, and a lot of research has been conducted on the swelling inhibition mechanism, but most of them have the high cost of swelling inhibition agents, complex synthesis, and poor stability. In-depth research on the hydration swelling of the clay minerals and the swelling inhibition mechanism needs to be further studied from the molecular level, with screening and developing of swelling inhibition agents with low cost, non-toxicity, easy biodegradation, and good stability and providing a theoretical basis for the development of green and high-efficiency swelling inhibition agents.

3.4.3. Seepage Promotion Leaching Agent

During the in situ leaching process, the clay minerals of the weathered crust elution-deposited rare earth ores are prone to hydration and expansion, which increases the distance between mineral sheets, and some sheets are detached from the mineral particles and are washed and broken into fine particles by the leaching agent solution. These fine particles will migrate in the clay pores and deposit, resulting in clogging and reducing the seepage velocity of the leaching agent in the ore body. When the solution accumulates seriously during in situ leaching, it will aggravate the slope stability of the deteriorated ore body, resulting in landslides [54]. He Zhengyan et al. [55] studied the hydrodynamics of weathered crust elution-deposited rare earth ores, and found that ore particle size is the main factor affecting ore permeability. The smaller the particle size is, the smaller the porosity is, and the poorer the permeability is. Diameter has a greater effect on permeability than porosity. Zhou Fang et al. [56] discussed the effect of the initial moisture content of the ore on improving the leaching process of weathered crust elution-deposited rare earth ores, especially impermeable rare earth ores, and found that rare earth has better mass transfer properties than aluminum.

At present, the permeation aid mainly studies the effect of ammonium salt leaching agents or ammonium salt leaching agents under the action of permeation enhancers. Luo Xianping et al. [57] investigated the effect of the fulvic acid on the leaching process of weathered crust elution-deposited rare earth ores using ammonium sulfate as lixiviant. The results showed that with the addition of fulvic acid at a concentration of 0.1 wt%, the leaching extraction of rare earth elements increased by 8.38% and the ammonium sulfate concentration decreased by 25%. The fulvic acid can enhance the leaching process effectively. Zou Hualiang et al. [58] found that when ammonium acetate, ammonium tartrate, and ammonium citrate were the three organic acid ammonium salts used as leaching agents, when their concentration was greater than 0.7 wt%, the permeability coefficient decreased with the increase in concentration and ammonium acetate. The maximum permeability coefficient was 2.92, the maximum permeability coefficient of ammonium tartrate was 1.91, and the maximum permeability coefficient of ammonium citrate was 2.70. This is because ammonium citrate and ammonium tartrate will react with rare earths to form precipitates, which block the pores and reduce the penetration effect.

In order to improve the permeability and mass transfer performance of the traditional ammonium salt leaching technology, Zhang Yongbing et al. [59] used the surfactant sodium dodecyl sulfate (SDS) to improve the seepage effect of weathered crust elution-

deposited rare earth ores and found that by adding 0.04 wt% SDS, the leaching rate of rare earth increased by about 5%. Fang Zhou et al. [60] added cetyl trimethyl ammonium bromide (CTAB) and dodecyl trimethyl bromide to $(NH_4)_2SO_4$ or NH_4Cl leaching agents. Ammonium chloride (DTAB), sodium dodecyl sulfate (SDS), sodium oleate, oleic acid, and five other surfactants were found to improve the permeability of weathered crust elution-deposited rare earth ores, improve leaching efficiency, and inhibit aluminum leaching. It shows that these five surfactants can promote the leaching of weathered crust elution-deposited rare earth ores.

Sesbania gum is a natural polymer compound, mainly composed of non-ionic galactomannan gum, which contains a large number of free hydroxyl groups and has a good affinity for water. Glue can significantly improve its permeability. In addition, sesbania gum is non-toxic and harmless. Tian Jun et al. [61] used $(NH_4)_2SO_4$ as the leaching agent and sesbania gum as the permeation aid. They found that sesbania gum is conducive to the seepage of the leachate and can improve the leaching efficiency of rare earth. Tian Jun et al. [62] also studied the permeation-promoting properties of the modified carboxylate gum and found that it enhanced the permeability of the leaching agent, enhanced the leaching efficiency of rare earth, and reduced the consumption of leaching agent.

For weathered crust elution-deposited rare earth ores with high clay mineral content and fine particles, the leaching agent solution penetrates slowly into the ore body, and the leaching cycle is long. Due to the water absorption and swelling of the clay minerals, it is extremely easy for landslides to occur in the in situ leaching process, resulting in the loss of leaching agent and rare earth. Therefore, the research on the mechanism of swelling inhibition and infiltration promotion should be strengthened at the same time, and the development of swelling inhibition leaching agents and infiltration promotion leaching agents suitable for in situ leaching is of great significance for the safe and efficient exploitation of weathered crust elution-deposited rare earth ores.

4. Prospect

After years of research and development of weathered crust elution-deposited rare earth ores, researchers have made great efforts in leaching technology, compound ammonium salt leaching agents, ammonia-free or low-ammonia leaching agents, impurity inhibition leaching agents, and swelling inhibition leaching agents and achievements have been obtained which have laid a good foundation for the safe and efficient exploitation of rare earth ores, but there are still deficiencies in the basic theory and engineering applications that need to be further improved, mainly as follows:

(1) Although there are many kinds of leaching technologies for weathered crust elution-deposited rare earth ores, each has its own advantages. Appropriate leaching technologies should be selected for rare earth ores with different ore body structures to improve the leaching rate and recovery rate of rare earth and reduce environmental pollution. At the same time, it is necessary to strengthen the research on the metallogenic theory of weathered crust elution-deposited rare earth ores, improve the prospecting ability of rare earth ores, develop new leaching technology, and enrich the geochemistry of rare earth elements.

(2) In order to eliminate or reduce the environmental pollution caused by ammonia–nitrogen, it is necessary to strengthen the development of ammonia-free or low-ammonia leaching agents (for example, magnesium salt leaching agents and metabolites of biosynthetic citrate) and leaching technologies (for example, extraction technology and bioleaching technology) and further study impurity inhibition, swelling inhibition, and percolation promotion mechanisms and develop green, safe, and efficient impurity inhibition leaching agents, swelling inhibition leaching agents, or infiltration-promotion leaching agents to improve the recovery rate of rare earth, enhance the safety of rare earth ores, shorten the leaching cycle, and provide green and safe weathered crust elution-deposited rare earth ores.

(3) When ammonium salt is used as a leaching agent, there will be ammonium salt residue in the tailings after in situ leaching, and its slow release will have an impact on the water system of the mining area. Therefore, it is necessary to conduct an environmental impact assessment on the residual ammonium salt in tailings, carry out studies on the occurrence states and distribution pattern of residual ammonium salt in ore body, explore the mechanism of in situ nitrogen removal, and develop the corresponding nitrogen removal technology and leaching technology.

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