Review

Review on the Development and Utilization of Ionic Rare Earth Ore

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Abstract: Rare earth, with the reputation of "industrial vitamins", has become a strategic key metal for industrial powers with increasingly significant industrial application value. As a unique rare earth resource, ionic rare earth ore (IREO) has the outstanding advantages of complete composition, rich resource reserves, low radioactivity, and high comprehensive utilization value. IREO is the main source of medium and heavy rare earth raw materials, which are in great demand all over the world. Since the discovery of IREO, it has attracted extensive attention. Scientists in China and the around world have carried out a lot of research and practical work and achieved a series of important breakthroughs. This paper introduces the discovery process, metallogenic causes, deposit characteristics, and the prospecting research progress of IREO, so as to deepen the understanding of the global distribution of ionic rare earth resources and the prospecting direction of ionic rare earth deposits. The leaching principle of IREO, the innovation of leaching process, the influencing factors and technological development of in situ leaching process, and the technical adaptability of in situ leaching process are reviewed. The development of leachate purification and rare earth extraction technology is summarized. We aim to provide guidance for the industrial development of IREO through the above review analysis. Additionally, the problems existing in the development of IREO are pointed out from the aspects of technology, economy, and the environment. Ultimately, a series of suggestions are put forward, such as the development of ammonium free extraction technology in the whole exploitation process of in situ leaching and leachate purification and rare earth precipitation, research on enhancing of seepage and mass transfer process, and research on the development of new technologies for impurity removal of leachate and extraction of rare earth, so as to promote the development of green and efficient exploitation new technologies and sustainable development of ionic rare earth ore.

Keywords: ionic rare earth ore; resource characteristics; leaching; impurity removal; rare earth extraction; development direction

1. Introduction

Rare earth elements are necessary raw materials for modern industry and important strategic resources. They are widely used in metallurgy, petrochemical industry, special glass, precision ceramics, catalysis, high-temperature superconductors, and photoelectric and magnetic new materials of photoelectromagnetic and other fields, giving them the reputation of "industrial vitamins" [1,2]. The world is rich in rare earth reserves. According

to the data of the U.S. Geological Survey, the global rare earth resource reserves are as high as 120 million tons. In nature, rare earth elements mainly exist in two forms: mineral rare earth and ion adsorption rare earth. The former occupies an absolute reserve advantage and is distributed on major continents in the world [3]. However, mineral rare earth ores are mainly light rare earth resources. Ionic rare earth ores are complete distribution and are rich in medium and heavy rare earth elements, which have become the main source of medium and heavy rare earth elements in the world [4].

Since their discovery, ionic rare earth ores have attracted extensive attention, provided urgently needed medium and heavy rare earth resources across the world, driven the rapid development of the rare earth industry and new materials, enriched the theories of rare earth geochemistry and hydrometallurgy, and deeply promoted the technological innovation of human science [5,6]. Ionic rare earth ores were first discovered in China and are the dominant mineral resource in China [7]. At present, China is the only country in the world that can supply all 17 rare earth elements, which makes China bear a heavy supply burden. China supplies more than 70% of the market demand with less than 40% of the global reserves [6].

Different from mineral rare earths, granite or volcanic rocks are gradually weathered under supergene and historical geological processes, and a thicker topsoil and weathered layer are formed. In this process, the fluorocarbon minerals and aluminosilicate minerals containing rare earth in parent rocks such as granite and volcanic rocks decompose and release rare earth elements [8,9]. The clay minerals formed by weathering have strong adsorption and cation exchange capacity on the surface or between layers. The rare earth elements released from the parent rock migrate under the leaching of rainwater, and adsorb in ionic phases on the surface of clay minerals such as kaolinite, montmorillonite, and illite in the weathering layer, and eventually enrich into ionic rare earth deposits [10].

In ionic rare earth deposits, the rare earth adsorbed on the surface of clay minerals has strong stability, which is difficult to elute with neutral solvents such as water to make it migrate again. In view of the occurrence form of rare earth elements, it is difficult to recover them by physical beneficiation methods such as flotation and magnetic separation. However, with the electrolyte solution, cations can desorb rare earth elements through ion interaction [11]. Long term practice has proven that sodium salt and ammonium salt have excellent ability to exchange rare earth ions. According to the characteristics of ionic rare earth ore, Chinese scientists put forward the rare earth extracting method of leaching, which has been successfully applied to production practice. In the leaching process, a large number of metal ions such as aluminum and iron are desorbed into the rare earth leachate, resulting in the complexity of the components of the solution. The existence of impurity ions has a significant effect on the precipitation, crystallization, or extraction of rare earth ions, which is not conducive to the recovery of rare earth elements. After long-term production practice, the leaching and extraction of ionic rare earth has formed a complete technical solution.

At present, among the proven ionic rare earth resources in the world, China has the most abundant reserves. The mineralized area of the five provinces of Nanling alone is only 100,000 square kilometers, of which the southern Jiangxi region accounts for the largest share. In recent years, with the shortage of rare earth resources in the international market, many countries in the world have carried out ionic rare earth ore prospecting in their own countries. Furthermore, scientists' enthusiasm for the research of ionic rare earth ores is also rising day by day, which promotes the efficient exploitation and utilization of rare earth resources. This paper reviews the exploitation process of ionic rare earth resources, and summarizes the main achievements and progress of the research on the exploitation technology of ionic rare earth ores, including the study of ionic rare earth ore deposit, prospecting, leaching technology, leachate purification, and rare earth extraction. At the same time, the main problems existing in the exploitation of ionic rare earth resources are pointed out, and the suggested research direction is given. The purpose is to promote green

and efficient technology development and resource sustainable exploitation of ionic rare earth ores.

2. Overview of Ionic Rare Earth Ore Resources

2.1. Discovery and Naming of Ionic Rare Earth Ore

In the 1960s, it was discovered that rare earth elements can significantly improve the properties of materials. At that time, China found abundant rare earth resources in the Bayan Obo mine area in Baotou city, Inner Mongolia Autonomous Region, but the rare earth resources in the mine are mainly medium and light rare earth, which cannot provide heavy rare earth raw materials in urgent need. In the mid-to-late 1960s, Chinese scientists detected a high content of rare earth elements in the "Clay-like" weathering crust in Ganzhou City, Jiangxi Province, especially Y, Gd, Dy, Er, Yb, and other heavy rare earth elements, which was the first time the world came into contact with "ionic rare earth ore" [12]. Scientists used the traditional gravity beneficiation method to separate the samples. However, the content of rare earth elements in the obtained heavy sand is only a few grams/ton, which is far from meeting the requirements of industrial application. Hence, the value of ionic rare earth deposits was once denied.

In the late 1960s, similar rare earth deposits were found in many places during the general prospecting in southern Jiangxi Province, China. In 1970, Ganzhou Institute of Nonferrous Metallurgy provided technical support to the geological survey unit and established the joint experimental group. However, the enrichment of rare earth elements could not be achieved effectively, even with the exhaustion of traditional beneficiation methods. Unexpectedly, it was noticed that there were discrepancies in the total amount of rare earth elements in raw ores and products, and analysis speculated that some of the rare earth elements infiltrated the electrolyte solution. Under the new idea, this conjecture was soon proven by experiments. Through the study of rock and ore identification, it was determined that rare earth in this type of deposit exists in the form of "ion adsorption". In-depth studies show that the rare earth elements mainly exist in the form of ion adsorption on the surface of clay minerals such as kaolinite in the weathering crust of granite, and can be recovered by active ion exchange into the solution. Thus, ionic rare earth ores have been discovered in the world, and the existence of ion-phase ores has been confirmed for the first time, deepening people's understanding of the occurrence form of minerals.

The research results affirmed the industrial application value of this type of rare earth deposit, and a detailed work of geological exploration and prospecting was carried out in China in the early 1970s, which unearthed the prospecting characteristics—low hills with sparse surface vegetation and exposed medium-coarse sand grains. A large ionic heavy rare earth deposit has been explored for the first time in southern Jiangxi [12]. In 1971, the resources were defined as "ionic phase" ores according to the occurrence characteristics of rare earth. This type of rare earth deposit is named "Weathering Crust Leaching Rare Earth Deposit" according to the genesis of the deposit and "weathering crust ion adsorption rare earth deposit" according to the occurrence characteristics of the deposit, and the abbreviation of "ionic rare earth deposit" is still used today.

2.2. Formation Conditions of Ionic Rare Earth Ore

The discovery of ion-type rare earth introduced a new "ionic phase mineral", and also provided a new raw material for the industrial development of the world. Due to its high industrial value, extensive research and development have been performed. At present, a consensus has been reached in the academic community on the reason behind the ore-forming of ionic rare earth, which is that granite or volcanic rocks with high rare earth content produced by historical geological processes evolved clay minerals, and the released rare earth ions are absorbed on the clay minerals by rain leaching and migration. Therefore, the following four important conditions must be met for the mineralization of ionic rare earth ore [11–15]. First of all, there are many rare earth minerals in the parent rock, as well the high content of REE to provide sufficient resources during weathering and mineraliza-

tion, which is the endogenetic material basis of ionic rare earth ore mineralization. Secondly, the occurrence form of rare earth in the parent rock must mainly be the minerals containing rare earth that are easily weathered. The weathering of medium rare earth minerals in parent rocks is an important prerequisite for the release of rare earth elements. In general, the main sources of rare earth elements in ionic rare earth ores are rare earth fluorocarbons such as bastnaesite, novel calcium yttrium ore and yttrium-cerium fluorocarbon ore, and silicate minerals containing rare earth such as epinite, sphene, and garnet [8,9,15]. In addition, there is a positive europium anomaly in plagioclase, and granodiorite and quartz diorite with high plagioclase content easily produce a high Eu weathering crust. Thirdly, the parent rock rich in weathering rare earth minerals must be located in the warm and humid subtropical region, which is the key factor for the exogenesis of ionic rare earth minerals. Fourth, the pH value formed by surface water infiltration and leaching is the determining factor controlling REE fractionation enrichment and orebody location. In general, ionic rare earth ore mineralization is mainly controlled by rock conditions, tectonic conditions, and supergene conditions.

The geological background of the geological bodies in the mining area has a significant impact on the mineralization of ionic rare earth deposits [16]. The geological bodies forming industrial deposits of ionic rare earth ores in China are closely related to three geological movements: Yanshanian, Himalayanian, and Caledonian, of which the most were formed during the Yanshanian movement. Taking the ionic rare earth deposit in Xunwu County, Jiangxi Province, China, as an example [17], the geological body in this area takes the Mesoproterozoic Neoproterozoic metamorphic rock stratum as the basement, and the Cretaceous and Quaternary strata as the caprock. The metamorphic rock stratum is the Nanhua Cambrian, the metamorphic degree of the early Cambrian is shallow, and the metamorphic process of Nanhua Sinian stratum is very uneven. The lithologic combination of medium and deep metamorphic rocks is called the Xunwu formation, which is schist, granulite, and gneiss mixed with residual feldspathic quartz sandstone. The geological body in this area has the characteristics of multi-stage activity, and the magmatic activity in this area is frequent, mainly including the Caledonian, the Hercynian, and the Yanshanian rock masses. The Caledonian rock mass mainly includes the white-faced rock mass and the Qishan independent rock mass, the Hercynian rock mass mainly includes the Guikeng rock mass, and the Yanshan rock mass mainly includes the Sanbiao rock mass, the hat top rock mass, the shangjia independent rock mass, the Shuitou rock mass, hat top rock mass and the Tuling rock mass. The Yanshanian period has the largest number of rock bodies, mainly acid and medium acid granite. The lithology includes the granulite, the schist, and the gneiss. Among them, mica schist has the highest content of rare earth elements, which is the most favorable metallogenic parent rock and belongs to light rare earth enrichment type parent rock.

The mineralization of rare earth elements in rocks belongs to a long time period, and generally the content of rare earth elements in weathered crusts tends to increase gradually with a later time of formation of the geological bodies. The process of mineralization of ionic rare earth ore geobodies is influenced by differences in the acidity of mineralization in combination with alkali metals and differences in calcium-controlled ore [14]. The mineralization of the rare earth element yttrium requires greater acidity than that of the rare earth element cerium. During metallogenesis, the rare earth element yttrium is often closely related to the sodic mineral composition. The calcareous content required for mineralization of yttrium group rare earth elements formed in the late magmatic evolution is lower than that of cerium group rare earth elements. Moreover, the type of ionic rare earth mineralization is closely associated with the kind and content of rock-forming minerals and rare earth mineral ores in the rock mass, and there is also a relationship with the scale of the rock mass.

In addition, geological tectonic activity is also very important for the influence of ionic rare earth mineralization [15,18,19]. Weathering has a significant correlation with tectonic activity and climate change. The relatively stable and intermittent rise of the Earth's

crust or the slow rise of the fractured block makes the groundwater fall slowly, which effectively prolongs the weathering time. During the mineralization of ionic rare earth deposits, the crustal rise rate and denudation rate of neotectonic activity are in balance, which is the root condition for weathering crust development and ore body preservation. Therefore, ionic rare earth deposits must have been formed during the long geological history, but the rate of crustal uplift was too high or too low to preserve the formed ionic rare earth depositions. Alternatively, the rare earth elements in the conserved ones were cemented again and difficult to be leached, and as such are no longer ionic deposits, such as the ancient weathering crust rare earth deposits in the basalt distribution area of Emei Mountain in southwest China [15].

The formation process of ionic rare earth deposits needs to go through two stages of endogenesis and exogenesis [20,21]; the former stage provides the material requirements for the onset of ionic rare earth ore, while the latter stage is directly responsible for the change of rock to weathering crust and the transformation process of mineral phase rare earths to ionic phase rare earths. Exogenesis provides sufficient weathering for the geological body, which is strongly related to the climatic environment and topography of the mine site. Climatically, the mining area needs to be tropical or subtropical, and the granite body should be exposed to long-term weathering and denudation by sun and rain [15]. In this respect, the dense vegetation in tropical and subtropical climates provides ample organic accelerates the chemical weathering of the geological body and makes it easier to form weathering crusts of higher thickness. In particular, the pH value of water has an effect on the migration and enrichment of rare earth elements. Rare earth elements migrate as hydrated cations in aqueous solutions containing organic acids, carbonic acid, etc. This is an important guarantee that rare earth ores can be enriched to form deposits. In terms of topography, most of the ionic rare earth mines are located in hilly areas with altitudes below 500 m and height difference of 60–250 m. The topography of the mine area is characterized by gentle low hills and water system development. However, small local undulations in the landscape are more favorable to mineralization. Chinese scholars Chi summarize the topography as ridges are more favorable to ionic rare earth ore formation than mountain ridges, mountain tops as compared to mountainsides, and gentle slopes as compared to steep slopes [13,14].

2.3. Distribution and Prospecting Progress of Ionic Rare Earth Resources

According to the metallogenic conditions of ionic rare earth ores, scholars summarized and found that the climatic conditions meeting the metallogenic conditions are mainly distributed in the south of 28° N, especially in the south of 26° N. Taking the distribution of ionic rare earth ores in China as an example, ionic rare earth ores are mainly distributed in Jiangxi, Fujian, Guangdong, Yunnan, Hunan, Guangxi, Zhejiang, and other provinces. Most of these deposits are distributed in the area of 22~29° N and 106°30′~110°40′ E. The density is highest between latitude 24~26° N [11–15].

In the context of the global shortage of rare earth resources, many countries have also increased the prospecting research of ionic rare earth ores [22,23]. At present, ionic rare earth deposits have been found in many countries in Southeast Asia. For example, several ionic rare earth deposits have been found in the border areas between Viet Nam and China, and ionic rare earth deposits rich in medium and heavy rare earths have been found in many states of Malaysia. Several ionic rare earth mines have also been found in Kachin state, Myanmar, and some mines are in the production stage. In addition, the discovery of ionic rare earth ores has also been reported in Thailand, Laos, the Philippines, the United States, Madagascar, and other countries or regions. Among them, the proven rare earth oxide reserves in Madagascar are 39,092 t, with an average content of 975×10^{-6}, the inferred treatment is up to 384,552 t, and the average content is 894×10^{-6}. The Rare earth Office of The Ministry of Industry and Information Technology of China has carried out an investigation on rare earth in Brazil and Chile. The proven rare earth resources are

75,600 t, and the average grade of ionic rare earth is as high as 0.3%. The distribution of global weathering crust, ionic rare earth deposits, and related projects is shown in Figure 1.
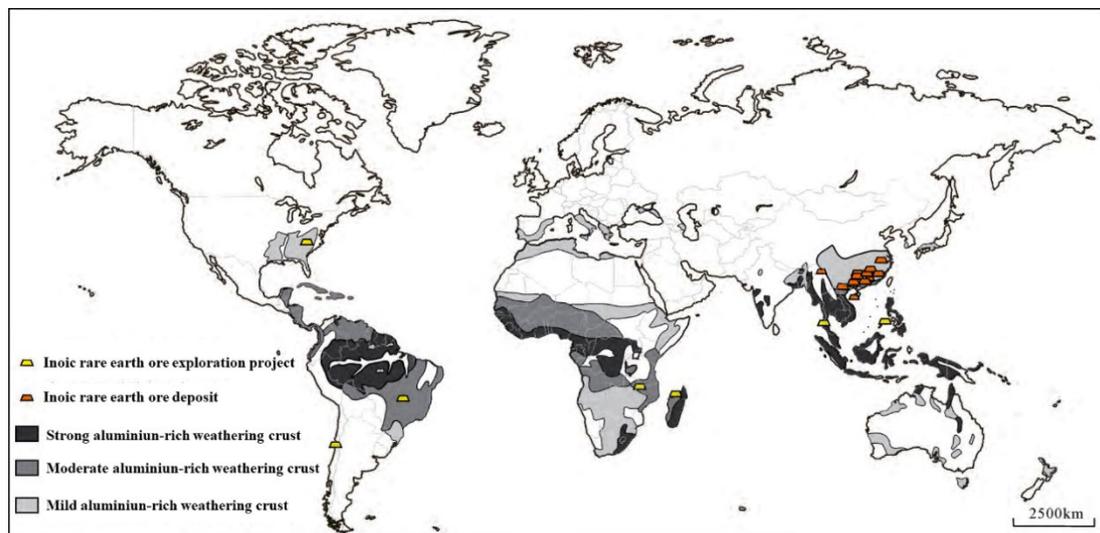

Figure 1. Distribution of global weathering crust, ionic rare earth deposits, and related projects [15].

Zhao et al. [15] compared various ionic rare earth deposits according to the relevant literature of ionic rare earth ores, as shown in Table 1, and discussed the influence of climate on the mineralization of ionic rare earth ores. In South China, which has a subtropical climate, the annual average temperature is 16~22 °C, the annual average precipitation is 1000~1800 mm, the thickness of the weathering crust is mostly 15~35 m, and the content of rare earth can reach thousands of ppm ($1000n \times 10^{-6}$). There are light and heavy rare earth deposits, mainly medium and heavy rare earth deposits. South Carolina, which also has a subtropical climate, has an annual average temperature of 17 °C and an annual average precipitation of 1150 mm. The thickness of the weathered crust in the area is between 10 m and 20 m, and the content of rare earth is 93×10^{-6}~757×10^{-6}. However, Thailand and other Southeast Asian countries have a tropical climate, with an annual average temperature of more than 25 °C and an annual average precipitation of more than 2000 mm concentrated in the rainy season, and the thickness of the weathering crust is usually only 1~10 m. There are mainly light rare earth deposits. In the Philippines, the thickness of the weathering crust is less than 5 m, and the rare earth content is only tens of ppm, even lower than that in bedrock. The thickness of the weathering crust and the content of rare earth elements are higher in subtropical areas. In the tropical climate, the weathering alteration coefficient of the weathering crust is significantly higher than that in the subtropical climate, and the rock weathering is more thorough. The strong weathering means that rare earth elements are more likely to migrate and lose with the surface water, which is not conducive to rare earth mineralization.

Table 1. Information of ionic rare earth deposits in various regions.

Country	Area	Climate	Precipitation (mm)	Rock Type	Mineral Character	REE ($\times 10^{-6}$)	Thickness of Weathering Crust (m)	Crust of WeatheringREE ($\times 10^{-6}$)	IREE (%)	Literatures
United States	South Carolina	Subtropics	1150	Medium-coarse-fine-grained biotite hornblende granite	Monazite-zircon-sphene-epanite-apatite-bastnaesite	123~451	10~20	93~757	3~77	[24]
Myanmar	Tanintharyi	Tropic	3000	Biotite granite-binary mica granite-garnet granite	Epinde-sphene-apatite zircon; Apatite-zircon-garnet-monazite-yttrium-rare earth fluorocarbons	130~328	1.5~5	30~364	1.5~59	[25]
Viet Nam	Nui Phao	Tropic	1800	/	/	155	10	/	18~67	[22]
Thailand	Phuket Island	Tropic	2200	Biotite granite	Rare earth fluorocarbon minerals-epinite-sphene-apatite-zircon	592	2~12	174~1084	34~85	[26]
Thailand	North Thai granitic pluton	Tropic	1200	Black cloud hornblende granodiorite-biotite granite-binary mica granite	Epinite-sphene-monazite-xenotime-apatite-zircon	152~450	4~7	53~726	0.1~61	[27]
Thailand	Western Province granitic pluton	Tropic	1600	Biotite granite-binary mica granite	Epinite-sphene-monazite-xenotime-apatite-zircon-rare earth fluorocarbonate-thorium	171~634	3~12	85~1430	0.4~94	[27]
Laos	Attapu, Boneng, Nape, Xaisomboum	Tropic	1834	Black cloud hornblende granodiorite-biotite granite-porphyry	Apatite-zircon-monazite-xenotime-epinite-sphene-thorium-garnet	36~339	1~10	38~817	14~73	[28]
Philippines	Palawan	Tropic	2200	Biotite granodiorite-biotite granite	Allanite-monazite-xenotime-zircon-apatite	77~243	1~5	26~94	53~74	[29]
Indonesia	Sulawesi	Tropic	2500	Mamasa and palu granite	Sphene-apatite-zircon-epinite	204~285	1~6	81~533		[30]
Madagascar	Antsirabe	Tropic	1200	Tonalite	Allanite-yttrite-monazite-yttrite fluoride	299~363	2~3	286~2194		[31]

2.4. Occurrence Form of Ionic Rare Earth

The occurrence state of rare earth elements in the weathering crust directly reflects the geochemical behavior of rare earth elements in the process of migration, enrichment, and differentiation. It is of great significance to the study of the genesis of ion adsorption rare earth ores, and it is also a problem that must be paid attention to in the development and utilization of such deposits. At present, the chemical phase analysis method (continuous chemical extraction method) is widely used in the research on the occurrence state of rare earth elements in weathered crust [32–35]. Based on the difference of solubility and dissolution rate of various minerals or compounds in chemical solvents, the content of rare earth elements in the form of various minerals or compounds in the sample is determined by selective dissolution and leaching. Substantial research shows that there are four forms of ionic rare earth deposits: ion adsorption phase, colloidal dispersion phase, independent mineral phase, and lattice impurity phase. They can be divided into exchangeable adsorptive state, specific adsorption state, colloid adsorbed state, gel state, supergene mineral state, residual mineral state, homogeneous phase, and internal submersible crystal state. Statistics of different ionic rare earth ores show that exchangeable adsorbed rare earth accounts for about 80%–96% of the total rare earth [12–14].

After long-term weathering, feldspar, mica, and other minerals in the rock are gradually transformed into clay minerals such as kaolinite, illite, halloysite, and montmorillonite [36]. Chi et al. [37] showed that rare earth was adsorbed on the surface of halloysite, kaolinite, and other clay minerals in the form of hydrated or hydroxyl hydrated ions by photoelectron spectroscopy (XPS). In addition, the adsorption capacity of clay minerals for rare earth ions is different, which is related to the specific surface area, structure, and number of active center sites of clay minerals. The adsorption capacity of clay minerals to rare earth elements in the weathering crust is montmorillonite, halloysite, illite, and kaolinite, from strong to weak. For different cations, the adsorption capacity of clay minerals is [37] RE^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, and Na^+, from strong to weak. According to the difference of rare earth ion activity, the adsorption intensity of clay minerals to each rare earth ion is Sc^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Y^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}, from strong to weak.

Synchrotron radiation studies in recent years have shown that rare earth elements also exist in the form of outer-sphere or inner-sphere hydrated complexes. Yamaguchi et al. [38] studied the occurrence state of yttrium in granite weathering crust sample in Japan through X-ray absorption fine structure spectroscopy, and proposed that yttrium is mainly adsorbed on the surface of clay minerals in the form of outer-sphere hydrated free ions complexes. Mukai et al. [39] proposed that nearly half of the rare earth elements in the single clay mineral particles in the granite weathering crust may exist in the form of inner-sphere hydrated complexes by methods of SEM, TEM, Nano-SIMS, and desorption test. Hiroki Mukai et al. [40] studied the micro adsorption of rare earth on the clay surface through (STEM)-EDS and Nano-SIMS, and found that illite is an important reason for the enrichment and mineralization of rare earth in granite weathering crust. In view of the spatial structure of clay minerals, rare earth elements will also form inner-sphere complexes on mineral particles, and the complexation of the heavy rare earth inner-sphere with small ion radius is stronger than that of light rare earth elements, which is not conducive to cation exchange desorption of rare earth elements. Borst et al. [41] used synchrotron radiation X-ray absorption spectrum and comparatively studied the occurrence states of Y and Nd (Y represents heavy rare earth and Nd represents light rare earth) on the surface of clay minerals in the weathering profile of granite in the Zhaibei mining area in Jiangxi Province and the weathering profile of ambohimirahavavy alkaline complex in northern Madagascar. It is considered that the occurrence of forms of rare earth elements in clay minerals include not only the outer-sphere complex form, but also the inner-sphere complex form combined with Al-O and Si-O bonds on the surface of clay minerals or with the edge of clay minerals. The distribution and combination modes of heavy rare earth elements and light rare earth elements represented by Y and Nd in clay minerals are detected by synchrotron radiation

X-ray absorption spectrometry. Through the qualitative comparison of K edge data between them, it is considered that Y element is likely to exist on the surface of kaolinite in the form of 8-coordinated or 9-coordinated outer-sphere hydrated complex, as shown in Figure 2.
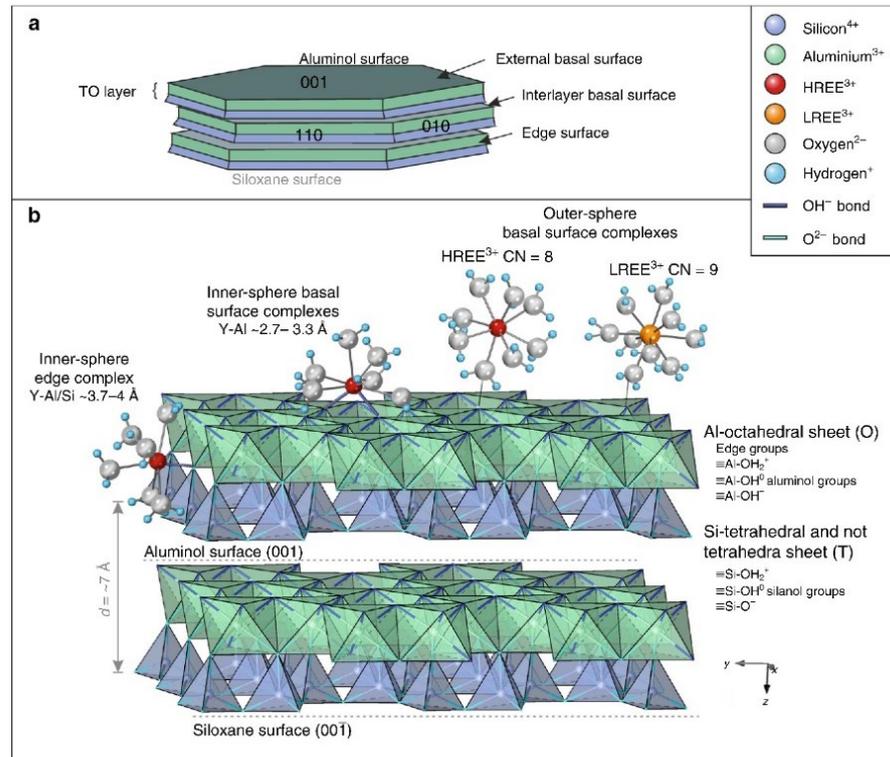

Figure 2. Occurrence characteristics of rare earth elements on the surface of kaolinite [41].

Quantum chemical calculation is widely used in the study of the occurrence form of ionic rare earth with the progress of computer. According to the research of relevant scholars [42], the d orbital of rare earth element in rare earth ion hydration ion or rare earth hydroxyl hydration ion can obtain electrons from the 2p orbital of O atom on the surface of clay minerals which are adsorbed on the surface of clay minerals by generating RE-O chemical bonds. In many rare earth element hydrates, the inner layer adsorption stability of hydrated rare earth ions is lower than that of monohydroxy hydrated rare earth ions, and the inner layer adsorption stability of dihydroxy hydrated rare earth ions is the strongest. In addition, rare earth hydrate can be adsorbed on the outer layer of aluminum hydroxyl surface and silicon oxygen surface of kaolinite through a hydrogen bond. Due to the repulsion of H atoms on the hydroxyl group of aluminum to rare earth hydrate, the outer layer adsorption of rare earth hydrate on silicon oxygen surface is more stable.

Generally speaking, scholars have carried out a large number of studies on the metallogenic mechanism of ionic rare earth ores and achieved many research results, especially in the aspects of parent rock properties, metallogenic conditions, geological characteristics and deposit characteristics, which have improved the cognition of the properties of ionic rare earth deposits and promoted the exploration and development of ionic rare earth deposits. However, the theory of metallogenic mechanism still needs to be supplemented and improved. The weathering path of minerals other than feldspar and mica, the difference of weathering rate of different minerals, the deep mechanism of mineral weathering evolution, the mass balance and migration law of the weathering process, the difference mechanism of dissolved element adsorption characteristics, the micro-occurrence characteristics, and differences of elements still need to be systematically studied.

2.5. Characteristics of Ionic Rare Earth Deposits

In the strong weathering environment, clay minerals are produced by the weathering of original rocks such as granite and volcanic rock. In addition, 20%~50% of quartz and feldspar are used as skeleton particles. The content of clay minerals in the raw ore [12] is halloysite (25%~50%), illite (5%~20%), kaolinite (5%~10%), and montmorillonite (<1%). Due to the different weathering degree of the original rock, the mineral composition of each horizontal position in the weathering crust is different. Showing a certain layered structure on the section, which can generally be divided into topsoil layer, weathered layer, semi-weathered layer, and bedrock [12–15]. The content of rare earth elements in the completely weathered layer is the highest.

The mineral species and content, structural characteristics, and rare earth occurrence location of ore body in the weathering crust are affected by the chemical composition of the original rock [15], as shown in Figure 3. Granite weathering crust is mostly sandy, with high content of quartz, feldspar, and other debris, coarse particle size, poor adhesion, and strong water permeability. Rare earth ions are easy to migrate downward, and often occur in the lower part of the completely weathered layer. On the contrary, the weathering crust of volcanic rock and shallow metamorphic tuff-tuffaceous sandstones is mostly soil-like structure, with less content of clastic particles such as quartz and feldspar, fine particle size, and poor water permeability. Rare earth ions often occur in the middle and upper part of the completely weathered layer. According to the relationship between rare earth grade and ore body depth, ionic rare earth ores can be divided into plutonic, hypabyssal and extrusive rock, as shown in Figure 4. According to the relationship between ionic rare earth deposits and primary rare earth deposits and the distribution characteristics of rare earth elements, ionic rare earth deposits can be divided into the following different deposit types [14], as shown in Table 2.

Figure 3. Structural characteristics of different weathering crusts: (**a**) Weathering crust of Zudong muscovite alkali feldspar granite in Jiangxi Province, (**b**) Weathering crust of Liutang rhyolite in Guangxi Province, and (**c**) Weathered crust of Getengzui metamorphic tuff in Jiangxi Province [15].
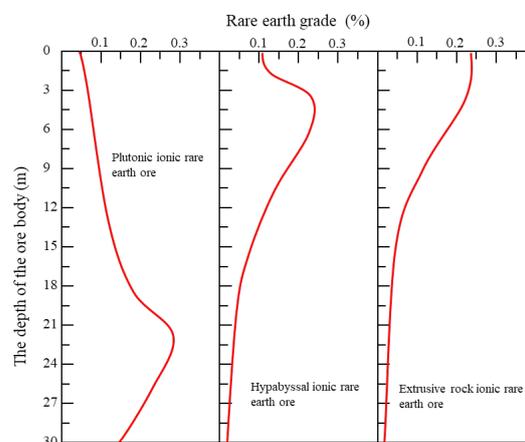

Figure 4. Ionic rare earth ore types according to the relationship between rare earth grade and ore body depth.

Table 2. Classification of ionic rare earth deposits in China.

Weathering Crust Type	Deposit Type	Parent Rock Type	Main Rare Earth Minerals in Parent Rock	Approximate Proportion of Ionic Phase Rare Earth in the Deposit/%
Plutonic weathering crust	Heavy rare earth type of yttrium rich	Fine grained muscovite granite	Fluorocarbon calcium yttrium ore	88
	Yttrium rich heavy rare earth type	Medium fine grained biotite granite	Fluorocarbon calcium yttrium ore	80
	Heavy rare earth type of medium yttrium content	Medium fine grained biotite granite	Fluorocarbon calcium yttrium ore	78
	Light rare earth type of europium rich and medium yttrium content	Medium fine grained biotite granite	Bastnaesite	85
	Light rare earth type of medium yttrium and low europium content	Medium fine grained biotite granite	Bastnaesite	80
	Non selective distribution type	Medium fine grained binary-mica granite	Fluorocarbon calcium yttrium ore	90
	Light rare earth type of cerium rich	Fine grained biotite granite	Bastnaesite	83
Hypabyssal weathering crust	Light rare earth type of lanthanum and europium rich	Granite porphyry	Bastnaesite	90
	Non selective distribution type	Lamprophyre	Bastnaesite	85
Extrusive rock weathering crust	Light rare earth type of lanthanum and europium rich	Rhyolite	Bastnaesite	92
	Light rare earth type of lanthanum and europium rich	Tuff	Bastnaesite	97

The grade of ionic rare earth deposits is generally low, which is mainly concentrated in fine grained clay minerals in the completely weathered layer. However, due to the tiny property differences in different rare earth elements, there will be significant differentiation in the process of migration and adsorption of rare earth elements in the weathering crust. This means that the distribution of rare earth elements in different depths of the weathering crust is different [13,14], which is also significantly different from that in the original rock. The relevant results show that the distribution of light rare earth decreases gradually with the increase in ore body depth, while the distribution of heavy rare earth increases with the deepening of ore body depth. It may be caused by the great interaction energy between rare earth ions and clay minerals; the greater the interaction, the easier it is to be adsorbed. It can be seen from Section 2.4 that the adsorption capacity of clay minerals for light rare earths is greater than that of heavy rare earths. In addition, under the influence of a large amount of organic acids and a small amount of atmospheric dissolved CO_2, rare earth elements also migrate in the form of carbonate complex ($REECO_3^+$) and bicarbonate complex ($REEHCO_3^{2+}$). As the stability of heavy rare earth carbonate complex ($REECO_3^+$) is higher than that of light rare earth [43], it is easier to move with the infiltration solution. Therefore, compared with light rare earth elements, heavy rare earth elements have stronger migration ability. The continuous water–rock reaction increases the pH of the infiltration solution, and more heavy rare earths are adsorbed on the surface of clay minerals in the lower part of the weathering crust, resulting in obvious rare earth differentiation. Therefore, in the long weathering environment and weak acid medium, the substitution reaction and migration variation between rare earths will occur. As a result, the heavy rare earths with poor adsorption capacity migrate down and accumulate in the deep weathering residual clay minerals, while the content of light rare earths is large in the upper layer of the ore body. The specific manifestation is that the weathered materials at the foot of the mountain are more rich in heavy rare earths than those at the ridge. However, if the weathering degree is very strong, light and heavy rare earths will tend to be enriched in the same layer, that is, they will all be enriched in the lower part of the weathering layer.

$$4Ce^{3+} + O_2 + 4H_2O + 8H^+ = 4Ce(OH)_4 \downarrow \tag{1}$$

$$Ce(OH)_4 = CeO_2 \downarrow + 2H_2O \tag{2}$$

Different from other rare earth elements, redox has a great influence on the enrichment and differentiation of variable valence rare earth element Ce by the redox conditions of weathered crust [14]. In the process of rock weathering, the trivalent cerium ions dissociated from the mineral lattice are prone to redox reaction to form tetravalent cerium ions, which exist as periclase or insoluble colloidal phase $Ce(OH)_4$. The specific process is shown in Equations (1) and (2). This leads to the enrichment of Cerium in the upper part of the weathering crust section, which is called cerium positive anomaly. The lower part shows cerium loss, which is called cerium negative anomaly. The negative anomaly of Cerium in weathered crust can be used as a good prospecting indicator.

3. Leaching Process of Ionic Rare Earth Ore

3.1. Reform of Leaching Process of Ionic Rare Earth Ore

It can be seen from the occurrence that rare earth elements exist in the form of ion adsorption, which is difficult to enrich and recover by conventional physical beneficiation methods. However, cations with more active chemical properties, such as Na^+, K^+, H^+, NH_4^+, and Mg^{2+} can be exchanged with rare earth elements adsorbed on the clay surface to make them resolve into the solution. In the process of rare earth recovery by using electrolyte solution as leaching agent, taking NH_4^+ as example, the chemical reaction in the leaching process can be expressed as Equation (3).

$$[Clay] \cdot nRE^{3+}_{(s)} + 3nNH^+_{4(aq)} \rightleftharpoons [Clay] \cdot (NH^+_4)_{3n(s)} + nRE^{3+}_{(aq)} \tag{3}$$
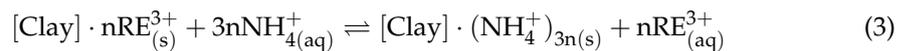
where [Clay] represents clay minerals, s represents solid phase, and (aq) represents liquid phase.

According to the above characteristics, in the process of long-term research and practice, Chinese scientific and technological workers have successively developed three generations of leaching processes of pool leaching, heap leaching, and in situ leaching [44]. At the same time, sodium chloride, ammonium sulfate, composite ammonium salt, and non-ammonium salt were screened out as leaching agents. These research results promote the green extraction technology of ionic rare earth resources.

In the 1970s, scholars had a preliminary understanding of the resource characteristics of ionic rare earth ores and successively developed the barrel leaching process and pool leaching process, as shown in Figure 5. The specific process is as follows: After stripping topsoil, the rare earth ore is mined and then transported indoors, screened, and placed in a wooden bucket or water tank. Next, under natural pH conditions, the rare earth is leached with sodium chloride solution as leaching agent and the obtained lixivium is precipitated with oxalic acid. The leaching agent sodium chloride used in this process has the advantage of low price and sufficient source. At the same time, oxalic acid can be used as precipitant to effectively separate rare earth from iron, aluminum, and other impurity ions. However, the consumption of the leaching agent in this process is large, and the leaching rate of rare earth is low. The concentration of leaching agent needs to be 6%~8%, while the leaching rate of rare earth is only about 60%. At the same time, a large amount of sodium chloride wastewater is produced, resulting in soil hardening and salinization. In addition, the process has low efficiency, high labor intensity, and requires a large number of workers.

In view of the above problems, the second generation leaching process was developed in the 1980s, as shown in Figure 6. At this time, pool leaching and heap leaching were coexisting. The specific process is as follows: heap the mined rare earth ore to the storage yard with a leak proof layer; ammonium sulfate is used as leaching agent; spray from the top of the ore heap at a low concentration of 1%–4% (at this time, the solution pH is about 5.5), so as to realize the leaching of the ore. The collected lixivium uses ammonium bicarbonate as the precipitant of rare earth. The process reduces the consumption of the leaching agent, reduces the pollution of agent to soil, and reduces the leaching of impurity metal ions. The

rare earth leaching rate of 80% to 90% and mixed rare earth oxides with a total amount of rare earth greater than 92% can be obtained. This process can optimize the leaching efficiency by changing the leaching process parameters such as leaching liquid–solid ratio, leaching liquid concentration, and leaching speed, as well as adjusting the storage yard construction parameters such as stacking height, bottom cushion inclination, and ore pile particle gradation, so as to obtain higher rare earth recovery in a shorter leaching cycle. However, in the long-term production practice, the heap leaching process has the following disadvantages. In the leaching process, due to the uneven particle size, the leaching agent solution has a "ditch flow" in the local part of the ore heap, while other parts with poor permeability form a "Dead zone", which increases the consumption of leachable agents and also affects the leaching effect. In addition, the first two generations of leaching processes need to strip the mine topsoil, which has seriously damaged the ecological environment. The results of long-term production practice show that for every 1 t of rare earth products, the mined surface area is 200~800 m^2, and the amount of stripped topsoil and tailings is 1200~1500 m^3. In addition, the ore below the hillside is basically covered by the discarded stripped topsoil and tailings and cannot be used. The semi weathered ore bed is usually not mined due to its high ore hardness and low rare earth grade, resulting in a great waste of resources.
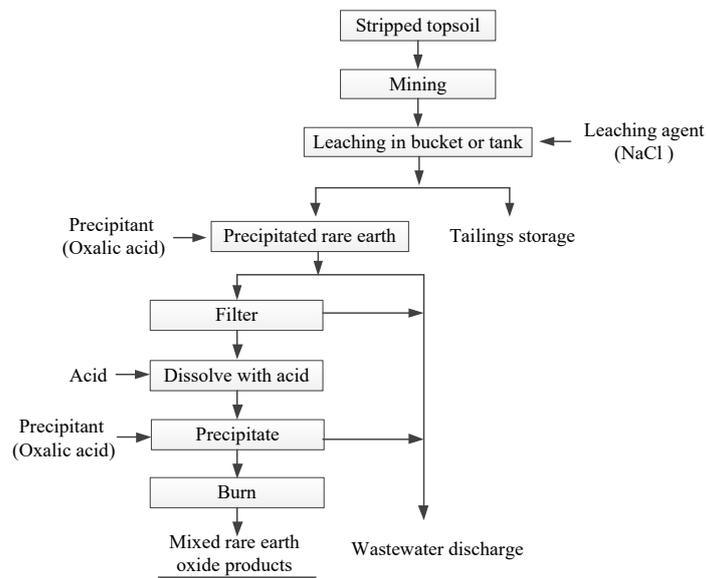

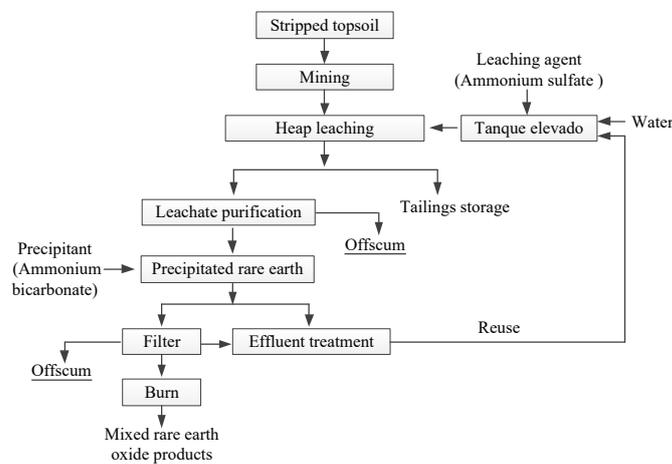**Figure 5.** First generation leaching extraction process.

Figure 6. Second generation leaching extraction process.

In the 1980s, Chinese scholars carried out key scientific and technological research on the above problems and developed an advanced and mature in situ leaching process, as shown in Figure 7. The technology has achieved great success in China and has been successfully promoted to southeast Asian countries. In this process, without damaging the surface vegetation of the mining area or excavating the topsoil and ore body, the lixiviant is injected into the closed liquid injection well from a high-level water tank. The lixiviant permeates and diffuses into the pores in the ore body. In this case, the rare earth ions adsorbed on the surface of clay minerals are desorbed to form the rare earth mother liquor into the liquid collecting ditch. After the rare earth leaching is completed, top water is added to make the ammonium sulfate and rare earth remaining in the ore body flow out, and the low concentration mother liquor formed is recycled after treatment. In this process, the lixiviant can also permeate and diffuse in the semi-weathered layer and slightly weathered layer. Thus, the rare earth can be better recovered and the resource utilization rate is improved. Under the concentration of 1%–3% leaching agent (leaching pH 5.5), the maximum rare earth leaching rate of 90%–95% can be obtained in engineering practice, and even 98% can be obtained in the laboratory. In addition, the in situ leaching process only needs to excavate liquid injection wells and liquid accumulation ditches and lay liquid injection pipelines, which greatly reduces the workload and improves the production efficiency. However, under the in situ leaching process, the re-adsorption of rare earth ions in the leaching solution is an important factor affecting the recovery effect of rare earth. To solve this problem, Chinese scholars have put forward solutions such as changing the liquid injection mode and optimizing the leaching parameters. The efficient leaching of rare earth elements is effectively realized by injecting the top of the mountain first, then the hillside and foot of the mountain, injecting the high concentration leaching agent first, then the low concentration leaching agent, and then injecting the top water to wash out the rare earth leachate remaining in ore body [45].
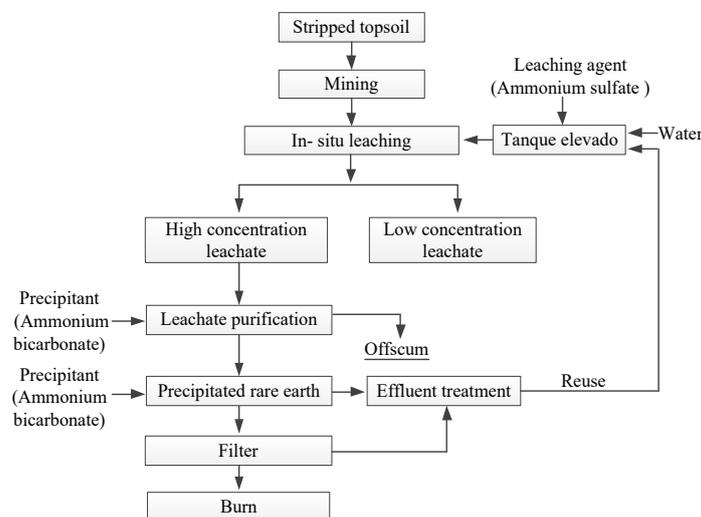

Figure 7. Third generation leaching extraction process.

3.2. In Situ Leaching Process Rare Earth Recovery Process

In the in situ leaching process, after the leaching agent is injected, it enters the ore body along the pores and fissures of the ore body. Under the action of gravity and pressure, the water in the pores and fissures is squeezed out and diffused in the pores of the ore body. In the diffusion process, the cations in the leaching agent reach the mineral surface and exchange with rare earth ions. The exchanged rare earth ions diffuse into the solution in the pores and continue to diffuse out of the ore body to become the mother liquor of rare earth leaching. Therefore, the leaching process of ionic rare earth ore is essentially a cyclic process of "leaching agent seepage ion dissolution mass transfer" [46,47].

As the chemical reaction process takes a short time, the seepage effect of leaching solution in the deposit is the most important factor to determine the leaching effect of in situ leaching. Ionic rare earth ore is an unconsolidated mineral particle group deposit. The seepage velocity of leaching solution in the ore body is small, and it is easy to be in a stable laminar flow state. The seepage law basically conforms to Darcy's law and can pass through the permeability coefficient σ Seepage effect of reaction ore body.

$$\sigma = \frac{Q\eta L}{F\Delta p} \tag{4}$$

where Q is the flow of leaching agent solution; η is the kinematic viscosity of leaching agent solution; L is the height of ore body in seepage process; F is the cross-sectional area of seepage area, which in fact represents the pore channel of ore body; and Δp is the pressure difference between liquid injection and liquid outlet.

According to Equation (4), the seepage velocity of leaching agent in the ore body is related to the injection parameters and the properties of the ore body. The kinematic viscosity of leaching agent solution and injection pressure are external factors, and the pore of ore body is the internal factor affecting the seepage effect. The type and concentration of leaching agent affect the kinematic viscosity of leaching agent solution. Generally, the viscosity increases with the increase in leaching agent concentration, and the seepage effect becomes worse.

The flow rate of the leaching agent has a significant impact on the seepage effect in the leaching process [48,49]. As the ionic rare earth ore body is mainly composed of skeleton particles with fixed positions and loose particles moving freely within a certain range, when the hydraulic gradient of leaching agent solution does not reach the critical hydraulic gradient started by loose particles, appropriately increasing the hydraulic gradient is conducive to improving the seepage effect. However, once the critical hydraulic gradient is exceeded, the fine loose particles migrate and block the pores driven by the leaching agent solution, which greatly reduces the permeability of the ore body, and the leaching blind area is formed due to the inability of seepage below the blocked part. Due to the heterogeneous property of ionic rare earth ore body, it is critical that the hydraulic gradient has no fixed value. The research results [50] show that the pore size of ore body increased by fine particle migration is smaller than that reduced by blockage. The water pressure of the leaching solution is small, which is conducive to maintaining the seepage of the leaching solution in the leaching process of the ore body.

The porosity of ore body is controlled by many factors, which is not only related to the pore distribution of ore body, but also related to the thickness of adsorbed liquid layer on the mineral surface. Due to the negative charge on the surface of clay minerals in the ore body, the mineral surface is wrapped by water, in which the outer water molecules wrap the mineral particles in the form of free water, while the inner water molecules are firmly adsorbed on the mineral surface [49,51] which is called adsorbed liquid layer. In the process of leaching, the adsorbed liquid layer on the particle surface has a viscous and blocking effect on the seepage of leaching solution. Therefore, the combined water film thickness affects the pore radius of the ore body. The results [52] show that the greater the thickness of the adsorbed liquid layer, the lower the permeability coefficient of the ore body. The cation concentration in the leaching solution determines the thickness of the adsorbed liquid layer. With the increase in cation concentration, the more rare earth and other metal ions are replaced, and the amount of negative charge on the surface of mineral particles increases, resulting in the increase in the thickness of the adsorbed liquid layer. The pore radius distribution of the primary ore body has a significant impact on the seepage. When the ore body is dominated by small radius pores, the combined water film occupies the effective pores, which will greatly hinder the seepage effect of the leaching solution.

Mass transfer is also one of the key factors affecting the leaching effect. Under the in situ leaching process, the leaching agent solution enters the free water layer to form a flowing layer. The cations such as NH_4^+ or Mg^{2+} in the flowing liquid layer reach the

surface of clay minerals through the adsorbed liquid layer and exchange reactions with rare earth ions. The exchanged rare earth ions reach the flowing layer through the adsorbed liquid layer. The mass transfer process of ionic rare earth ore is the material transfer between the flowing liquid layer and the mineral particle adsorbed liquid layer, as shown in Figure 8. The solute concentration difference between the adsorbed liquid layer and the flow layer is an important driving force of the mass transfer process [48,53].
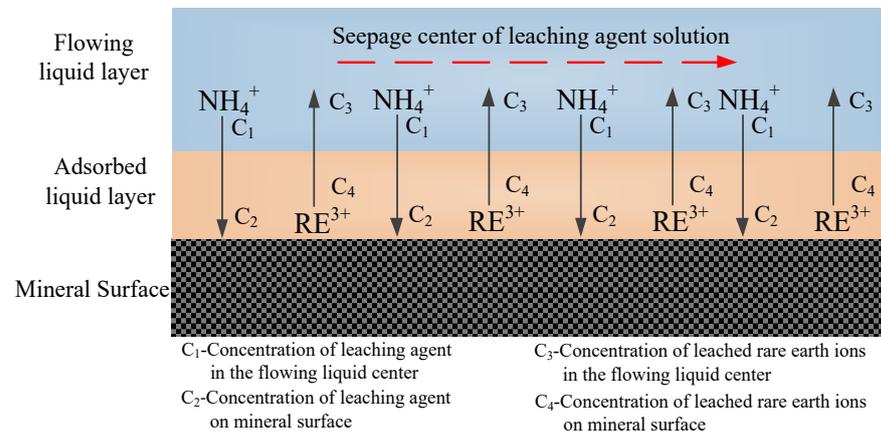

Figure 8. Schematic diagram of mass transfer process of ionic rare earth ore.

As the reaction is carried out on the surface of clay minerals, the concentration of leaching agent on the mineral surface decreases due to reaction consumption, and the concentration of a leaching agent in the flowing liquid layer, far away from the reaction zone, is high. On the contrary, the reaction product (RE^{3+}) is the largest near the mineral surface, while the concentration of the flowing liquid layer is low. The concentration difference between the flowing liquid layer and the reaction interface promotes the migration of reactants and leaching agent at the phase interface, and realizes the mass transfer process of leaching agent cations from solution to solid phase and rare earth ions on clay surface from solid phase to mobile liquid phase [48,54,55]. Scholars have found that the leaching process of ionic rare earth ore can be regarded as the color layer leaching process. The theoretical tray height reflects the mass transfer effect. The greater the theoretical tray height is, the stronger the lateral diffusion effect is, the worse the leaching mass transfer effect is. The theoretical tray height and the influencing factors of leaching can be described by the van Deemter equation (Equation (5)), and a theoretical tray height curve with leaching operation parameters is shown in Figure 9 [48].

$$\text{HETP} = A + \frac{B}{u} + Cu \tag{5}$$

where A is the seepage diffusion term, which depends on the uniformity and porosity of the ore body; B is the longitudinal diffusion coefficient, which depends on the longitudinal concentration gradient; C is the mass transfer impedance coefficient, which depends on the equilibrium distribution of rare earth ions between liquid and solid phases; and u is the flow velocity of leaching agent in the ore body.
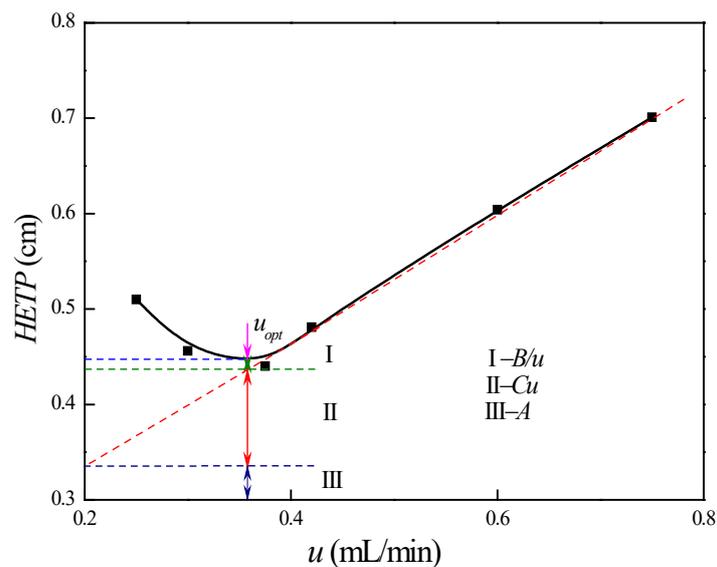
Figure 9. Theoretical tray height curve at different flow rates.

Chromatography tray theory and the van Deemter equation explain the leaching mass transfer process and point out the main mass transfer influencing factors such as the initial concentration of leaching agent, the flow rate of leaching agent, the height of ore column, the ratio of leaching column to diameter, and the particle size of ore. A large number of scholars have studied the effects of various factors on the mass transfer process of leaching based on the theory of chromatographic tray. It shows that the theory can be used to guide industrial practice.

In the leaching process of ionic rare earth ore, there is a relationship between the law of seepage and mass transfer, and the leaching parameters often have a significant impact on the effect of seepage and mass transfer. In order to clarify the speed control steps of leaching reaction process of weathered crust leaching rare earth ore, scholars have carried out research from the perspective of dynamics to find a way to strengthen the leaching process. Scholars regard clay mineral particles as regular spherical particles, and the seepage diffusion process follows the "shrinking unreacted core model" [48,56], which is shown in Figure 10. It was found that $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$; a series of straight lines passing through the origin can be obtained by plotting the leaching time t (where α is the leaching rate, in %). It is considered that the leaching seepage process of rare earth can be characterized by the diffusion control model in the solid film [48,56], and the dynamic equation of the leaching process is $1 - (2/3)\alpha - (1 - \alpha)^{2/3} = kt$. This suggests that, in the actual production process, we should pay attention to the factors restricting leaching, such as leaching agent concentration and liquid adding speed, so as to achieve high efficiency, low consumption, and high quality leaching dilution. Some scholars believe that the "shrinking unreacted core model" regards particles as an idealized spherical shape, which is not rigorous. The Kerr model (Equation (6)) used to describe the solid–liquid ion exchange process of soil science is introduced to reflect the adsorption capacity of NH_4^+ to RE^{3+} through the selectivity coefficient K_k [51,57,58]. Through this model, they studied the optimal concentration of ammonium sulfate and the migration process of rare earth elements.

$$K_k = \frac{[RE^{3+}]_{lg}[NH_4^+]_s^3}{[RE^{3+}]_S[NH_4^+]_l^3} \tag{6}$$
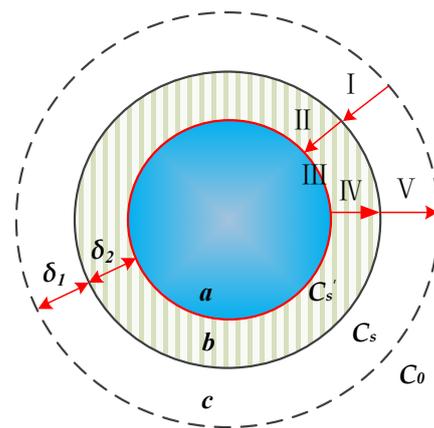
*a:Unleached ore particles, **b:**solid residue, **c:**Solvent diffusion zone*
***C₀:**Leaching agent concentration in liquid phase, **Cₛ:**Leaching
agent concentration on particle surface, **Cₛ':**Leaching agent
Concentration in the reaction area, δ₁:Thickness of diffusion zone,
δ₂:Thickness of solid residue, Ⅰ Ⅱ Ⅳ Ⅳ : Direction of mass transfer,
Ⅲ: The reaction interface.*

Figure 10. Illustrative diagram of shrinking unreacted core model.

3.3. Adaptability Evaluation of In Situ Leaching Process

Since the advent of the in situ leaching process, the mining of ionic rare earth resources has entered a high-speed development stage which not only protects the resources and environment, but also improves the level of comprehensive utilization of resources. However, in situ leaching process is not suitable for all ionic rare earth deposits. Its applicability is different according to the permeability of the deposit, hydrogeological conditions, and engineering geological conditions.

The permeability of the deposit is controlled by the type of deposit [59]. For the granite weathering crust type rare earth ore, the deposit has coarse, medium and fine particles and good permeability. It is the rare earth deposit with the largest mining scale and the largest output at present. The in situ leaching process has good adaptability and has achieved great success in production. For the weathered crust type rare earth ore of complex rock mass, because its rock mass is formed many times, the rock mass characteristics of different stages are different, the ore particle size changes in a large range, and its permeability is uneven. This kind of deposit has poor adaptability to the in situ leaching process and small mining scale. For the tuff weathering crust type rare earth deposit, the in situ leaching process cannot be suitable for this kind of deposit because the ore particles are very fine and the permeability is very poor. In order to evaluate the influence of permeability on the adaptability of in situ leaching process in detail, the deposits are divided into four categories according to permeability. The ore deposit with permeability rate of 1–3 m/d has good permeability. The particle size of large particles in the ore deposit can reach more than 5 mm, and the proportion of particles with particle size of more than 2 mm can reach 25%. The in situ leaching process has good adaptability to this kind of ore deposit. The permeability rate of deposits with particles above 1 mm, accounting for about 25%, is usually between 0.5–1 m/d. Most of these deposits are granite weathering crust rare earth ores with good permeability, so the in situ leaching process can be adopted. For the deposit with ore particle D_{25} of 0.5 mm, due to its fine composition and particle size, its permeability rate is usually 0.25–0.5 m/d. If the in situ leaching process is adopted, the mining cycle is long and the permeability is poor. In contrast, when the deposit is tuff weathering crust type, most of its constituent particles are less than 0.074 mm, and the permeability of the ore body is very poor. The in situ leaching process cannot adapt to the exploitation of such resources.

In the in situ leaching process, bedrock or semi-weathered layer with poor permeability is usually used as the baseplate of the deposit, and the leachate flows out of the ore body along the baseplate. Therefore, the relationship between the ore body baseplate

and groundwater table has a significant impact on the in situ leaching process [59]. An illustrative diagram of the relationship between ore body floor and groundwater level is shown in Figure 11. When the deposit baseplate is combined with the groundwater table, the hydrogeological conditions are very favorable for the in situ leaching process, and the required leaching liquid–solid ratio is small. For the exposed rare earth deposit, because the baseplate is above the groundwater table, the liquid–solid ratio required for in situ leaching is large, resulting in large consumption of leaching agent and reducing the technical and economic index of the process. On the contrary, in the low hilly area, the weathering degree of ionic rare earth ores is deep, and the groundwater table of such deep submersible deposits is mostly above the baseplate. Therefore, when adopting the in situ leaching process, a deep effusion ditch needs to be excavated, and the groundwater needs to be drained in advance before liquid injection. In general, the engineering cost of in situ leaching process for such deposits is high, but has a good adaptability.
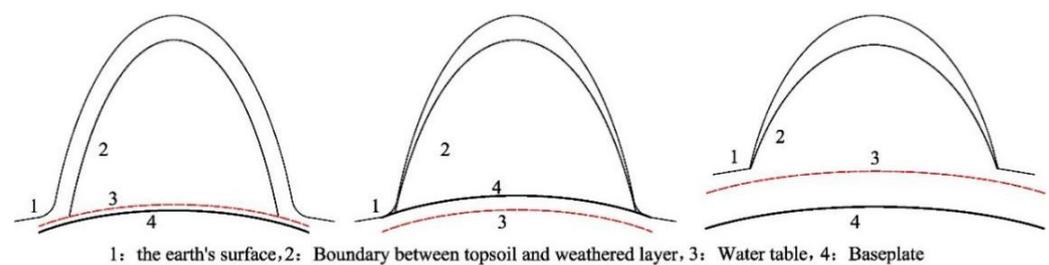

1: the earth's surface, 2: Boundary between topsoil and weathered layer, 3: Water table, 4: Baseplate

Figure 11. Relationship between ore body floor and groundwater level.

In geological conditions, the relationship between the baseplate of the deposit and the foot of the mountain is another important factor affecting in situ leaching. When the bedrock is exposed at the foot of the mountain or valley, this deposit is called barefoot deposit. Its bedrock is a good natural baseplate. The recovery of rare earth leachate can be realized only by excavating a liquid collecting channel below the bedrock base level. There are obvious differences between fully covered deposits and barefoot deposits. The fully covered deposit is deeply weathered, the bedrock is deeply buried, and the deep rare earth content of deposits is low or does not contain rare earth. The rock mass at the bottom of the rare earth ore body has good permeability and cannot be used as the baseplate to guide the rare earth leachate out of the ore body. At this time, it is necessary to arrange artificial baseplate at the bottom of rare earth ore body, and set up liquid collecting culvert in the ore body to lead rare earth leachate out [59]. The schematic diagram of the artificial baseplate concealed ditch net liquid collection method is shown in Figure 12.

1: Topsoil layer, 2: Weathered layer, 3: Deep baseplate, 4: Liquid injection well
5: the earth's surface, 6: Artificialbaseplate, 7: Underdrain for liquid collection
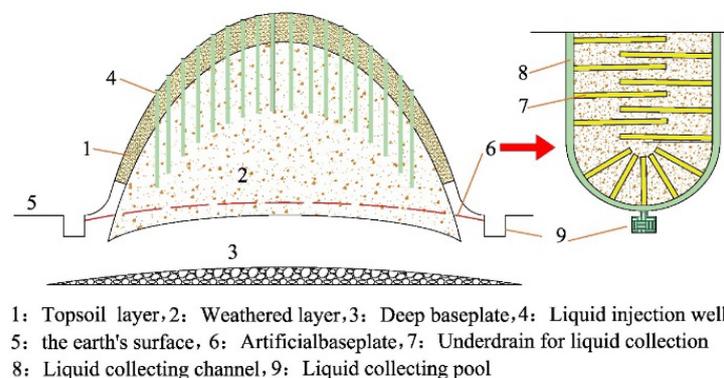8: Liquid collecting channel, 9: Liquid collecting pool

Figure 12. Schematic diagram of fully covered ionic rare earth mine artificial baseplate concealed ditch net liquid collection method.

In addition, the dip angle and thickness of ore body also affect the process adaptability [59]. According to the dip angle, it can be divided into horizontal ore body (less than

10°), gentle tilt ore body (10–30°) and tilt ore body (more than 30°). The dip angle of ore body affects the layout of liquid injection and liquid collection engineering. The smaller the dip angle, the stronger the adaptability of in situ leaching process. According to the thickness of the weathered layer of the ore body, it can be divided into thin ore body (less than 5 m), relatively thick ore body (5–15 m), thick ore body (15–25 m), and extremely thick ore body. The greater the thickness of the weathered layer of the ore body, the stronger the adaptability of the in situ leaching process. According to the nature of ore body, relevant scholars have summarized the adaptability of in situ leaching process, as shown in Table 3.

Table 3. Adaptability evaluation of in situ leaching process [59].

Deposit Conditions			Applicability Evaluation	Remarks
Geological conditions of deposit	Metallogenic parent rock	Granite weathering crust	Excellent	Successful production and Application
		Weathering crust of complex	Not applicable	Small scale production test but unsuccessful
		Tuff weathering crust	Not applicable	No mines use this technology for mining
	Deposit permeability	Fine (1~3 m/d)	Excellent	Granite weathering crust
		Barely good (0.5~1 m/d)	Good	Granite weathering crust
		Poor (0.25~0.5 m/d)	Good	Weathering crust of complex
		Extremely poor (<0.25 m/d)	Commonly	Tuff weathering crust
Hydrogeological conditions		The groundwater level coincides with the baseplate	Excellent	Latent deposit
		The groundwater level is below the baseplate	Commonly	Outcrop deposit
		The groundwater level is above the baseplate	Commonly	Deep buried deposit
Engineering geological conditions	Occurrence of baseplate	Barefoot	Excellent	
		Full cover	Good	
	Dip angle of ore bed	horizontal	Excellent	
		Gentle tilt	Excellent	
		Tilt	Commonly	
	Thickness of ore bed	Thin	Commonly	
		Relatively thick	Good	
		Thick	Excellent	
		Extremely thick	Excellent	

4. Leachate Purification and Rare Earth Extraction of Ionic Rare Earth Ore

4.1. Leachate Purification Technology of Ionic Rare Earth Ore

Under the leaching action of ionic rare earth ore, while the rare earth ions on the mineral surface are exchanged and desorbed, the clay minerals are also weathered and dissolved, so that the metal elements such as aluminum, calcium, iron, potassium, and sodium in the minerals are dissolved and enter the rare earth leachate together. The rare earth leachate obtained by the in situ leaching process has the remarkable characteristics of low concentration of rare earth elements and high content of metal impurities and complex species. The main impurities in the leachate are Al^{3+}, Fe^{3+}, and Ca^{2+}, and heavy metal ions, especially the content of Al^{3+}, can be as high as 1000~3000 mg/L. A large number of theoretical and practical studies have been carried out at home and abroad on the influence of impurity ions on the extraction of rare earth elements and removal methods. The results show that impurity ions not only affect the formation and morphology of rare earth crystals, but also lead to the amorphous precipitate of rare earth carbonate. Additionally, the recovery of rare earth products and the production cycle was also affected [60,61]. The influence of impurity aluminum ions on rare earth precipitation is shown in Figure 13.
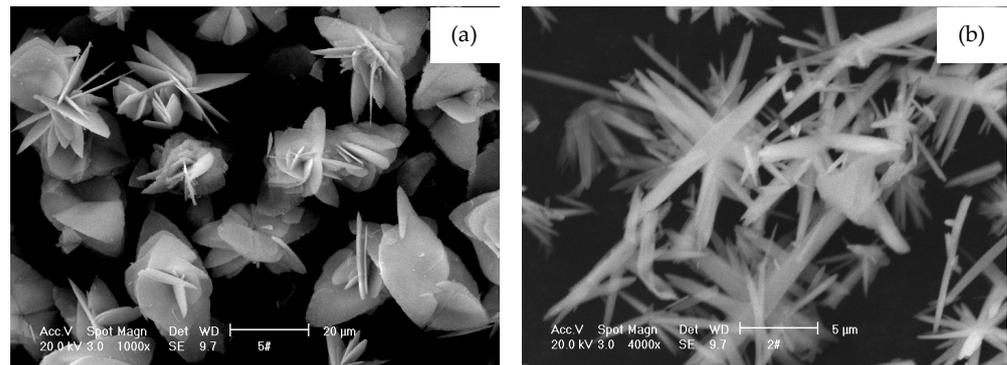
Figure 13. SEM of rare earth carbonate precipitate in the absence (**a**) and presence (**b**) of aluminum ions.

For the removal of impurity ions in the leachate of ionic rare earth ore, the method of hydrolysis neutralization and impurity removal is currently widely used in production. This method uses the difference of precipitation pH value between impurity ions and rare earth ions in the leachate to achieve the purpose of impurity removal. The method uses ammonium bicarbonate or ammonia to adjust the pH value of the solution to about 5.0, so that impurity ions such as Al^{3+} form hydroxide precipitation for removal, while rare earth remains in the solution in ionic state [62,63] as shown in Figure 14. Long term practice shows that under the ammonium bicarbonate impurity remover system, when the pH of the solution is greater than 4.8, impurity ions such as Al^{3+} and Fe^{3+} can form hydroxide precipitation which have a small solubility product, while rare earth ions gradually form precipitation when the pH is greater than 5.2. Therefore, by adjusting the pH value of rare earth leachate to 4.8~5.2, the rare earth and impurity ions can be differentially separated. However, when ammonium bicarbonate (NH_4HCO_3) was used as impurity remover, the side reaction between rare earth ions and carbonate ions easily to occurred, and some rare earth ions enter the impurity precipitation in the form of $RE_2(CO_3)_3$ precipitation, which caused the high loss rate of rare earth (Equation (8)) [64]. Scholars have studied the reaction entropy and solubility product of aluminum hydroxide, and proposed using ammonia as impurity remover. Li et al. [65] investigated ammonia and ammonium bicarbonate precipitant, respectively, found that the ammonia could cause a lower loss rate of rare earth than that of ammonium bicarbonate. In addition, other pH buffer solutions also have good impurity removal effects. Luo et al. [64] investigated the removal effects of ammonia, ammonium bicarbonate, hexamethylenetetramine, sodium acetate, and sodium sulfide on aluminum ions. The results showed that the hexamethylenetetramine could effectively improve the removal of aluminum ions, avoid the side reaction of formed rare earth carbonate, and greatly reduce the loss of rare earth.
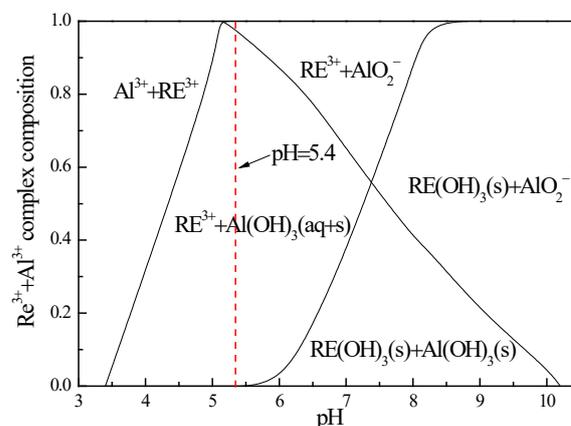

Figure 14. Composition of Al^{3+} and RE^{3+} in rare earth leaching solution varies with pH.

Due to the tiny difference of the precipitation pH value between rare earth and impurity ions, it is easy to increase the rare earth loss rate when ensuring the impurity removal rate, especially for the leachate with low rare earth concentration and high impurity concentration. In recent years, complex precipitation methods were applied more and more to the removal of impurity ions in rare earth leachate. Using the high selectivity of complex agent, the impurity ions were precipitated and separated in the form of insoluble complex. Li et al. [66] selectively reacted with impurity aluminum by adding 8-hydroxyquinoline to the leachate to generate insoluble 8-hydroxyquinoline aluminum, so as to realize the effective separation of rare earth ions and aluminum ions. This method has the advantages of good selectivity and easy filtration of impurity removal products. At the same time, the impurity removal product 8-hydroxyquinoline aluminum is also a good photoelectric material. After further purification, the impurity ions can be used as resources to avoid the harm of impurity removal products to the environment and form secondary pollutants [67,68]. Using TA [69] as aluminum remover, the leachate containing high concentration of aluminum can be purified. The results show that TA has good selectivity, the removal rate of impurity aluminum in the leachate is high, and the loss rate of rare earth is significantly reduced. Benzoate and naphthenate have a good effect of complexing aluminum ions [70,71].

In addition, we found [72] that many natural plant polysaccharides can also remove impurity ions from rare earth leaching solution, and their impurity removal effect is better than that of ammonium bicarbonate. Using lauroyl glucoside (LG) as impurity removal agent, our team carried out the purification and impurity removal test on low concentration rare earth leachate from southern Jiangxi (rare earth concentration 777 mg/L, impurity aluminum ion concentration 184 mg/L, impurity iron ion concentration 5 mg/L), and compared the impurity removal effect with ammonium bicarbonate. The results show that when ammonium bicarbonate is used as an impurity removal agent, at the optimal pH value of 5.4, the removal rate of aluminum ion can reach $91.03 \pm 0.1\%$ and the removal rate of iron ion can reach $92.53 \pm 0.2\%$, but the loss rate of rare earth is as high as $23.27 \pm 1.3\%$. With low concentration of rare earth leachate, the disadvantage of rare earth loss caused by side reaction of ammonium bicarbonate will be further amplified. When LG is used as an impurity remover, 99.09% aluminum ion removal rate and 93.13 iron ion removal rate can be obtained under the condition of pH 5.4. The results of solution chemical analysis show that under this pH condition, Fe^{3+} and Al^{3+} ions basically exist in the form of hydroxyl compounds, while rare earth ions still exist in the form of RE^{3+} free ions. Further DFT calculation (Table 4) results show that LG has strong chemical interaction with aluminum hydroxide, and the adsorption energy is as high as -114.82 kJ/mol, while the adsorption energy with rare earth ions and rare earth hydroxide is only -45.94 kJ/mol and -70.58 kJ/mol, respectively. Therefore, LG can show a strong selective complexation adsorption effect in the impurity removal of low concentration rare earth leachate.

Table 4. The chemical interaction intensity of lauryl glucoside with aluminum ion and rare earth ion by DFT calculation.

| Compound Composition	LG + Al(OH)$_3$	LG + La^{3+}	LG + La(OH)$_3$
Adsorption energy (KJ·mol^{-1})	-114.82	-45.94	-70.58
Reaction band	Al$_1$-O$_3$	La$_1$-O$_3$	La$_1$-O$_3$
Band population	0.26	0.01	0.10

In general, the complexation precipitation method could effectively reduce the content of impurity ions in leachate and reduced the loss of rare earth in the process of impurity removal, which provided a direction for the purification and impurity removal of ionic rare earth ore leachate. This method has a good application prospect. However, there are great differences in the chemical properties of the rare earth leachate produced by different weathered deposits. Sometimes, complex precipitants only target specific impurity ions, or

partially complex rare earth ions, due to lack of selectivity. At present, there are few reports on the application of complex precipitation in industrial production.

4.2. Extraction Technology of Rare Earth Ions from Leachate

At present, the extraction methods of rare earth in the leaching mother liquor after impurity removal are mainly divided into crystallization precipitation method, solvent extraction method, liquid membrane separation method, and so on, among which the crystallization precipitation method is the mainstream extraction process.

According to the development of rare earth precipitant, the crystallization precipitation method can be divided into the oxalic acid precipitation process and the ammonium bicarbonate precipitation process [44]. The oxalic acid precipitation process is a traditional process, mostly studied and practiced in the early development and utilization of ionic rare earth ore. In this process, oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) was used as a precipitant, which was added into the rare earth leachate after purification according to a certain proportion (generally, the ratio of rare earth amount to oxalic acid amount = 1:2). Rare earth ions reacted with oxalic acid to form a rare earth oxalate precipitation according to Equation (7).

$$2RE^{3+} + 3H_2C_2O_4 + xH_2O \rightarrow RE_2(C_2O_4) \cdot xH_2O + 6H^+ \tag{7}$$
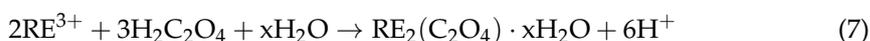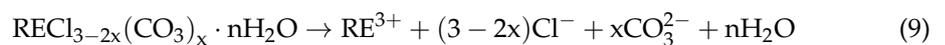
The oxalic acid precipitation process has the advantages of good separation effect between rare earth and coexisting ions, coarse Precipitation Crystallization particle size, and high product purity. It has been well popularized in early industrial applications. However, it was found that the actual consumption of oxalic acid was larger, which was much higher than the proportion required in theory. Chi et al. [73] calculated the solution chemistry of the oxalic acid precipitation rare earth process and found that the consumption of oxalic acid mainly occurs in three aspects: precipitation of rare earth ions, maintenance of complete rare earth precipitation, and complexation of impurity ion aluminum and iron. Increasing the concentration of rare earth in the leachte and strictly controlling the reaction conditions are the key to reducing the amount of oxalic acid.

The oxalic acid precipitation process has prominent disadvantages such as high cost, large dosage, and strong toxicity, which is completely inconsistent with the development trend of green extraction of rare earth. Therefore, scholars developed the ammonium bicarbonate precipitation process by replacing oxalic acid with ammonium bicarbonate. Academic circles generally believe that ammonium bicarbonate is an excellent agent to realize the crystallization and precipitation of rare earth ions, and its reaction conditions and mechanism have been deeply studied. Li et al. [74,75] found that rare earth ions began to form precipitation when ammonium bicarbonate was used to adjust the pH value of the leachate between 4.0 and 5.0. Furthermore, when the rare earth content was high, the rare earth carbonate precipitation could also be formed when the pH value of the leachate was less than 4.0, and could exist stably when the pH value was less than 7.0. Through the study on the change of pH value and composition in the precipitation process, he found that the rare earth ions first formed amorphous flocculent precipitation in the initial precipitation stage. In the aging process, with the decrease in pH value of the system and the release of CO_2 gas, the flocculent precipitation began to gradually transform into crystalline rare earth carbonate precipitation.

The crystallization process of rare earth carbonate is essentially an aging process, which is composed of metastable phase transformation and Ostwald ripening. The factors affecting the crystallization process and crystal morphology characteristics of rare earth carbonate are very complex, such as rare earth concentration, temperature, pH value of the system, content of non rare earth impurities, aging time, stirring conditions, additives, and other factors [76]. At present, the academic community has formed a consensus on the crystallization mechanism of rare earth carbonate. When the rare earth ions were nearly precipitated but not completely precipitated, the rare earth carbonate crystal core was initially formed. During the long aging process, the grains grow along the crystal nucleus, and the solution was accompanied by the production of H^+ (Equation (8)). With the decrease

in pH value of the system, amorphous flocculent precipitation gradually transformed into crystalline precipitation. The greater the decrease range of pH value, the better the crystallization and the faster the decrease speed, the faster the crystallization speed. The change of pH value of the system can be used as a good criterion for the crystallization and precipitation effect of rare earth. At the initial stage of nucleation, the solubility of rare earth Crystal nucleus was larger, and it was in the dynamic equilibrium of formation, dissolution, and reformation (Equation (9)). The free rare earth ions and carbonate ions were reoriented to form crystalline rare earth carbonate. The total reaction was shown in Equation (10). The Precipitation Crystallization Process of crystalline rare earth carbonate was a process involving HCO_3^- and releasing H^+, which could be summarized as crystal nucleation→crystal dissolution→recrystallization [62].

$$2RE^{3+} + 2HCO_3^- + nH_2O \rightarrow RE_2(CO_3)_3 \cdot nH_2O \downarrow + H^+ \tag{8}$$

$$RECl_{3-2x}(CO_3)_x \cdot nH_2O \rightarrow RE^{3+} + (3-2x)Cl^- + xCO_3^{2-} + nH_2O \tag{9}$$

$$2RECl_{3-2x}(CO_3)_x \cdot nH_2O + (3-2x)NH_4HCO_3 \rightarrow RE_2(CO_3)_3 \cdot 2H_2O + (3-2x)NH_4Cl + (3-2x)HCl \tag{10}$$

The ammonium bicarbonate precipitation process was easy to produce a large amount of amorphous flocculent precipitation during rare earth precipitation, with large floc volume and difficult to solid–liquid separation. Scholars have found that adding a certain amount of fresh crystal seeds during the precipitation and crystallization of rare earth carbonate could effectively strengthen the crystallization process of rare earth carbonate and prepare a crystalline rare earth carbonate. In addition, some studies also found that adding a certain amount of organic solvent, neutral surfactant, flocculant, and other additives in the process of rare earth precipitation and crystallization could promote the crystallization of metal ion carbonate [62,77]. The crystal seeds usually added are fine-grained rare earth carbonate crystals. In the precipitation process, the seed crystal provides the initial crystal nucleus required for crystallization, promotes the rapid directional arrangement of particles, and can effectively adjust the supersaturation of precipitated substances. Controlling the number, particle size, and activity of crystal seeds can improve the crystal precipitation and obtain ideal rare earth carbonate products. Qian [68] studied the effect of crystal seed on the crystallization process of actual leaching solution. The results show that when there is no crystal seed, the flocculent precipitation of rare earth carbonate is accumulated in a disorderly manner and gradually changes to crystalline rare earth carbonate after a long aging process. After adding crystal seed, the crystallization precipitation process of rare earth carbonate is significantly accelerated and the crystallization particle size is significantly increased, as shown in Figure 15. There are some differences in the action mechanism between surfactant and crystal seed. Taking sesbania gum as an example, due to the force between its rich hydroxyl and rare earth carbonate, it is easy to form a stable network winding structure and form stable flocs in the process of rare earth precipitation, which improves the concentration of rare earth carbonate around the flocs and reduces the driving force required for rare earth crystallization so as to promote the transformation of rare earth crystallization [62,77].

In addition to the crystallization precipitation method, the solvent extraction method has become a research hotspot for many experts and scholars because it can achieve the separation of rare earth elements and non rare earth elements and can directly prepare rare earth classification products. The extractants suitable for extracting rare earth ions from ionic rare earth ore leachate include naphthenic acid and organic phosphonic acid, among which P204 and P507 are the representatives. Chi et al. [78] used P507-kerosene extractant with saponification degree of 30% and concentration of 40% to extract the rare earth leachate after impurity removal. The extraction rate of rare earth was more than 95%. After three-stage countercurrent back extraction, rare earth chloride rich solution with REO of more than 150 g/L could be obtained. The disadvantage of solvent extraction method is that when the concentration of REO in rare earth leachate is low, the extraction rate is low,

multi-stage extraction is required, and the production cost is high. Moreover, the extractant needs saponification, consumes a lot of alkali, and the recycling rate of extractant is low. Therefore, this method is mainly used for rare earth extraction and separation in smelters.
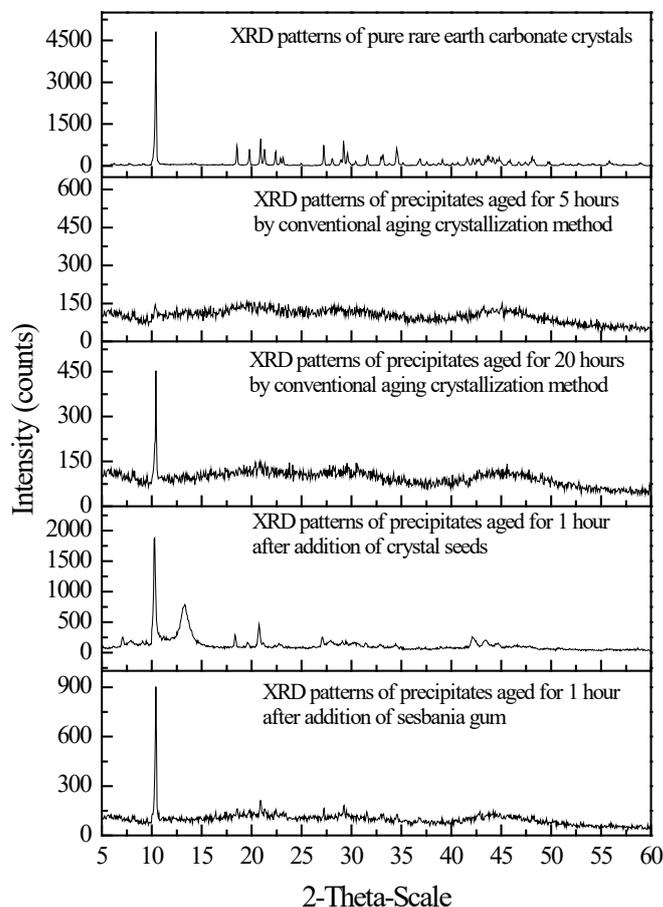

Figure 15. XRD diffraction patterns of rare earth carbonate precipitates under different conditions.

The process of rare earth enrichment by liquid membrane was to add an emulsion composed of membrane solvent, surfactant, mobile carrier, and internal water into the leachate. Rare earth elements could enter the emulsion from the leachate and then separate the leachate from the emulsion. The extraction and back extraction were carried out simultaneously. Deng et al. [79] developed a new extractant Cyanex272 for the enrichment of rare earth by liquid membrane method. After one-time intermittent enrichment, the concentration of rare earth in the internal phase could be as high as 90 g/L, and the recovery rate of rare earth could reach 99%. However, the stability of liquid membrane separation was not high, and there were still many technical problems. For example, it is difficult to realize the industrial application and popularization due to the technical problems such as eliminating swelling phenomenon, inhibiting the transmission of impurities in the membrane, and the selection of flow carrier and surfactant.

Generally, the removal of impurities by hydrolysis neutralization and the preparation of crystalline rare earth carbonate by ammonium bicarbonate precipitation are still the mainstream leachate purification and rare earth extraction technologies at present. These technologies are stable and mature. However, with the grade of the mined ionic rare earth ore decreasing, the rare earth content of the leachate decreasing, and the impurity ion content increasing, the inherent shortcomings of the above methods were becoming increasingly prominent, which presented difficulties in meeting the green development needs of ionic rare earth resources. Therefore, technical innovation is imminent.

5. Development Direction of Ionic Rare Earth Exploitation Technology

After nearly 50 years of development, the exploitation technology of ionic rare earth resources has made great progress and gradually moved towards becoming green, but there are still many deficiencies to be further improved. At present, the green exploitation of ionic rare earth resources can be carried out in the following directions.

5.1. Ammonium Free in "Leaching, Impurity Removal and Precipitation" Process of Ionic Rare Earth Ore

After long-term development, ammonium salts such as ammonium sulfate have become typical leaching agents for the in situ leaching process, especially the composite ammonium salts combined with ammonium sulfate and ammonium chloride, which reduce clay swelling to a certain extent [11] and are widely used in leaching operations. A large amount of ammonium bicarbonate is also used in the process of impurity removal and precipitation extraction of rare earth. However, in the process of extracting ionic rare earth, the ammonium salts used cause serious ecological and environmental problems such as soil acidification, water eutrophication, and excessive ammonia nitrogen in rare earth mining areas [51].

In view of the above problems, a large number of scholars have carried out the research work of non-ammonium salt leaching agents and precipitants and achieved some research progress. In terms of leaching agents, a large amount of the literature shows that high rare earth leaching rate can be obtained when magnesium sulfate is mixed with ammonium salt or used alone [80]. At present, the leaching effect of magnesium sulfate on rare earth ions has been verified, and has been gradually applied in the exploitation of some ionic rare earth mines. In addition to magnesium salt, aluminum sulfate and ferrous sulfate can also efficiently leach rare earth elements [81,82]. Using the reducibility of ferrous ions, rare earth ions in colloidal deposition phase can even be leached, which further improves the rare earth leaching rate. Aluminum ion has a stronger exchange capacity for rare earth ions, and it has a good anti expansion effect on clay minerals, which can significantly reduce the landslide risk in the process of in situ leaching. Relevant reports show that adding a certain amount of organic Leaching Aids [47,83,84], such as sesbania gum, LPF, and especially ascorbic acid with its strong reducibility, can effectively improve the rare earth leaching effect.

In terms of impurity removal from leachate and rare earth extraction, highly selective complexation precipitant is a research direction with great development prospects. Combined with non-ammonium salt pH regulator, it is expected to achieve efficient separation of rare earth and impurity ions through selective complexation of impurity ions or rare earth ions. Additionally, in recent years, non-ammonium salt precipitants, such as sodium carbonate, sodium bicarbonate, calcium oxide, and magnesium oxide, have also proved to be effective in recovering rare earth [85,86]. Taking magnesium oxide and calcium oxide as examples, alkaline oxide was added into the mother liquor to make the rare earth ions and a part of impurity ions in the solution form precipitates. One simply has to filter and wash the precipitates, add dilute acid and adjust pH, and selectively remove impurity ions such as aluminum by using solubility difference so as to realize the separation and recovery of rare earth and impurity ions. The ammonium free coprecipitation-selective impurity removal technology of leaching mother liquor has been formed [87].

It can be seen that the use of non-ammonium salts can also realize the efficient leaching and recovery of rare earth ions, which avoid the problem of ammonia nitrogen pollution from the source. However, the above methods are only in the laboratory research stage, and have different disadvantages, such as the introduction of impurity ions and low purity of rare earth products. At present, ammonium sulfate and ammonium bicarbonate are still the main agents in industrial production. Looking for and developing high-efficiency leaching agents and ammonium free precipitants is an important research direction for the green development of ionic rare earth mines in the future. Among them, magnesium salt leaching agent and ammonium free coprecipitation-selective impurity removal technology

are expected to achieve a great breakthrough in the short term and solve the problem of ammonia nitrogen pollution in the process of ionic rare earth extraction.

5.2. Enhancement of Seepage and Mass Transfer Process of In Situ Leaching of Ionic Rare Earth Ore

At present, the exploitation of ionic rare earth ore is becoming more and more difficult. The most significant changes are the increase in the content of fine minerals in the ore body, the decrease in the porosity of the ore body, and the obvious decrease in the permeability. As a result, the effect of seepage and mass transfer becomes worse, the leaching period is prolonged, and the leaching rate is reduced, which affects the efficient utilization of ionic rare earth resources.

It can be known from Section 3.3 that the main factors affecting the seepage of leaching agent in the ore body are the kinematic viscosity of leaching agent solution and the pores of the ore body. The main factors affecting the mass transfer effect are the adsorption strength of rare earth on the clay minerals' surface and the thickness of adsorbed liquid layer on the clay minerals' surface. Therefore, the regulation research on enhancing the seepage and mass transfer process of in situ leaching can be carried out from the above direction.

In terms of strengthening the seepage process of ionic rare earth ore, He et al. [11] found that reducing the concentration of leaching agent and increasing the temperature can greatly reduce the viscosity of leaching agent solution. Through the test, it is verified that the permeability coefficient of increases greatly, and the temperature has a greater impact. However, in reality, the above methods are difficult to be effectively realized. At present, a feasible scheme is to find the surfactant with strong hydrophilicity as the leaching aid to reduce the viscosity of the leaching agent. A large number of research results show that the use of anionic surfactant can effectively reduce the surface tension and viscosity of leaching agent solution and improve its seepage effect. The method has been verified in the leaching tests of ionic rare earth ore, uranium ore, and laterite nickel ore [88–90]. Natural and green surfactants such as sesbania gum and its carboxymethylation modification products have a significant effect on the seepage strengthening of ionic rare earth minerals [47]. Zhang et al. [88] used cheap sodium dodecyl sulfate to reduce the surface tension of leaching agent solution, significantly improving the seepage effect, which reduced the amount of leaching agent and shortened the leaching cycle.

Another way to improve the seepage effect of ionic rare earth ore is to prevent the excessive expansion of clay minerals, reduce the migration of fine clay particles and protect the pore channel of ionic rare earth ore. The leaching process is accompanied by the expansion of clay minerals and the migration of colloidal fine clay minerals, and the fine clay minerals usually deposit in the place with small porosity, blocking the throat and affecting the seepage [91]. Regulating the zeta potential of clay minerals and compressing the electric double layer on the clay minerals surface are effective methods to reduce the expansion of clay [92,93]. Agents such as ammonium acetate and magnesium salt have a good effect [93,94], and small molecular quaternary ammonium salt ore such as dimethyl diallyl ammonium chloride has an anti-swelling effect [95] which has more potential. In the future, it is important to study the influence of anti-swelling agents on ore body pores by combining high-resolution computer tomography and three-dimensional visualization technology [91,96].

In terms of mass transfer process enhancement of ionic rare earth ores, adding leaching aids that coordinate with rare earth ions can effectively reduce the adsorption strength of rare earth ions on the clay minerals surface and improve the mass transfer effect. Luo et al. [97] studied the effect of fulvic acid on rare earth leaching and found that it can form complexes with rare earth elements to improve the leaching effect of rare earth. Through DFT calculation, Zhang et al. [88] found that for rare earth elements adsorbed on the surface of clay minerals in the form of chemical bond, the interaction between sodium dodecyl sulfate and rare earth elements greatly reduces the RE-O chemical bond strength between rare earth and O atoms on the mineral surface, which is conducive to improving

the mass transfer effect. The coordination of LPF with rare earth ions can also reduce the concentration of rare earth ions in the flowing liquid layer, improve the diffusion concentration difference between the flowing liquid layer and the adsorbed liquid layer, and improve the mass transfer efficiency [83]. Theoretically, adding leaching aids and regulating the electric double layer of clay minerals surface can reduce the thickness of adsorbed liquid layer on the mineral surface and improve the diffusion concentration difference, which is another research direction to improve the mass transfer effect.

To sum up, it is urgent to carry out the regulation research on enhancing the seepage and mass transfer process of in situ leaching of ionic rare earth ores. The screening and development of green and efficient leaching aids is the main research direction, and the leaching aids that can reduce the viscosity of the leaching agent solution and coordinate with rare earth ions are the focus of the research. Cheap industrial surfactants or natural macromolecular surfactants such as plant polysaccharides have great application prospects.

5.3. New Technology of Impurity Removal and Rare Earth Extraction from Leachate

At present, the purification of ionic rare earth ore leachate and rare earth extraction rely on ammonium bicarbonate. However, a series of problems such as slow precipitation speed, difficult filtration, difficulty in forming crystalline rare earth carbonate in the precipitation process, and the ease of the process to cause ammonia nitrogen pollution are the increasingly prominent technical disadvantages of this process [87]. In the future, in addition to strengthening the research on the mechanism and exploring an effective way to solve the problem of ammonium bicarbonate precipitation method, we should also carry out research on the new technology of impurity removal and rare earth extraction from the leachate.

Microbial adsorption was proposed by C. C. Ruchhoft in the late 1950s and has been applied in many fields. Microbial adsorption selectively adsorbs a component from the solution according to its specific chemical structure and component characteristics. The adsorbed component can be quickly and effectively resolved. It is a reversible process of "adsorption desorption". At present, the research on microbial adsorption of rare earth elements is in its infancy. Xu et al. [98] studied the biosorption of rare earth ions La and Ce by agrobacterium R strain, and confirmed that it has good adsorption effect on La and Ce. Yin et al. [99] studied the adsorption of aspergillus oryzae and yeast on rare earth ions in the leachate of ionic rare earth ore, and found that both strains can effectively adsorb and enrich rare earth ions in the leachate, and aspergillus oryzae has stronger adsorption capacity and can be reused. Compared with other methods, microbial adsorption method has the advantages of low operation cost, high dilute solution treatment efficiency, good selectivity, and environmental friendliness. It has great potential and opens up a new way for the efficient extraction of rare earth from low concentration leachate.

In addition, solvent extraction is another feasible research direction. On the basis of solvent extraction, Huang Xiaowei, academician of the Chinese Academy of engineering, developed a new process of non-saponification and non-equilibrium coupling centrifugal extraction and enrichment of low concentration rare earth leachate [100]. Using the characteristics of selective extraction of rare earth ions with P507 and P204 extractants, non-saponified P507 was used to extract rich heavy rare earth, and the light rare earth in the remaining solution was extracted with non-saponified P204. Hydrochloric acid back extraction was used to obtain chlorinated medium heavy rare earth liquid and chlorinated light rare earth liquid, respectively. Eventually, the concentration of rare earth in the liquid reached 240 g/L, the total extraction rate of rare earth was 99.5%, and the content of heavy rare earth in light rare earth liquid was low. This process can extract rare earth without emulsification under the condition of low acidity, save saponification cost, and realize efficient and clean extraction of low concentration rare earth solution. Compared with the traditional rare earth extraction and enrichment process, it has the advantages of shortening the process flow, improving the recovery rate of rare earth, reducing the production cost, and causes no ammonia nitrogen wastewater discharge. Xiamen Institute of rare earth

materials, Haixi Research Institute, Chinese Academy of Sciences [101] developed ABC-BIL ionic liquid impregnation resin to recover rare earth ions based on solvent extraction and ion exchange principle. ABC-BIL ionic liquid extractant was adsorbed on macroporous polymer resin. The acid-base coupling bifunctional group of ABC-BIL ionic liquid was used to effectively adsorb rare earth ions in low concentration rare earth solution under strong acid conditions. This method has the high selectivity of solvent extraction and the simplicity and high efficiency of ion exchange technology.

In order to solve the pollution of high ammonia nitrogen waste liquid produced by ammonium bicarbonate and its inherent technical problems, the research and development of new technologies for impurity removal and rare earth extraction from leachate is an important direction for the green and efficient development of ionic rare earth resources in the future. From a long-term perspective, solvent extraction has a good prospect, but due to the low concentration of rare earth in the leachate, the effect will be better when it is used together with ammonium free coprecipitation technology. The combination of the two technologies is expected to achieve green and efficient rare earth extraction and change the current situation of ion rare earth extraction.

6. Conclusions

Ionic rare earth ore is a unique rare earth resource first discovered and developed in China. In the past 50 years, it has made an important contribution to meeting the world demand for rare earth resources. According to the unique metallogenic conditions and occurrence mechanism of ionic rare earth, it is of great significance to carry out resource prospecting all over the world to meet the increasingly vigorous market demand. According to the characteristics of this kind of resource, scholars have made significant research progress; developed a complete set of development and utilization technologies such as the in situ leaching process, hydrolysis neutralization, impurity removal, and precipitation and crystallization extraction; and carried out in-depth basic research on each process of rare earth extraction, which promoted the development of this kind of resource towards green methods. In the face of low-grade complex ionic rare earth deposits, the existing extraction technology still has a series of problems, such as long leaching period, low leaching efficiency, large rare earth loss in impurity removal process, lower rare earth crystal particle size, difficult dehydration of rare earth precipitate, and ammonia nitrogen pollution in rare earth extraction process, which still need to be improved further. At present, the research on the ammonium free process of ionic rare earth development, the enhancing of in situ leaching seepage and mass transfer process, and the new technology of impurity removal and rare earth extraction from leachate are important research directions for the green and efficient development of ionic rare earth resources.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Li, F.; Xiao, Z.; Zeng, J.; Chen, J.; Sun, X. Recovery of REEs from leaching liquor of ion-adsorbed-type rare earths ores using ionic liquid based on cooking oil. *Hydrometallurgy* **2020**, *196*, 105449. [CrossRef]
2. Qiu, T.; Yan, H.; Li, J.; Liu, Q.; Ai, G. Response surface method for optimization of leaching of a low-grade ionic rare earth ore. *Powder Technol.* **2018**, *330*, 330–338. [CrossRef]
3. Dushyantha, N.; Batapola, N.; Ilankoon, I.; Rohitha, L.; Dissanayake, D. The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. *Ore Geol. Rev.* **2020**, *122*, 103521. [CrossRef]
4. Kanazawa, Y.; Kamitani, M. Rare earth minerals and resources in the world. *J. Alloys Compd.* **2006**, *408*, 1339–1343. [CrossRef]
5. Deng, Y.; Ding, Y.; Huang, Z.; Yu, Y.; Zhang, Y. Boosting the extraction of rare earth elements from chloride medium by novel carboxylic acid based ionic liquids. *J. Mol. Liq.* **2021**, *329*, 115549. [CrossRef]
6. Yu, S.; Duan, H.; Cheng, J. An evaluation of the supply risk for China's strategic metallic mineral resources. *Resour. Policy* **2020**, *70*, 101891. [CrossRef]

7. Zhou, F.; Liu, Q.; Feng, J.; Su, J.; Liu, X.; Chi, R. Role of initial moisture content on the leaching process of weathered crust elution-deposited rare earth ores. *Sep. Purif. Technol.* **2019**, *217*, 24–30. [CrossRef]

8. Bao, Z. A geochemistry study of the granitoid weathering crust in southeast China. *Geogeochemistry* **1988**, *10*, 83–85. (In Chinese)

9. Ichimura, K.; Sanematsu, K.; Kon, Y.; Takagi, T.; Murakami, T. REE redistributions during granite weathering: Implications for Ce anomaly as a proxy for paleoredox states. *Am. Mineral.* **2020**, *105*, 848–859. [CrossRef]

10. Feng, J.; Zhou, F.; Chi, R.; Liu, X.; Xu, Y.; Liu, Q. Effect of a novel compound on leaching process of weathered crust elution-deposited rare earth ore. *Miner. Eng.* **2018**, *129*, 63–70. [CrossRef]

11. He, Z.; Zhang, Z.; Chi, R.; Xu, Z.; Yu, J.; Wu, M.; Bai, R. Leaching hydrodynamics of weathered elution-deposited rare earth ore with ammonium salts solution. *J. Rare Earths* **2017**, *35*, 824–830. [CrossRef]

12. Ding, J. Review of some important issues in the history of research, exploration, exploitation and utilization of ion-adsorbed rare earths. *Rare Earth Inf.* **2017**, *03*, 25–29. (In Chinese)

13. Chi, R.; Liu, X. Prospect and Development of Weathered Crust Elution-Deposited Rare Earth Ore. *J. Chin. Soc. Rare Earths* **2019**, *37*, 129–140. (In Chinese)

14. Chi, R.; Tian, J.; Luo, X.; Xu, Z.; He, Z. The basic research on the weathered crust elution-deposited rare earth ores. *Nonferrous Met. Sci. Eng.* **2012**, *3*, 1–13. (In Chinese)

15. Zhao, Z.; Wang, D.; Wang, C.; Wang, Z.; Zou, X.; Feng, W.; Zhou, H.; Huang, X.; Huang, H. Progress in prospecting and research of ion-adsorption type REE deposits. *Acta Geol. Sin.* **2019**, *93*, 1454–1465. (In Chinese)

16. Dill, H.G.; Buzatu, A. From the aeolian landform to the aeolian mineral deposit in the present and its use as an ore guide in the past. Constraints from mineralogy, chemistry and sediment petrography. *Ore Geol. Rev.* **2022**, *141*, 104490. [CrossRef]

17. Liu, H.; Chen, B.; Peng, L.; Zhao, Z.; Zhang, X. Characteristics and genesis of the ion Adsorption REE deposit in Jiangbei Metamorphic was recognized crust, Southern Jiangxi Province. *East China Geol.* **2020**, *41*, 315–324. (In Chinese)

18. Luo, X. Metallogenic conditions and formation mechanism of ion-adsorption rare earth deposits in Hunan Province. *J. Min.* **2011**, *1*, 332–333. (In Chinese)

19. Yang, D.; Xiao, G. Regional Metallogenic Regularities of the Ion Adsorption Type of Rare-Earth Deposits in Guangdong Province. *Geol. Resour.* **2012**, *20*, 462–468. (In Chinese)

20. Wu, C.; Huang, D.; Guo, Z. Geochemical study of rare earth elements in granite weathering crust in Longnan area, Jiangxi Province. *Acta Geol. Sin.* **2012**, *20*, 462–468. (In Chinese)

21. Bao, Z.; Zhao, Z. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. *Ore Geol. Rev.* **2008**, *33*, 519–535. [CrossRef]

22. Mentani, T.; Ohmura, T.; Watanabe, Y.; Urabe, T. So-Called "Ion-Adsorption Type" REE Deposits Found in Weathered Crust of Ilmenite-Series Granite in Northern Vietnam. Master's Thesis, The University of Tokyo, Tokyo, Japan, 2010.

23. Li, Y.; Zhao, W.; Zhou, M. Nature of parent rocks, mineralization styles and ore genesis of regolith-hosted REE deposits in South China: An integrated genetic model. *J. Asian Earth Sci.* **2017**, *148*, 65–95. [CrossRef]

24. Bern, C.R.; Yesavage, T.; Foley, N.K. Ion-adsorption REEs in regolith of the Liberty Hill pluton, South Carolina, USA: An effect of hydrothermal alteration. *J. Geochem. Explor.* **2017**, *172*, 29–40. [CrossRef]

25. Sanematsu, K.; Watanabe, Y.; Verplanck, P.L.; Hitzman, M.W. Characteristics and Genesis of Ion Adsorption-Type Rare Earth Element Deposits. In *Rare Earth and Critical Elements in Ore Deposits*; Society of Economic Geologists: Littleton, CO, USA, 2016; Volume 18.

26. Sanematsu, K.; Kon, Y.; Imai, A.; Watanabe, K.; Watanabe, Y. Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization in Phuket, Thailand. *Miner. Depos.* **2013**, *48*, 437–451. [CrossRef]

27. Sanematsu, K.; Kon, Y.; Imai, A. Influence of phosphate on mobility and adsorption of REEs during weathering of granites in Thailand. *J. Asian Earth Sci.* **2015**, *111*, 14–30. [CrossRef]

28. Sanematsu, K.; Murakami, H.; Watanabe, Y.; Duangsurigna, S.; Siphandone, V. Enrichment of rare earth elements (REE) in granitic rocks and their weathered crusts in central and southern Laos. *Bull. Geol. Surv. Jpn.* **2009**, *60*, 527–558. [CrossRef]

29. Padrones, J.T.; Imai, A.; Takahashi, R. Geochemical Behavior of Rare Earth Elements in Weathered Granitic Rocks in Northern Palawan, Philippines. *Resour. Geol. Off. J. Soc. Resour. Geol.* **2017**, *67*, 231–253. [CrossRef]

30. Maulana, A.; Yonezu, K.; Watanabe, K. Geochemistry of rare earth elements (REE) in the weathered crusts from the granitic rocks in Sulawesi Island, Indonesia. *J. Earth Sci.* **2014**, *25*, 460–472. [CrossRef]

31. Berger, A.; Janots, E.; Gnos, E.; Frei, R.; Bernier, F. Rare earth element mineralogy and geochemistry in a laterite profile from Madagascar. *Appl. Geochem.* **2014**, *41*, 218–228. [CrossRef]

32. Li, M.; Zhou, M.F.; Williams-Jones, A.E. The Genesis of Regolith-Hosted Heavy Rare Earth Element Deposits: Insights from the World-Class Zudong Deposit in Jiangxi Province, South China. *Econ. Geol.* **2019**, *114*, 541–568. [CrossRef]

33. Sanematsu, K.; Kon, Y. Geochemical characteristics determined by multiple extraction from ion-adsorption type REE ores. *Bull. Geol. Surv. Jpn.* **2013**, *64*, 313–330. [CrossRef]

34. Fu, W.; Li, X.; Feng, Y.; Feng, M.; Lin, H. Chemical weathering of S-type granite and formation of Rare Earth Element (REE)-rich regolith in South China: Critical control of lithology. *Chem. Geol.* **2019**, *520*, 33–51. [CrossRef]

35. Li, M.Y.H.; Zhou, M.F. The role of clay minerals in forming the regolith-hosted heavy rare earth element deposits. *Am. Mineral.* **2020**, *105*, 92–108. [CrossRef]

36. Banfield, J.F. The Mineralogy and Chemistry of Granite Weathering. Master's Thesis, The Australian National University, Canberra, Australia, 1985.

37. Chi, R.; Xu, J.; He, P.; Zhu, Y. REE geochemistry of granitoid weathering crust and properties of ores in southern China. *Geochimica* **1995**, *24*, 261–269. (In Chinese)

38. Yamaguchi, A.; Honda, T.; Tanaka, M.; Tanaka, K.; Takahashi, Y. Discovery of ion-adsorption type deposits of rare earth elements (REE) in Southwest Japan with speciation of REE by extended X-ray absorption fine structure spectroscopy. *Geochem. J.* **2018**, *52*, 415–425. [CrossRef]

39. Mukai, H.; Kon, Y.; Sanematsu, K.; Takahashi, Y.; Ito, M. Microscopic analyses of weathered granite in ion-adsorption rare earth deposit of Jiangxi Province, China. *Sci. Rep.* **2020**, *10*, 20194. [CrossRef]

40. Kosmulski, M. pH-dependent surface charging and points of zero charge. IV. Update and new approach. *J. Colloid Interface* **2009**, *337*, 439–448. [CrossRef]

41. Borst, A.M.; Smith, M.P.; Finch, A.A.; Estrade, G.; Geraki, K. Adsorption of rare earth elements in regolith-hosted clay deposits. *Nat. Commun.* **2020**, *11*, 4386. [CrossRef]

42. Yan, H. First-Principles Study on the Adsorption of Hydrated Rare Earth Ions on the Surface of Kaolinite. Ph.D. Thesis, Jiangxi University of Science and Technology, Ganzhou, China, 2019.

43. Lee, J.H.; Byrne, R.H. Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. *Geochim. Cosmochim. Acta* **1993**, *57*, 295–302.

44. Luo, X.; Wen, C.; Xu, J.; Ma, P.; Tang, X.; Chi, R. Research Progress on and Development Trend of Exploitation Technique of Ion-absorbed Type Rare Earth Ore. *Met. Mine* **2014**, *43*, 83–90. (In Chinese)

45. Tang, X.; Li, M.; Yang, D. T The problem of reabsorption of ion-absorbed rare earth mineral in situ leaching mining and the measure to overcome it. *J. Cent. South Univ. Technol. Sci. Technol.* **1998**, *29*, 13–16. (In Chinese)

46. Tian, J.; Tang, X.; Yin, J.; Luo, X.; Rao, G.; Jiang, M. Process opitimisation on leaching of a lean weathered crust elution-deposited rare earth ores. *Int. J. Miner. Process.* **2013**, *119*, 83–88. [CrossRef]

47. Tian, J.; Tang, X.; Yin, J.; Chen, J.; Luo, X.; Rao, G. Enhanced leachability of a lean weathered crust elution-deposited rare-earth ore: Effects of Sesbania Gum Filter-Aid Reagent. *Metall. Mater. Trans. B* **2013**, *44*, 1070–1077. [CrossRef]

48. Tian, J.; Chi, R.; Yin, J. Leaching process of rare earths from weathered crust elution-deposited rare earth ore. *Trans. Nonferrous Met. Soc. China* **2010**, *20*, 892–896. [CrossRef]

49. Tian, J.; Tang, X.; Yin, J.; Luo, X. Present situation of fundamental theoretical research on leaching process of weathered crust elution-deposited rare earth ore. *Nonferrous Met. Sci. Eng.* **2012**, *3*, 48–52. (In Chinese)

50. Wang, X.; Li, Y. Experimental study on permeability characteristics of rare earth ore body under seepage and chemical coupling action. In Proceedings of the 2017 Annual Conference of China Rare Earth Society, Beijing, China, 11–13 May 2017. (In Chinese).

51. Nie, W.; Zhang, R.; He, Z.; Zhou, J.; Wu, M.; Xu, Z.; Chi, R.; Yang, H. Research progress on leaching technology and theory of weathered crust elution-deposited rare earth ore. *Hydrometallurgy* **2020**, *193*, 105295. [CrossRef]

52. Li, Y.; Fu, Y.; Chen, J. Analysis on the Changes of Permeability of Rare Earth and Its Causes under Different Concentrations of Ore. *Min. Res. Dev.* **2018**, *12*, 117–120. (In Chinese)

53. Tian, J.; Yin, J.; Chen, K.; Rao, G.; Jiang, M.; Chi, R. Optimisation of mass transfer in column elution of rare earths from low grade weathered crust elution-deposited rare earth ore. *Hydrometallurgy* **2010**, *103*, 211–214.

54. Chi, R.; Li, Z.; Peng, C. Partitioning properties of rare earth ores in China. *Rare Met.* **2005**, *24*, 205–210.

55. Tang, X. Optimization of Mass Transfer Process of Leached Rare Earth Ore with Low Grade Weathering Crust. Master's Thesis, Jiangxi University of Science and Technology, Ganzhou, China, 2013.

56. Tian, J.; Yin, J.; Chi, R.; Rao, G.; Jiang, M.; Ouyang, K. Kinetics on leaching rare earth from the weathered crust elution-deposited rare earth ores with ammonium sulfate solution. *Hydrometallurgy* **2010**, *101*, 166–170.

57. Hu, S.; Cao, X.; Wang, G.; Long, P.; Zhou, X. An Ion Exchange Model for Leaching Process of Weathered Crust Elution-deposited Rare Earth. *Min. Metall. Eng.* **2018**, *38*, 1–5. (In Chinese)

58. Long, P.; Wang, G.; Tian, J.; Hu, S.; Luo, S. Simulation of one-dimensional column leaching of weathered crust elution-deposited rare earth ore. *Trans. Nonferrous Met. Soc. China* **2019**, *29*, 625–633. [CrossRef]

59. Zhao, B.; She, Z.; Kang, Q. Applicability Evaluation and Classification of In-situ Leaching Mining for Ion-absorbed-type Rare Earth Deposit. *Min. Metall. Eng.* **2017**, *37*, 6–10. (In Chinese)

60. Judge, W.D.; Azimi, G. Recent progress in impurity removal during rare earth element processing: A review. *Hydrometallurgy* **2020**, *196*, 105435. [CrossRef]

61. Hu, P.; Jiao, X.; He, X.; Gu, Z.; Li, M.; Li, Y. Effect of Impurity Ions on the Crystallization of Yttrium-Base-Heavy Rare Earth Carbonate. *Chin. Rare Earths* **2000**, *21*, 1–4. (In Chinese)

62. Qian, Y. Precipitation and Crystallization of Ammonium Bicarbonate in Low Concentration Rare Earth Solution. Master's Thesis, Jiangxi University of Science and Technology, Ganzhou, China, 2013.

63. Chi, R.; Li, X.; Xu, J.; He, P.; Zhu, Y. Theoretical analysis of ammonium bicarbonate used to separate rare earth from aluminum-containing solution. *Multipurp. Util. Miner. Resour.* **1993**, *4*, 39–42. (In Chinese)

64. Luo, X.; Zou, L.; Ma, P.; Luo, C.; Xu, J.; Tang, X. Removing aluminum from a low-concentration lixivium of weathered crust elution-deposited rare earth ore with neutralizing hydrolysis. *Rare Met.* **2017**, *36*, 685–690. [CrossRef]

65. Li, X.; Chi, R. Study on removing impurities in the exchanged liquor of rare earth ores. *Multipurp. Util. Miner. Resour.* **1997**, *2*, 10–13. (In Chinese)

66. Li, J.; Chen, Z.; Wang, G. The Invention Relates to a Complexation Precipitation Method for Removing Aluminum from Rare Earth Solution. CN. Patent CN105624440B, 3 October 2017. (In Chinese)

67. Wang, Y.; Ren, Y.; Liu, J.; Zhang, C.; Xia, S.; Tao, X. Crystal growth, structure and optical properties of solvated crystalline Tris(8-hydroxyquinoline)aluminum(III)(Alq3). *Dye. Pigment.* **2016**, *133*, 9–15. [CrossRef]

68. Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sironi, A. Correlation between Molecular Packing and Optical Properties in Different Crystalline Polymorphs and Amorphous Thin Films of mer-Tris(8-hydroxyquinoline)aluminum(III). *J. Am. Chem. Soc.* **2000**, *122*, 5147. [CrossRef]

69. Mao, Y.; Zhang, C.; Wu, N.; Zeng, L. Study on elimination of aluminum in ion adsorption type rare earth ore. *Shanghai Met. (Nonferrous Fasclcule)* **1993**, *14*, 16–19. (In Chinese)

70. Ge, X. Method for Removing Aluminum from Rare Earth Solution by Benzoate Precipitation. CN. Patent ZL201210542546.0, 14 December 2012. (In Chinese)

71. Han, Q.; Liu, Z.; Yan, J.; Li, J. A new technology of aluminum removal from rare earth feed liquid with naphthenic acid. *Chin. Rare Earths* **2013**, *34*, 74–77. (In Chinese)

72. Luo, X.; He, K.; Zhou, H.; Zhang, Y.; Xie, F. Enhanced impurity removal of ionic rare earth leaching solution through the use of lauryl glucoside. *Miner. Eng.* **2022**, *181*, 107551. [CrossRef]

73. Chi, R.; Xu, Z. A solution chemistry approach to the study of rare earth element precipitation by oxalic acid. *Metall. Mater. Trans. B* **1999**, *30*, 189–195. [CrossRef]

74. Li, Y.; Li, M.; He, X.; Hu, P.; Gu, Z. Precipitation and crystallization process of rare earth carbonate. *Chin. J. Nonferrous Metals.* **1999**, *9*, 165–170. (In Chinese)

75. Li, Y.; Li, M.; Hu, P.; He, X. Study on the precipitation and crystallization process of rare earth carbonate. In Proceedings of the International Symposium on Industrial Crystallization, Tianjin, China, 21–25 September 1998; Volume 9, pp. 85–90.

76. Luo, X.; Qian, Y.; Chen, X.; Liang, C. Crystallization of Rare earth solution by Ammonium bicarbonate. In Proceedings of the 52nd Conference of Metallurgists, Rare Earth Elements, Montreal, QC, Canada, 27–31 October 2013; pp. 289–297.

77. Liu, Y. Precipitation Crystals Technology and Mechanism Research on Ion-Absorbed Rare Earth Ore. Master's Thesis, Jiangxi University of Science and Technology, Ganzhou, China, 2014.

78. Chi, R.A.; Xu, J.M.; He, P.J.; Zhu, Y.J. Recovering re From Leaching Liquor of Rare Earth Ore by Extraction. *Trans. Nonferrous Met. Soc. China* **1995**, *4*, 36–40.

79. Xu, D.; Zeb, S.; Yu, C.; Jin, L.; Peng, X.; Hao, Z.; Sun, G. Recovery of rare earths from nitric acid leach solutions of phosphate ores using solvent extraction with a new amide extractant (TODGA). *Hydrometallurgy* **2018**, *180*, 132–138. [CrossRef]

80. Xiao, Y.; Feng, Z.; Huang, X.; Huang, L.; Chen, Y.; Wang, L.; Long, Z. Recovery of rare earths from weathered crust elution-deposited rare earth ore without ammonia-nitrogen pollution: I. leaching with magnesium sulfate. *Hydrometallurgy* **2015**, *153*, 58–65.

81. Yang, L.; Li, C.; Wang, D.; Li, F.; Liu, Y.; Zhou, X.; Liu, M.; Wang, X.; Li, Y. Leaching ion adsorption rare earth by aluminum sulfate for increasing efficiency and lowering the environmental impact. *J. Rare Earths* **2019**, *37*, 429–436. [CrossRef]

82. Xiao, Y.; Feng, Z.; Guhua, H.U.; Huang, L.; Huang, X.; Chen, Y.; Long, Z. Reduction leaching of rare earth from ion-adsorption type rare earths ore with ferrous sulfate. *J. Rare Earths* **2016**, *34*, 917–923. [CrossRef]

83. Luo, X.; Ma, P.; Luo, C.; Chen, X.; Feng, B.; Yan, Q. The effect of LPF on the leaching process of a weathered crust elution-deposited rare earth ore. In Proceedings of the 53rd Conference of Metallurgists, Vancouver, BC, Canada, 27 September–1 October 2014.

84. Yanfei, X.; Fuguo, L.; Li, H.; Zongyu, F.; Zhiqi, L. Reduction leaching of rare earth from ion-adsorption type rare earths ore: II. Compound leaching. *Hydrometallurgy* **2017**, *173*, 1–8. [CrossRef]

85. Nagashima, K.; Wakita, H.; Mochizuki, A. The Synthesis of Crystalline Rare Earth Carbonates. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 152–156. [CrossRef]

86. Meng, X. No-Ammonia Precipitation Enrichment Technology and Process Control of Low Concentration Rare Earth Sulfate Leaching Solution. Master's Thesis, General Research Institute for Nonferrous Metals, Beijing, China, 2017.

87. Zhu, D. Behavior and Process of Ion-Type Rare Earth Ore Leaching Liquor Coprecipitation and Aluminum Selective Removal with No-Ammonium. Ph.D. Thesis, Jiangxi University of Science and Technology, Ganzhou, China, 2019.

88. Zhang, Y.; Zhang, B.; Yang, S.; Zhong, Z.; Zhou, H.; Luo, X. Enhancing the leaching effect of an ion-absorbed rare earth ore by ameliorating the seepage effect with sodium dodecyl sulfate surfactant. *Int. J. Min. Sci. Technol.* **2021**, *31*, 995–1002. [CrossRef]

89. Tan, K.; Li, C.; Liu, J.; Qu, H.; Xia, L.; Hu, Y.; Li, Y. A novel method using a complex surfactant for in-situ leaching of low permeable sandstone uranium deposits. *Hydrometallurgy* **2014**, *150*, 99–106. [CrossRef]

90. Zhang, P.; Sun, L.; Wang, H.; Cui, J.; Hao, J. Surfactant-assistant atmospheric acid leaching of laterite ore for the improvement of leaching efficiency of nickel and cobalt. *J. Clean. Prod.* **2019**, *228*, 1–7. [CrossRef]

91. Luo, X.; Zhang, Y.; Zhou, H.; He, K.; Zhang, B.; Zhang, D.; Xiao, W. Pore structure characterization and seepage analysis of ionic rare earth orebodies based on computed tomography images. *Int. J. Min. Sci. Technol.* **2022**, *32*, 411–421. [CrossRef]

92. Zhang, Z.; He, Z.; Zhou, F.; Zhong, C.; Sun, N.; Chi, R. Swelling of clay minerals in ammonium leaching of weathered crust elution-deposited rare earth ores. *Rare Metals.* **2018**, *37*, 72–78. [CrossRef]

93. Chen, Z.; Zhang, Z.; Liu, D.; Chi, X.; Chi, R. Swelling of clay minerals during the leaching process of weathered crust elution-deposited rare earth ores by magnesium salts. *Powder Technol.* **2020**, *367*, 889–900. [CrossRef]

94. Chai, X.; Li, G.; Zhang, Z.; Chi, R.; Chen, Z. Leaching Kinetics of Weathered Crust Elution-Deposited Rare Earth Ore with Compound Ammonium Carboxylate. *Minerals* **2020**, *10*, 516. [CrossRef]

95. He, Z.; Zhang, R.; Sha, A.; Zuo, Q.; Xu, Z.; Wu, M. Anti-swelling mechanism of DMDACC on weathered crust elution-deposited rare earth ore. *J. Rare Earths* 2022, *in press*. [CrossRef]

96. Yin, S.; Chen, X.; Yan, R.; Wang, L. Pore structure characterization of undisturbed weathered crust elution-deposited rare earth ore based on X-ray micro-CT scanning. *Minerals* **2021**, *11*, 236. [CrossRef]

97. Luo, X.; Feng, B.; Wang, P.; Zhou, H.; Chen, X. The Effect of Fulvic Acid on the Leaching of a Weathered Rare-Earth Ore. *Metall. Mater. Trans. B* **2015**, *46*, 2405–2407. [CrossRef]

98. Xu, S.; Wang, H.; Zhang, S.; Wu, K. Biosorption of lanthanum and Cerium ions by Soil bacterium R strain. In Proceedings of the 10th National Symposium on Environmental Microbiology, Guangzhou, China, 30 November–4 December 2007. (In Chinese)

99. Yin, J. Study on Microbe Adsorption of Rare Earth from the Leach Liquid of the Weathered Crust Elution-Deposited Rare Earth Ore. Master's Thesis, Nanchang University, Nanchang, China, 2012.

100. Xiao, Y.; Long, Z.; Huang, X.; Feng, Z.; Cui, D.; Wang, L. Study on non-saponification extractionprocess for rare earth separation. *J. Rare Earths* **2013**, *31*, 512–516. [CrossRef]

101. Zhao, Z.; Sun, X.; Dong, Y.; Wang, Y. Synergistic effect of acid−basecoupling bifunctional ionic liquids in impregnated resin for rare earth adsorption. *ACS Sustain. Chem. Eng.* **2016**, *4*, 616–624. [CrossRef]