

RESOURCES AND EXPLOITATION OF RARE EARTH ORE IN CHINA

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Keywords: Exploitation; Rare Earth Ore; Endogenic Deposit; Exogenic Deposit; Processing Techniques

Abstract

As the major rare earth supplier in the world, China is very rich in the mineral resources. The distributions and characteristics of endogenic and exogenic rare earth deposits are concretely described. The important endogenic rare earth deposits, dominated by light rare earths, are located in Baiyunebo, Weishan and Sichuan Mianning, and most of the exogenic rare earth deposits, concentrated in heavy rare earths, are weathered crust elution-deposited rare earth deposits. Exploitation and utilization value of different rare earth ores are compared in detail and the various processing techniques are discussed according to different mineral species, components and structures.

Introduction

It is an indisputable global consensus that rare earths are not rare. Rare earth deposits are found in 37 countries and distributed in Asia, Europe, Africa, Oceania, North America and South America. The main rare earth countries are China, United States of America, Australia, Russia, Brazil, Canada, South Africa, Greenland, Mongolia, Kazakhstan, Kyrgyzstan, Malaysia and India which possess many large scale or super-large scale rare earth deposits [1]. According to the report of the US Geological Survey in 2011, the proved rare earth resources in the world is about 110 million tonnes (REO) in which China is 55 million tonnes, the former Soviet Union is 19 million tonnes and the United States of America is 13 million tonnes. China issued its White Paper on Rare Earths in 2012 and claimed that China accounts for 23% of the total RE reserves of the world. The rare earth mines are mainly distribute in Inner Mongolia, Jiangxi, Guangdong, Guizhou, and Sichuan etc. Most light rare earth ores are in the north, and most heavy rare earth ores are in the south. The principal exploited rare earth ores are the Baiyunebo, Sichuan Mianning, Shandong Weishan, and the weathered crust elution-deposited rare earth ore [2]. Among them, Baiyunebo is the richest rare earth resources [3]. With years of endeavor, China has become the biggest rare earth producer, user and exporter [4].

The application of rare earth makes a great contribution to the development of industry, but the exploiting of rare earth also brings serious resource and environment problems. For the past few

years, many measures have been taken on the mining, producing and exporting of rare earth to protect the resources and environment and achieve the sustainable and healthy development of the rare earth industry.

Main Rare Earth Deposits in China and the RE Partitioning

The Mineral Type Rare Earth Ore

The Baiyuneboite Rare Earth Ore in Inner Mongolia: Baiyunebo rare earth deposit is a large multi-metal deposit containing iron, rare earth and niobium etc. The orebody consists of west deposit, main deposit, high magnetic deposit, east deposit, east Jie Le Gele, dulahala and the east contact zone going from west to the east. Baiyunebo rare earth deposits derive from the metamorphic sedimentation (hydrothermal replacement) and the composition of the ores is quite complex containing 170 kinds of minerals. About 17 elements are found in the minerals including iron, rare earth, niobium, thorium, calcium fluoride, potassium, phosphorus, sulphur and scandium etc [5] The same element can exist in several forms or even more than a dozen of minerals, so the mineral species are multiplied and also with a relatively complicated structure. The minerals are intimately associated with each other in sub-sieve size ranges. Therefore, Baiyunebo deposit is a unique large multi-metal deposit that is rich in iron, rare earth and niobium all over the world. The reserve of rare earth at Baiyunebo is first and the reserves of niobium and thorium are second in the world [6].

The reserves of iron ore in Baiyunebo deposit are as follows: 716 million tonnes in main deposit and east deposit, 912 million tonnes in West deposit. The prospective reserve of REO is 135 million tonnes, industrial reserve is 43.5 million tonnes which occupies 83% of the national one (52 million tonnes). The prospective reserve of Nb₂O₅ and ThO₂ is 6.6 and 2.2 million tonnes, respectively.

More than 90% of the rare earth elements in Baiyunebo ores are present as independent ore phase, and about 4~7% are distributed in the iron ore and fluorite. Light rare earth occupies 88.5~92.4% of the total rare earth oxide, while the yttrium group elements are rare. Therefore, Baiyuneboite is a typical light rare earth ore with a high ratio of $\sum CeO_2/\sum Y_2O_3$ (27.11~64.41).

Bastnaesite, Bunsite, Cebaite, Huangheite, Carbocerine, Barium-parisite and Cryptolite etc., are the primary rare earth minerals in Baiyunebo, and the dominated bastnaesite and monazite, whose ratio is 6:4~7:3, accounts for 73.14~96.05% of the rare earth minerals. The particle size of rare earth mineral is between 0.01~0.07 mm and almost 70~80% are below 0.04 mm. The mixed rare earth ore contains other useful minerals such as magnetite, hematite, colombite and fluorite. The main gangue minerals are beloeilite, crocidolite, biotite, calcite, dolomite, barite, apatite, pyrite, feldspar, and quartz, etc.

Sichuan Liangshan Rare Earth Ore: Rare earth resources are relatively rich in Sichuan. Maoniuping rare earth ore with a high industrial value is located in the rare earth metallogenic belt with a length of 150 km in Liangshan. The rare earth reserve is about 2 million tonnes and mainly distribute in Maoniuping in the western Mianning and Dalu village in the southwest of Dechang county. The representative rare earth distribution is listed in Table I.

Table I. Rare Earth Distribution of Mianning and Dechang Rare Earth Ore (%)

Rare earth oxides	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃
Mianning Maoniuping	29.49	47.56	4.42	15.18	1.24	0.23	0.65	0.12	0.21	0.05	0.06	0.04	0.05	0.007	0.7
Dechang Dalu	35.63	43.81	4.73	13.06	1.22	0.225	0.52	0.06	0.09	0.045	0.04	0.01	0.055	0	0.40

*Note: Quoted from CSRE Yearbook 2011 [7]

Maoniuping rare earth ore is the largest one in Sichuan. The main industrial mineral is bastnaesite with 80% REO, only followed by parisite and a small amount of tschewkinitite. It is a typical light rare earth ore with a high content of light rare earth (96%). The ore in the rare earth ore usually associated with lead, molybdenum, barite (BaSO₄), barian celestine (Sr, Ba(SO₄)), fluorite etc which can be recovered, and the radioactive elements are at a low level. Except the Dalu rare earth ores, all other rare earth minerals in Liangshan occur in coarse mineral crystals and with a high weathered dissociation degree, so they are easily beneficiated.

Shandong Weishan Rare Earth Ore: Shandong Weishan rare earth ore is a quartz-barite- carbonate rare earth deposit with a reserve of 0.9 million tonnes. The mineral and gangue components of the deposit are simple, and the main mineral is bastnaesite, associated with a small amount of bunsite, quartz, barite etc. The particle size of Weishan rare earth ore is about 0.5~0.04 mm and can be easily enriched. The single RE element can be easily separated from the rare earth concentrate through beneficiating and 98% of the rare earth can be recovered. The original ore in Weishan contains 3.5~5% REO, and lanthanum, cerium, praseodymium, neodymium occupies more than 95% of the total amount, as shown in Table II.

Table II. Rare Earth Distribution of Weishan Rare Earth Ore (%)

Rare earth oxides	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃
Distribution (%)	35.46	47.76	3.95	10.90	0.79	0.13	0.53	0.14	-	-	-	-	0.03	-	0.76

*Note: Quoted from CSRE Yearbook 2011 [7]

The Weathered Crust Elution-deposited Rare Earth Ore

The weathered crust elution-deposited rare earth ore (ion-absorbed type rare earth ore) is a unique ion-absorbed rare earth ore only exploited in China, and it is mainly located in Jiangxi, Guangdong, Fujian, Hunan, Guangxi, Hainan, Yunnan and Sichuan province. The formation of the weathered

rare earth ores could be due to physical, chemical and biological weathering processes of the granodiorite and volcanic rocks [8]. Rare earth in the ores mainly exists as the hydration ions and hydroxyl hydration ions adsorbed on the clay minerals. Four major effects of ion phase RE partitioning are Ce loss, rich Eu, fractionation and Gd broken [9].

Weathered crust elution-deposited rare earth minerals are the yellow, light red and white mixture of sand and clay, which can be directly exploited by manual work. The rare earth grade is about 0.05~0.3% of REO, and more than 50% of REO enrich in the minerals with a particles size below -0.78 mm but which only account for 24~32% of the total mineral mass. The separated clay minerals of kaolin and halloysite have a REO grade of 1%. The rare earth grade along the depth of the deposit is low in the upper and bottom level but rich in the middle, but higher than rare earth grade of the bedrock at all depths. As for the transverse direction in a scale of 0~50 m, the rare earth grade has a small fluctuation, and rare earths is rich in the topographic high areas but poor in the valleys. The REO grade of different mines in the deposit greatly differs from each other with a difference of 2~6 times, and showed no apparent rules.

According to the RE partitioning, the weathered ores can be classified into three types: heavy rare earth ores, light rare earth ores and Middle Y and Rich Eu ores.

Heavy Rare Earth Ore: The weathered crust elution-deposited rare earth ore in Longnan Zudong, Jiangxi province is a typical heavy rare earth ore. The original rocks are muscovite-granite and biotite-granite, in which the major independent RE minerals are gadolinite and yttrapatite. The heavy rare earth ores is formed after weathering of the original rocks, and it is end member mineral deposit of heavy rare earth featured with rich yttrium. The reserve of such resource is 37 thousand tonnes, and the average rare earth grade is about 0.09% with 7% of light rare earth, 8% of middle rare earth and 85% of heavy rare earth. As seen in Table III Y_2O_3 occupies more than 60% of the total amount and Dy_2O_3 about 7%.

Table III. Rare Earth Partition of Longnan Rare Earth Ore in Jiangxi (%)

RE oxides	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
Partition	2.18	<1.09	1.08	3.47	2.34	<0.37	5.69	1.13	7.48	1.60	4.26	0.60	3.34	0.47	64.90

*Note: Quoted from CSRE Yearbook 2011 [7]

Light Rare Earth Ore: The weathered crust elution-deposited rare earth ore in Xunwu, Gannan, Jiangxi province is poor in yttrium and rich in cerium [10]. It has a reserve of 22 thousand tonnes, and the rare earth grade is about 0.1%. Light rare earth occupies about 70% of the total REO, middle rare earth is 10% and heavy rare earth is 14%. Lanthanum accounts for 30~40% as listed in Table IV.

Table IV. Rare Earth Partition of Xunwu Ore in Jiangxi (%)

RE oxides	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃
Partition	38.00	3.50	7.41	30.18	5.32	0.51	4.21	0.46	1.77	0.27	0.88	0.13	0.62	0.13	10.07

*Note: Quoted from CSRE Yearbook 2011 [7]

Mid-Heavy Rare Earth Ore: The weathered crust elution-deposited rare earth ore in Ganzhou Xinfeng, Jiangxi province is a typical mid-heavy rare earth ore. It has a reserve of 22 thousand tonnes, and the average rare earth grade is about 0.05%. Light rare earth occupies about 50% of the total REO, middle rare earth is 10% and heavy rare earth is 35%. The partitioning of Eu₂O₃ is very high with an average value of 1.0% and the highest value can reach 1.4%, and this kind of minerals also contain 25% of Y₂O₃, as shown in Table V. Mid-heavy rare earth ores were also found in Guangdong, Fujian, Hunan, Yunnan and Guangxi, which usually contains 20~30% of Y₂O₃ and 0.5~1% of Eu₂O₃.

Table V. Rare Earth Partition of Xinfeng Ore in Jiangxi (%)

RE oxides	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃
Partition	27.56	3.23	5.62	17.55	4.54	0.93	5.96	0.68	3.71	0.74	2.48	0.27	1.13	0.21	24.26

*Note: Quoted from CSRE Yearbook 2011 [7]

Enrichment and Extraction Technology

The Mineral Type Rare Earth Ore

Baiyunebo Rare Earth Ore in Inner Mongolia: It is difficult to separate rare earth from Baiyunebo ore due to the complex minerals. The specific gravity, magnetic ratio susceptibility and floatability of the minerals are relatively close just like the bastnaesite and monazite, and the mineral particles are very fine. Numerous research institutes and universities in China have put forward many new schemes and techniques for better utilization of the rare earth resource. Baogang rare earth dressing plant has improved its enrichment techniques several times during the 40 years of operation. More than ten processes have been used as follows: the mixed flotation-selective flotation and mixed flotation-gravity separation processes, the weak magnetic dressing-mixed flotation-selective flotation process, weak magnetic dressing-selective flotation to remove fluorite-bulk flotation-gravity separation with shaking table, and weak magnetic separation-strong magnetic separation- flotation process [11].

Particularly, the improved weak magnetic separation-strong magnetic separation- flotation process improve the recovery ratio of REO by 4~6 times compared to the weak magnetic separation-half selective half bulk flotation-gravity separation-flotation process. The raw material used in the process is strong magnetic middlings which contains 12% REO with a recovery ratio of 25~30%

from the original ores, and a mixture of H205, sodium silicate and H103 is used as the flotation agents. It can obtain rare earth concentrate containing REO 50~60% with a rare earth recovery ratio of 52.20% and secondary rare earth concentrate containing REO 34.48% with a rare earth recovery ratio of 20.55%, and the total recovery ratio of REO is 72.75% to the middlings and 18.37% to the original ores [12].

In the present beneficiation process in Baogang rare earth dressing plant, the operation conditions are as follows: sodium silicate (baume degree: 20, usage: 4.5~5.0 kg/t) is used as the inhibitor, LF-8 which has double activating group is used as the collector, the pH is about 7.0~8.5, the pulp density is 60~65%, mineral particles with the size of 85~90% -0.074 mm, and the flotation temperature is about 70⁰C. After one roughing and two cleaning, the REO grade can be up to 50% from the original 7%, and the recovery of REO is about 55% [13].

Zeng Yongjie et al. [14] carried on an industrial experiment of getting the rare earth from the magnetic ore tailings which contains 7.0% of REO, and obtained a flotation concentrate containing 45.69% of REO. The recovery ratio of REO is 28.87% to the original ores and 32.24% to the ore tailings.

The beneficiation work of Baotou Damao Rare Earth Co., Ltd and Boyu company of Baiyunebo iron mine concerns ores which have a great amount of magnetite using the weak magnetic separation-flotation technique. The original ores are ground to 90% -0.074 mm. After the weak magnetic separation of the magnetite, the tailings are concentrated in rare earths which are floated with a combined reagent of sodium silicate, J102 and H205. The REO grade of the concentrate can be 50~60% and the secondary concentrate is 34~40% [15].

Zhang Xinmin et al. [16] has carried on experiments about the pH, collector, inhibitor and frother used in the flotation of Baotou rare earth ore. When pH is 5~6, alums is used as the inhibitor of monazite and phthalandione or 802 as the collector, bastnaesite can be separated from monazite.

Ren Jun and Lu Shouci [17] use H894 (a kind of methanoic acid) as the collector, H103 (a kind of alcohol) as the frother, and aluminum potassium sulfate as the modifier in the separation of bastnaesite and monazite. When pH of the mineral pulp is 4.5~5.5, bastnaesite can be effectively separated from monazite.

Wang Guoqiang and Xu Gencan [18] have found a new collector L247. After adjusting the pH to 4.5~5, mineral pulp density 24%, flotation temperature 24⁰C, one roughing and two cleaning were carried out. The final bastnaesite concentrate has a REO grade of 66.43% with rare earth recovery ratio of 27.82%, and the content of bastnaesite is about 97.36%.

Li Mei et al. [19] have put forward a new theory of fractional mineral processing. Under the guidance of this theory, the tailing with 7.02% of rare earth (REO) was chosen as the raw material. The crude concentrate with 18.80% REO was obtained after the bulk flotation and foam separation. Then, from the crude concentrate of rare earth, the flotation process was used to separate high-grade rare earth concentrate whose REO content is greater than or equal to 65%, and the recovery ratio of this method is not smaller than 85%.

Sichuang Liangshan Rare Earth Ore: The conventional beneficiation processes for the

bastnaesite-featured rare earth ore are mainly gravity separation, magnetic separation, flotation, and the combination of the three methods. Bastnaesite usually co-exists with the gangue minerals such as calcite and fluorite, and their physical and chemical properties are similar. So the normal flotation agents or beneficiation methods do not provide a satisfactory result, and special enrichment methods are needed to effectively separate bastnaesite from the complex minerals. For example, heat the mineral pulp before flotation, use aromatic acid hydroxyl oxime and its salt as the flotation collector and so forth [20].

Ganzhou non-ferrous metallurgy research institutes [21] has proposed a magnetic separation-gravity separation process, and achieved good results. The original ore with a rare earth grade of 5.72% is chosen as the raw material, and a great amount of tailings were removed in the magnetic separation process. Finally, a rare earth concentrate containing 53.11% of REO with a recovery ratio of 55.36% was obtained.

Xiong Shuqin [22] has adopted a combined technique of primary grinding-classification- tabling and middlings regrinding flotation to the beneficiation of the rare earth ore, and obtained a rare earth concentrate with a REO grade of 61.18%, REO recovery ratio of 75.74%.

Xiong Wenliang and Chen Bingyan [23] use sodium silicate as modifier, derivative of hydroxamic acid as collector, at pH value within 7.15~8, and recovered a rare earth concentrate with REO content of 62.11% and REO recovery ratio of 86.98%.

Shandong Weishan Rare Earth Ore: Weishan rare earth dressing plant is a small one that was built in 1982. From 1991 to 2001, the rare earth concentrate it produced was high grade at 45~50% REO. But when the mining work switched to the underground in 2002, the REO grade of the original ores decreased. The output of the rare earth concentrate declined sharply, and so did the market share [2].

Zeng Xinnan and Li Fangji [24] recently selected reverse flotation-flotation-gravity separation process according to the floatability and the difference of specific gravity of the minerals. Firstly, NaOH, L101 (hydroxy oximino acid floating agent) and Na_2SiO_3 mixture is used for beneficiation of rare earth ore. To guarantee a satisfactory recovery ratio of rare earth, a small amount of carbonate mineral enters the rare earth rougher concentrate. This is upgraded to a high quality rare earth concentrate containing REO 68% and a middle grade concentrate containing REO 30% using a shaking table. The total recovery ratio of rare earth is 77~84%. After 3~4 times cleaning, a barite concentrate containing BaSO_4 92~95% is also obtained and its recovery ratio is 61~68%.

Feng Jie and Lv Dawei [25] adopted a single flotation technique in which Na_2CO_3 was used as modifier of pH value, CH and xp-2 as mixed collectors, Na_2SiO_3 and Na_2SiF_6 as mixed inhibitors, and produced a high grade concentrate containing 68.48% REO and medium grade containing 38.60% REO. The total recovery of rare earth elements is 81.05%.

Weathered Crust Elution-deposited Rare Earth Ore

The generation of the weathered crust elution-deposited rare earth ore could be due to weathering processes of the granite and volcanic rocks which were rich in rare earth. The ore deposit is shallow and the mineral particle is loose and fine. More than 80~90% of the rare earths are

adsorbed on the clay minerals of kaolin, halloysite and hydromica as hydration ions and hydroxyl hydration ions. It is not extracted by water and alcohol, but can be extracted in electrolyte solution (NaCl, $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NH_4Ac etc) through ion exchanging and it is a reversible process.

In 1970s, China had begun to exploit and utilize the ion-absorbed type rare earth ore. After over twenty years development and substantial practice of production, in-situ leaching has been partly utilized in which the electrolyte solution is directly permeated into ore body underground, after removing impurities, adjusting pH value, precipitating with oxalic acid (or other precipitating agents) and roasting etc., a rare earth mixture containing REO over 92% is obtained. Separating the solution which has been removed impurities in factory, the necessary rare earth product can also be obtained [26]. Compared with the heap leaching technology, there are many obvious advantages of in-situ leaching technology such as a high recovery ratio of RE resources (75%), a low cost of production, and especially a great decrease in environmental pollution and ecological destruction. Using heap leaching technology to producing one tonne of RE product, 200~800 m³ of the surface area would be exploited, and 1200~1500 m³ of ore would be mined and left on the surface, all of which is not needed in in-situ leaching.

The geological structure and subsurface drainage of weathered crust elution- deposited rare earth mines are complicated. Different leaching processes should be appropriately used in accordance with the structure of deposits. It is suggested that the in-situ leaching technology can be applied only in an orebody with solid bedrock without fissures or cracks otherwise, the leaching agents may leak away and pollute the ground water. Therefore, it is appropriate for an orebody without a solid bedrock to select the heap leaching technology combining with land leveling and tailings-reclamation [20, 25].

Conclusions

Rare earth resources in China have the characteristics as follows:

1. The resource distribution features light rare earths mainly in the north and heavy rare earths in the south. Light rare earth ores mainly occur in Baotou, Inner Mongolia, and Sichuan Liangshan. Weathered crust elution-deposited mid-heavy rare earth ores mainly distribute in Jiangxi Ganzhou, Fujian Longyan and some other regions in the south;
2. The industrial categories of rare earth minerals are abundant, including bastnaesite, monazite, ion-adsorbed minerals, xenotime, fergusonite and so on. The RE resource is varietal and covers every RE element. The weathered crust elution-deposited mid-heavy rare earth ore play an important role in the world;
3. There are various enrichment and extraction technologies for the rare earths that should be reasonably applied according to the different characteristics of the RE deposit and form of the RE mineralization.

Acknowledgements

Financial support for this work from National Natural Science Foundation of China (no. 50974098, 51274152) and Changjiang Scholars and Innovative Research Team in University (no. IRT0974) is

greatly appreciated.

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