POLITECNICO DI TORINO

MASTER OF SCIENCE IN PETROLEUM AND MINING ENGINEERING

MASTER’s DEGREE THESIS

Title

The impacts of the world transition to electrical energy: the role of rare earth minerals mining

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Abstract

A comprehensive literature review of the rare earth minerals is provided in this document. The topics covered are different processes from the mining of the ore to the production of the market valued product. The document provides an introduction of REE, the geological environment in which they exist and their chemical form of existence. The distribution of the reserves and the recoverable REEs are highlighted in this work.

An overview of the mining methods used for the extraction of rare earth ore from the ground is also discussed. The processing of extracted ore like beneficiation, separation and chemical treatment are enlightened. A brief discussion on the importance and uses of the REEs is done. The possible harmful effects of the different processes throughout the life cycle of REEs on the environment are also discussed. The prospects of recycling of REEs from scrap are explored which can help solving the supply issues. A geopolitical context of REEs trade is also discussed in this document.

The growing concerns from environment-related organizations and local populations of the area where REEs are mined and processed due to the damages that it causes to the ecology of the area is also presented. It is supported by the wrong practices of some mines during the past and the problems that were encountered as well as the damages that occurred to the local resources are looked at. It also provides an overview of the best practices and remedies to avoid the problems.

The document highlights the advantages and disadvantages of the REEs in technological sectors: new technological advances in the extraction processes provide much better and efficient recovery of the REEs with very minimal ecological and environmental damages. This can be achieved by setting high standards of safety and by constantly upgrading the infrastructure with technological and instrumental advances.

Acknowledgements

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I would also like to thank all my friends and family who supported me spiritually in this time of need. I would like to thank them for believing in me. In the end, I would like to pay my regards to my colleagues of Politecnico Di Torino for the affection they showed throughout.

Summary

Introduction

REE is a group of 17 elements. They show strong contradiction and similarities in physical and chemical properties at the same time. The group that occurs together in the periodic table contains Yttrium, Scandium, and 15 other lanthanide elements. They are often found together in the geologic deposits due to similar properties. As many of them are sold as oxides, they are often termed as rare earth oxides. Despite being similar in many ways there cannot be one to one substitution between them. This difference allows us to use them in a huge range of applications [1].

In the past few years, rare earth elements have come to limelight with increasing scientific and public interest. They find extensive usage in climate-friendly systems like electric vehicles, energy-saving lamps, or wind turbines. The usage of REE has helped reduced the size and weight of the structures and has also helped in increasing efficiency. Apart from this, they are significant to the medical and defense sectors.

For several years China had a monopoly as the sole producer and supplier of REE. It has controlled trade and prices of REE but now the situation is changing. For example, according to the US Geological survey, REE has a static range of more than 850 years. The name “rare” can be misleading as they are abundant in the earth's crust [2].

In this thesis, we will try to cover geological, geopolitical, and economical aspects of REE mining and their effects on the transition towards green energy. According to United States Geological Survey, the current gap between demand and supply of rare earth minerals is because the world production is short. We have enough resources to meet the current demand. The availability of rare earth minerals also depends upon mineralogy for example Cerium has a similar abundance to copper at 60-70 ppm. If we have rich ore bodies, mining and processing of elements become easier. In the first part of the thesis, geological occurrence and mineralogy of the reserves of REE across the world are discussed. REEs are discussed as economic commodities. Their price trends and market values are assessed.

In the second part, we discuss technical and environmental issues related to the processing of the ores. Processing of ores begins with deposit exploration and is followed by the mining of the ores. Extracted product from mining is subjected to beneficiation process which increases the concentration of the desired product. Beneficiation is followed by the chemical treatment of the ores. After chemical treatment, the ore is subjected to the separation and refining steps before being ready for the sale in the market. Technologies and practices used throughout the processing are of focus in this part. Environment-related issues associated with the processing of the ores and their remedies are studied. Energy requirements for the REE processing and mining and subsequent usage of local resources like water etc are discussed. The economics involved in this process are studied.

There are currently only a few operating mines for rare earth element extraction despite the identification of about a thousand deposits around the world. There are 34 countries with rare earth elements reserves. At present, 55% of the rare earth deposits are in China. As a result, China, provides 95% of REE to the world. The availability is currently undergoing a decrease because of the quotas forced by the China to control the illegal mining operation and exports. Prices increased by it have come under control, but the situation will likely remain uncertain until the former mines are opened, or new sources become operational. The world is looking for alternatives to decrease this gap in supply and demand. Several solutions to this problem have been presented. Most promising and the environment-friendly being the recycling of the REE. In this part, political, technical, and geological problems related to the supply and demand of the REE are studied.

Abundance Of REE

The word "rare" is often misleading that these elements are rare contrary to the fact these elements are more abundant than gold. According to International Union of Pure and Applied Chemistry they are a 17 elements group. They are Scandium (Sc), yttrium(Y), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Th), ytterbium (Yb), lutetium (Lu). The last 15 are defined using lanthanides or sometimes as lanthanoids. The word "oid" is to state that they behave the same whereas "id" defines a specific chemical structure. They are further divided into the HREE (Heavy Rare Earth Elements) or LREE (Low Rare Earth Elements) [3].

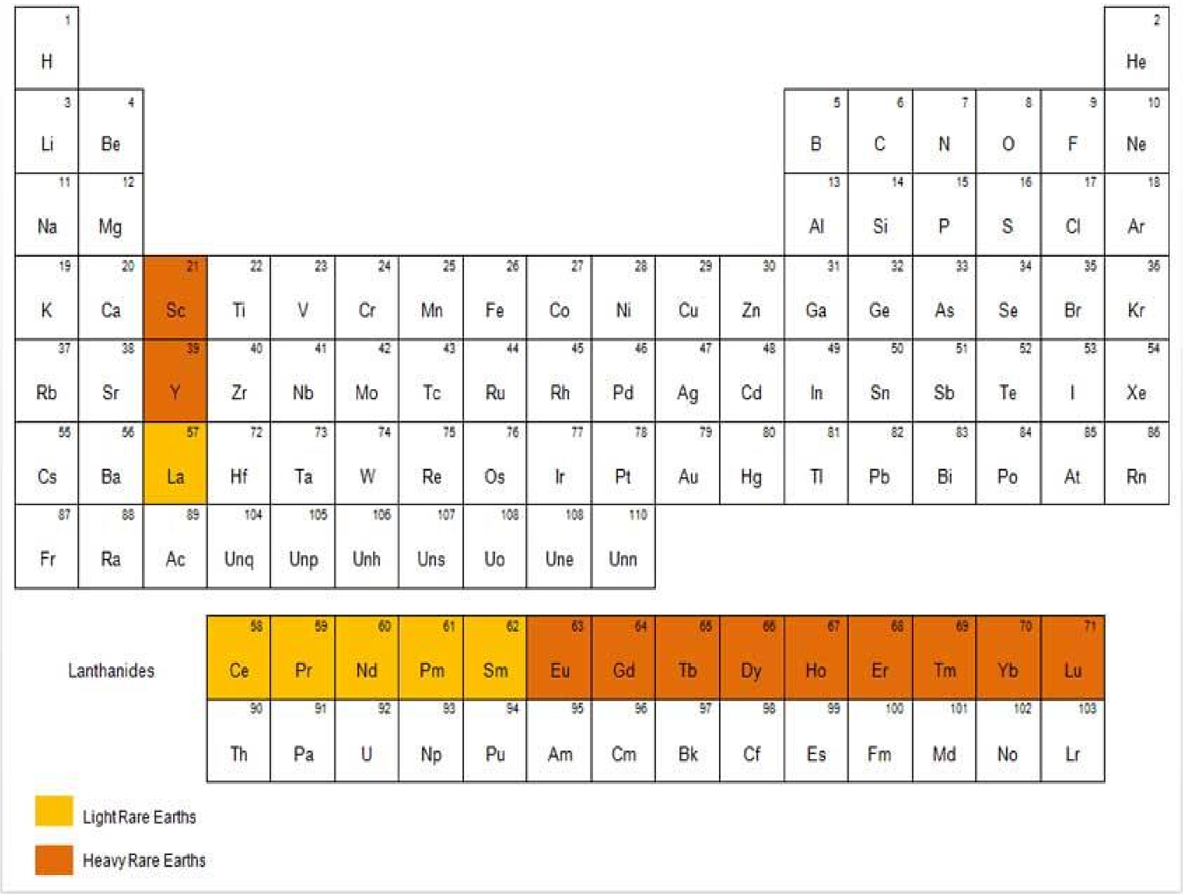

Figure 1 Schematic representation of the Periodic Table of elements

If we perform analogy of the word REE, the part "rare" comes from the 15th Century. According to Reiners (2001), from the 15th century, the term rare was used to describe something astonishing, extraordinary, and strange. He believes that the word rare is in the name because of this fact as these elements are not rare. The easiest part is to explain the word "Earth". To denominate an oxidic material, the word earth was used. Another explanation can be from the German word "Erden" which is often mistaken for quarry and pit industry material. Cerium is the most abundant REE having an abundance of 43ppm which is even higher than lead (11ppm) and copper (27ppm). This does not imply all REE. For instance, the crustal abundance of thulium is 0.28ppm. Heavy REE is relatively rare as compared to Lighter REE but they are more economic importance [4].

The table explains chondritic and average abundances of REE (μg/g) [5].

Elements	**Taylor and Melennan (1985)**	**Wedepohl (1995)**	**Lide (1997)**	**Chondritic Abundance**	
				Wakita et al. (1971)	**Pourmand et al. (2012)**
Lanthanum	16.0	30	39	0.34	0.2469
Cerium	33.0	60	66.5	0.91	0.6321
Praseodymium	3.90	6.7	9.2	0.121	0.0959
Neodymium	16.0	27	41.5	0.64	0.4854
Samarium	3.51	5.3	7.05	0.195	0.1556
Europium	1.11	1.3	2	0.073	0.0599
Gadolinium	3.31	4	6.2	0.26	0.2093
Terbium	0.61	0.65	1.2	0.047	0.0378
Dysprosium	3.71	3.8	5.2	0.30	0.2577
Holmium	0.81	0.81	1.31	0.079	0.0555
Erbium	2.21	2.11	3.51	0.22	0.1668
Thulium	0.31	0.31	0.53	0.033	0.0263
Ytterbium	2.21	2.0	3.21	0.23	0.1696
Lutetium	0.31	0.351	0.81	0.035	0.0258
Yttrium	20.0	24	33	-	1.395
Scandium	30.0	16	22	-	5.493
Total	**137**	**184.3**	**242.ww**	**-**	**9.5118**

Table 1 Chondritic and average abundances of REE

Country-wise distribution of REE Reserves

They are quite abundant in the earth's crust but are not always minable. There are three main stages for developing an REE deposit. The first stage is the discovery of the resource. In the second stage, we explore the discovered resource. In the final stage, we have produced. Out of 851 discovered rare earth element deposits, only a few have been developed as a potential source and are in the production phase while most are still in the first phase. As a result of the disruption of REE supply, many companies started to explore potential REE reserves. As of 2017, 178 deposits have been developed and identified. 59 projects have gone into productions based on feasibility results. The current amount of REE reserves around the world stand at 478 Mt REO according to the data published. China contains 164 Mt whereas Greenland, Brazil, Russia, and Australia have 43 Mt, 55 Mt, 48 Mt, 49 Mt respectively of the total reserves. Remaining 119 Mt is in the USA, Sweden, Vietnam, Canada, and other countries [6].

The following graph shows the latest world status regarding REE reserves according to United States Geological Survey report published in 2019 in Tons.

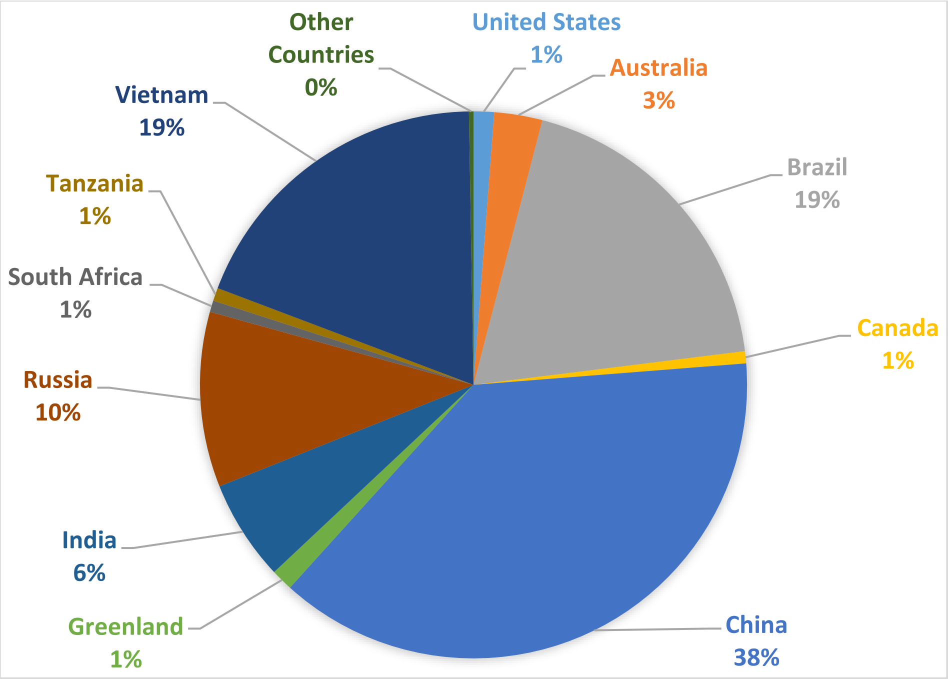

Figure 2 Distribution of reserves[7].

Below, is a brief breakdown of the reserves of each country:

1. China

88% of the Chinese deposits are in the three mining areas including Baotou, Sichuan, and Jiangxi. Bayan Obo is in Mongolia and is accountable for 83 percent of the country's total deposit and is affiliated to the Baotou region. Southern deposits and Sichuan province Accounts for 3% each of the total whereas the rest of the deposits are dispersed throughout the country [8].

The largest mine Bayan Obo is a huge REE-Fe-Nb polymetallic deposit. Niobium and rare earth elements are by-products from the mine. Monazite and bastnaesite minerals are present with Nd, La, and Ce contents. Bastnaesite and monazite are about 50% Ce_2O_3, 26% La_2O_3,16 % Nd_2O_3, 5% Pr_2O_3, 1%Sm_2O_3 and the remaining REE accounts for 1% each. Mianning, Sichuan has located 5 carbonatite deposits. They are 37% La_2O_3, 47% Ce_2O_3, 4% Pr_2O_3, 10% Nd_2O_3 and all others below 1% [9]. Sichuan region lies in potential earthquake regions therefore additional dangers from tectonics are kept in mind.

Lateritic clays containing REE are found in southeastern China where mining products are Lutetium, Yttrium, and Scandium. Studies suggest that by 2025, this reserve will be depleted which makes xenotime deposit in Guangdong as the only deposit with heavy rare earth as their primary product. Further research is being conducted in the Tsagaan region for potential REE reserves [10].

2. India

Indian Rare Earth Limited operates 4 units, the Chavara Mineral Division, Orissa Sand complex, and the Manavalakurichi Mineral Division. All three units are working on mineral sand deposits. 4th unit is located Aluva where monazite produced from one of the three units is processed. Different grades and states of REE products including Ce, Nd, Pr, and Sm are offered. REEs are not the main products. The main products are thorium and uranium in mantle grade. Despite USGS enlisting India as the REE producer with constant REE production of 2700t annually, there is no proof and validity of the provided data [7].

3. Brazil

Brazil has five main locations in the southern and southeast regions which have rich REE sands besides being rich in thorium and uranium. The locations are named Cumuruxatiba, Guarapari, Buena, Sapucai, and Mato Preto. The problem associated with monazite mining is because of the presence of radioactive material. These radioactive materials have not been treated cautiously which often leaves behind polluted sites requiring remedial actions. But things are progressing as today, the mining of monazite is being conducted under Industrias Nucleares do Brazil (INB), the national atomic agency of the country [11]. As per USGS records, Brazil produces 1000 tons of REE per year, but it does not state the percentage of individuals.

4. Russia and Central Asian Countries

Several sources list Russia and CIS as REE producers and potential deposit bearer despite any reliable data availability. Afrikanda complex, Koala peninsula being the potential reserve sights along with eastern Siberia located Tomtor Massif. The Tomtor massif site has three possible locations of the REE deposits. These all three positions lack infrastructure and are located on the permafrost soil and if these potential reserves are to be exploited, the weather and logistics are going to play an important role. No reliable data is available for Kyrgystan and Kutessay's possible deposits [12][13][14].

5. Australia

In 2018, Australia produced 0.019Mt of rare earth elements. Mount Weld mine in Western Australia produced 18556t of REO. Lynas Corporation’s Advanced Materials Plant in Malaysia process the concentrates from Mount Weld to produce REO products. Northern Minerals limited produced 2.6tons of rare earth carbonates from Brown range project in the Kimberley region of Western Australia. These produced Carbonates were exported to China. Several projects are developing throughout the country to enhance the production of REE. Currently, Australia Produces 3000 tons of REE through mining [15].

6. USA

United States of America was the leading REE producer outside China from 2012 to 2015 due to the mine production from Mountain Pass mine in San Bernardino County, California which belongs to Molycorp Inc’s. The company had a vision of production capacity of 19000 metric tons of REOs but due to a substantial decrease in the prices in 2015, idled the production. Exploration and development projects are underway throughout the country. According to an estimate, domestic REOs production in the country has reached 1.8 million metric tons [16].

7. Malaysia

Cassiterite mine in the states of Perak contains REE bearing minerals in the tailings. The mine is referred to as “amang” by the Malaysian mining industry had a production of about 500 metric tons per year. With 30,000 metric tons of REO, Malaysia’s reserves constitute less than 1% of the world reserves [16].

According to USGS, there has been an increase of 11% in REE mine production in 2019 compared to 2018. The production stands at 210,000 tons of REE oxide equivalent. China dominated most of the production and therefore supply of REE. The following graph shows the mine production of REE as of the year 2019 in Tons [7].

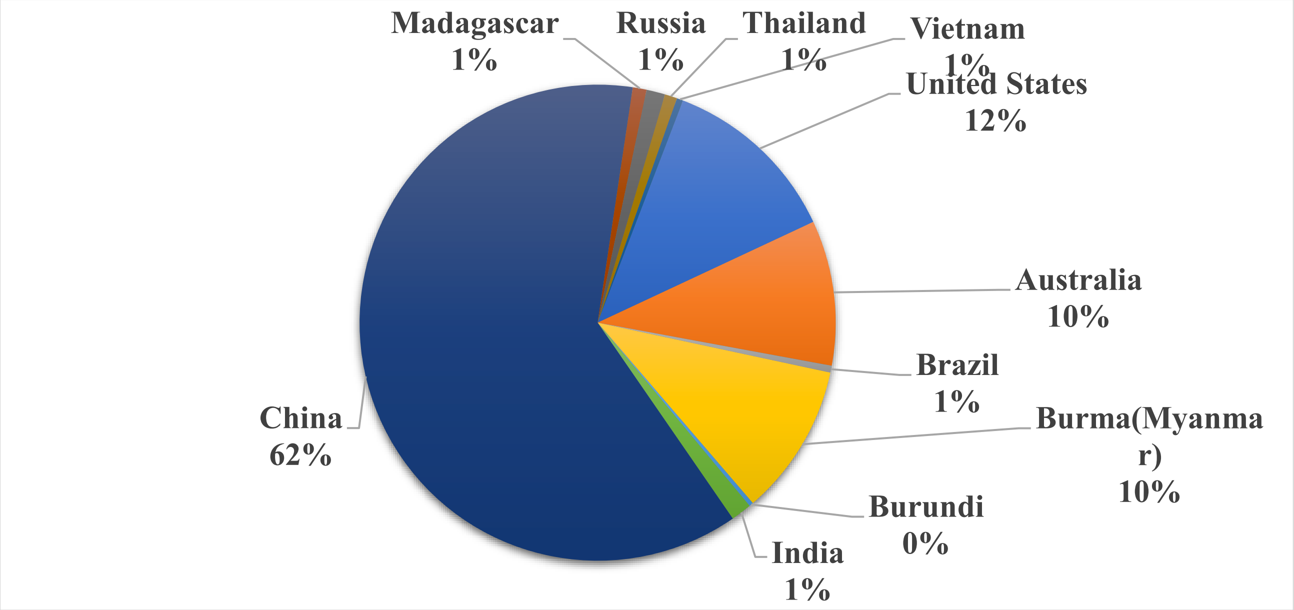

Figure 3 Production of REE in different countries[7].

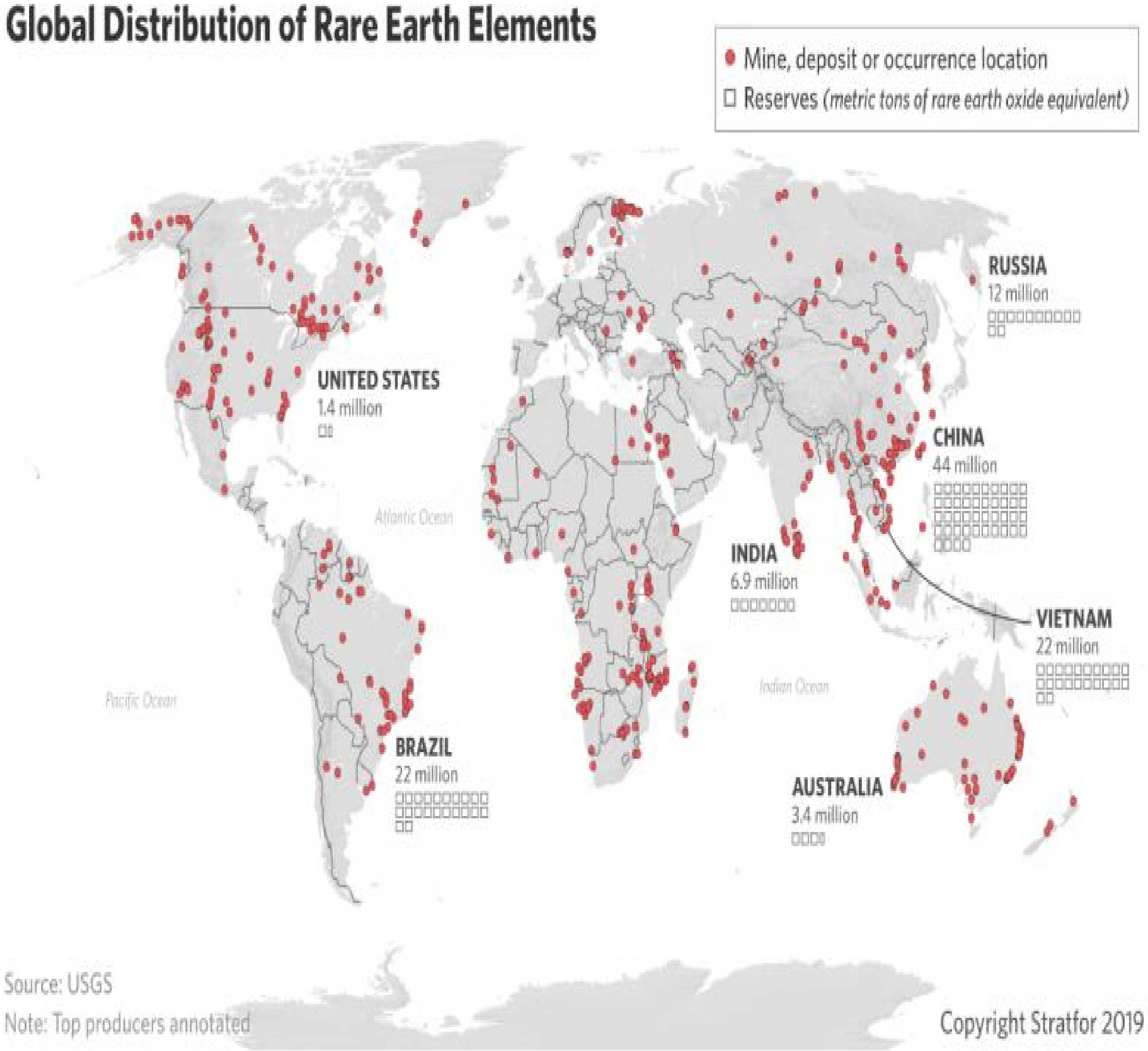

Figure 4 Global Distribution of REE reserves courtesy (Source: USGS)

Minerology of Rare Earth Elements

Rare earth elements are reactive and due to their reactivity and are found as ores unlike silver, copper and gold. They can be major or minor constituent of the ores. Even though they can be found in a wide range of minerals with some of them being the most common like phosphates, oxides, carbonates, and silicates, they are found in a limited geological environment. REE can be found in over 250 minerals. Monazite, bastnaesite, lateritic ion absorption clays, and loparite are the key sources of rare earth element containing minerals in terms of economics. Biotite and amphiboles also host a small amount of REE [17].

REE-bearing mineral deposits are mostly dominated by LREE (Light Rare Earth Elements) and HREE (Heavy Rare Earth Elements). Both can contain each REE. In some zones, abundance can reach more than 10% of the volume. In alkaline igneous complexes, pseudomorphs of pre-existing phases are produced due to late magmatic to hydrothermal overprinting of the primary minerals. This mineralization normally contains a variety of rare earth element-bearing minerals that exhibit complex texture. But not all the mineral reserves can be exploited due to economic problems. As listed in the table, the economically feasible minerals are monazite, xenotime, synchysite, loparite, bastnnäsite, parasite, and eudialyte. Bastnäsite, xenotime, and monazite are mostly associated with REE-rich minerals. Xenotime is the main source of Yttrium and Heavy rare earth elements. LREE dominates monazite and Bastnäsite. The problem with other minerals is that either they are difficult to extract REE from or they are sparse. In alkaline igneous rocks, the grain size varies from coarse-grained to fine-grained.

Table 2. Names and formula of the REE bearing minerals [17].

Mineral	**Formula**	**Approx. TREO (wt%)**
Allanite	$(Y, Ln, Ca)_2(Al, Fe^{3+})_3(SiO_4)_3(OH)$	39.0
Apatite	$(Ca, Ln)_5(PO_4)_3(F, CL, OH)$	19.0
Bastnäsite	$(Ln, Y)(CO_3)F$	75.0
Eudialyte	$Na_4(Ca, Ln)_2\ (Fe^{2+}, Mn^{2+}, Y)ZrSi_8 0_{22}(OH, Cl)_2$	9.0
Fergusonite	$(Ln, Y)NbO_4$	53.0
Gittinsite	$CaZrSi_2O_7$	
Limoriite	$Y_2(SiO_4)(CO_3)$	68.0
Kainosite	$Ca_2(Y, Ln)_2Si_4O_{12}(CO_3).H_2O$	38.0
Loparite	$(Ln,Na,Ca)(Ti,Nb)O_3$	30.0
Monazite	$(Ln, Th)PO_4$	65.0
Mosandrite	$(Na, Ca)_3Ca_3Ln(Ti, Nb, Zr)\ (Si_2O_7)_2(O, OH, F)_4$	33.0
Parisite	$Ca(Ln)_2(CO_3)_3F_2$	61.0
Pyrochlore	$(Ca, Na, Ln)_2Nb_2O_6(OH, F)$	
Rinkite (rinkolite)	$(Ca, Ln)_4Na(Na, Ca)_2Ti(Si_2O_7)_2(O, F)_2$	20.0
Steenstrupine	$Na_{14}Ln_6Mn_2Fe_2(Zr, Th)(Si_6O_{18})_2(PO_4)_7.3H_2O$	31.0
Synchysite	$Ca(Ln)(CO_3)_2F$	51.0
Xenotime	YPO_4	61.0
Zircon	$(Zr, Ln)SiO_4$	4.0

Table 2 Names and formulas of REE-bearing minerals.

Types of REE Deposits

Based on economics these are the types of rare earth element deposits[16]:

1. Alkaline Igneous Rocks

Deep mantle rocks melt partially and rise, cooling of this molten rock within earth crust form alkaline igneous rocks. Zirconium (Zr), Niobium (Nb), Strontium (Sr), Barium (Ba), and Lithium (Li) are also found in alkaline magma along with REE. Ascending magma experiences changes in temperature, pressure, and the surrounding rock chemistry which forms a great variety of REE deposits. Ytterby in Sweden, Bayan Obo (China), and Mountain Pass (California, USA) are the prime examples of alkaline igneous rocks. Chinese Bayan Obo has about 80% of the world's igneous alkaline deposit. LREE values ranging between 896.17 µg/g to 1265.85 µg/g and HREE ranging from 62.98 µg/g to 82.92 µg/g have been identified in carbonatite of ultramafic-alkaline-carbonatite Complex in Northeast India [17].

2. Residual Deposits

Deep weathering of pegmatites, copper-gold, igneous rocks, and iron-oxide results in residual deposits. Some studies suggest the formation of concentrated residual REE mineral deposits from intense weathering of peralkaline intrusive and carbonatite. Ion absorption ores are located in China only, fall under this category.

3. Carbonatites

There is a wide range of forms and carbonate compositions for carbonatite intrusion. They can be irregularly shaped masses, veins, dikes, stocks, and tabular bodies in terms of form. Whereas composition varies from calcic to dolomitic or siderite. As proven from geochemistry, a single region can have various distinct events of magma interruption which results in carbonatite masses having different chemistry and mineralogy. Monazite, ancylite, Synchysite, parisite, and bastnaesite are the principle REE ore minerals in carbonatites. Carbonate minerals are the non-ore minerals. Non-ore minerals can be accompanied by fluorite, hematite, magnetite, and quartz.

4. Magmatic magnetite-hematite Bodies

REE-bearing minerals can be found in this type of environment. They may not be the primary product but can be iron mining by-product. The main examples can be Pea ridge iron district deposit located in southeast Missouri and New York’s Mineville iron district in the upstate.

5. Iron Oxide-copper-gold deposits

They can be argued to be the same as Magmatic magnetite-hematite Bodies with slight modifications. They can be described as a magmatic-hydrothermal iron deposit that contains potential REE ores of economic value along with gold and copper. IOCG was first discovered in 1975 in Olympic Dam copper-uranium-gold deposit in South Australia. These types of deposits can extend for several Kilometers.

6. Ion Adsorption Clay Deposit

This type of deposit also known as "South China Clays" is the main source of heavy rare earth elements located in southern China. They are usually located in tropical region with moderate to heavy rainfall. They follow the process described as below:

I. From the bedrock(granites), the ground leaches REE.
II. Granites are covered in laterite soil and contain an abundance of clays.
III. In the soils, as a result of ion absorption, the REE are weakly fixed onto the clays [18].

The following graph shows the distribution of reserves by type:

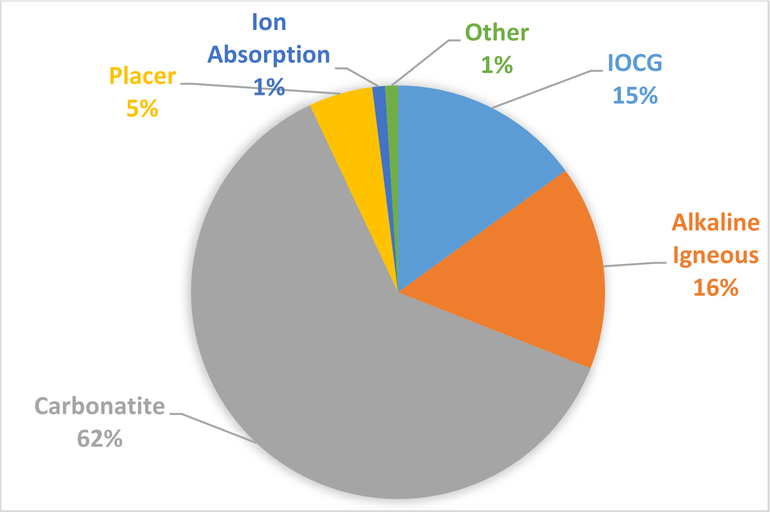

Figure 5 Distribution of reserves based on types[17].

The following table describes active rare earth mines by deposit type[16]:

Deposit	**Location**	**Reported Resource (Mt)**	**Reported Grade in weight percent**
Carbonatites			
Bayan Obo	Nei Mongol autonomous region, China	805	6.4
Daluxiang (Dalucao)	Sichuan, China	15.5	5.2
Maoniuping	Sichuan, China	50.5	2.90
Weishan	Shandong, China		
Mountain Pass	California, United States	17	8
Mount Weld	Western Australia, Australia	24	8
Pre-alkaline igneous			
Karnasurt Mountain, Lovozero deposit	Northern region, Russia	-	-
Heavy Mineral sand			
Buena Norte mining district	East coast of Brazil	-	-
Ion-Adsorption clay			
Dung Pao Mine	Vietnam	-	-
South China Clay Deposits	Jiangxi, Hunan, Fujian, Guangdong and Guangxi provinces, Southern China	-	0.07 to 0.6

Table 3 Active rare earth mines around the world

Continental shelf and land have similar mineral resources. It is possible that the minerals eroded from land may end up on the beaches and farther offshore. The table gives REE range in µg/g

Ocean	REE range(µg/g)	Matrix
Alfansay Nikitin Seamount in Eastern Equatorial Indian Ocean	1727-2511	Cobalt Crust[19]
Mid-Pacific Seamount	2085	Cobalt-Rich Crusts[20]
Indian Ocean	930-1572	Ferromanganese Crust[21]
Indian Ocean	920	Marine Mud
Scotia Sea	3400	Ferromanganese Crust
Eastern South Pacific	1005-2225	Deep-sea mud[22]
North Pacific (east and west of Hawaiian Islands)	403-1005	Deep-sea mud[22]
Mid-Pacific Ocean	1180-1435	Iron Magnesium nodules[23]
Pacific Ocean	1400	Shallow water Mn [24]
Pacific Ocean	1330	Deep-sea Mn [24]

Table 4 REE ranges in different environments.

Processing of REE

Following diagram explains the overall steps for processing of rare earth elements.

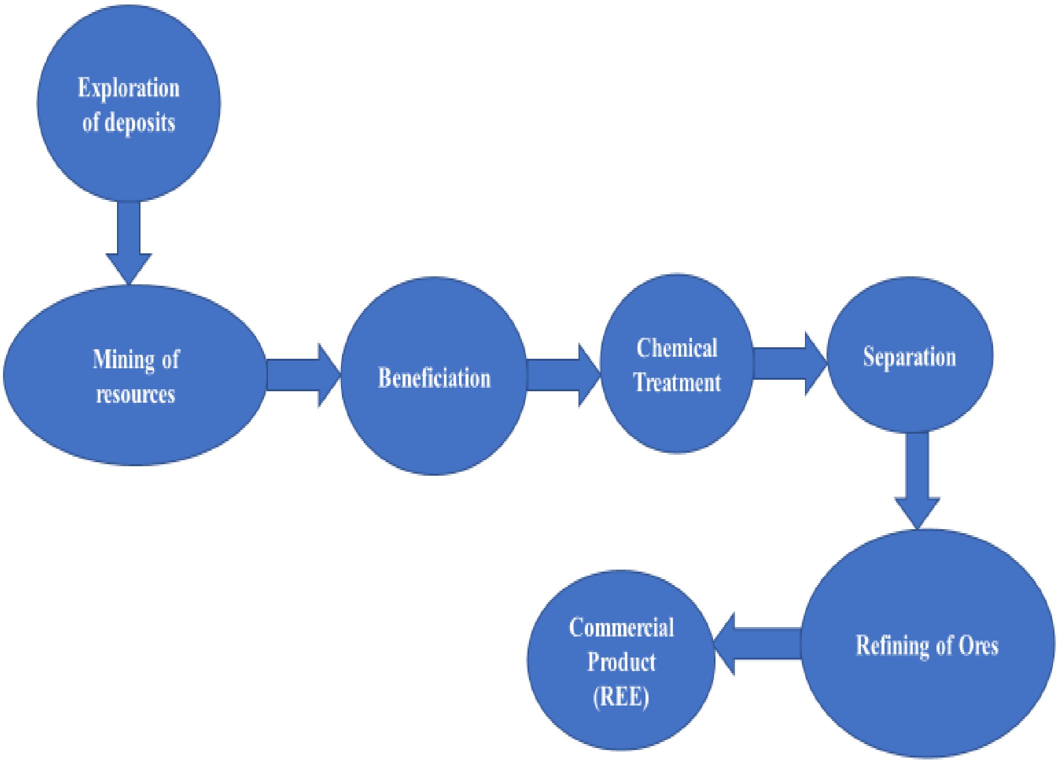

Figure 6 Processing of REE

Here we define each process in detail and in the sequence in which they occur [25].

1. Exploration of Deposits

The exploration begins with the identification of possible rare earth elements deposits that are of economic value. Because of the expensive geophysical surveys, most companies opt for geochemical sampling of the possible reserves. This can be accomplished in one of the two possible activities[26][5]:

- Brownfield Exploration
- Greenfield Exploration

There are still arguments to be made about which one is better. Some studies suggest that brownfield exploration is less risky than greenfield exploration method.

Greenfield exploration involves five further steps which are as follows:

- We have evidence from mineralogy that they often exist with radioactive elements, therefore the first step is to study radiation.

- The second step involves use of magnetometer to detect magnetism because evidence show that REE often exist with iron deposits.
- The third step involves studying the disparities in the magnetic field which can identify different densities in the earth crust.
- Fourth step involves satellite photography. Satellites are used to snap the footages of the area of the deposit.
- In the last step, geologists employ geological mapping which can be used to look out for structures bearing REE located in the area.

Following table explains the summary on brownfield and greenfield exploration:

Category	Description
Greenfield Exploration	This type of exploration involves greater risk because it is used for the prediction of new area. There are further two types: • This type utilizes different methods to confirm the mineral deposit. This is referred to as Grassroot Exploration Project. It can cost around above 10 million US$. • In this type, we ensue to drilling because the mineral deposit has been confirmed. It can cost around 100 million US$.
Brownfield Exploration	This activity involves very low risk an economics as it is employed on already existing or producing mine.

Table 5 A comparison of brownfield and greenfield exploration methods

Once the geological, environmental and safety standards are fulfilled, mining process begins.

2. Mining of the Deposits

Most common mining techniques are:

- Surface Mining
- Underground Mining
- In-Situ leaching

1) Surface Mining

This is the most common technique employed to extract the minerals from the earth. Open pit mining is employed when the ore body lie near the earth surface. This technique is used when the overburden rock is week or unstable for tunneling. Sometimes, it is difficult to retrieve mineral due to hard rock, so we go for open pit mining. The overburden rock body is removed, and the ore is exposed which is then extracted to the surface. Some pits can be about 1km deep. Mining rate can be between 20,000 to 100,000 tonnes per day. It is non-selective type of mining which means that all the zones are mined without distinguishing between grades. It is usually performed in benches that can be between 4 to 60 cm. Some mines require just a single bench whereas other can require several benches. The bench provide security against the rock falling [27][28].

There are two types of waste. The first the non-economic overburden rock that is removed to access the ore body. The second is the tailing which results from mineral separation and processing. It often requires large investment but is highly, productive, low operating cost and better safety conditions.

2) Underground Mining

Underground mining is adopted when the ore body is located at a considerable distance from the earth crust. It is economic, safe, and very little waste. To reach the ore body we build a tunnel that can be horizontal and vertical.

We use underground mining when[29]:

- It is not economical to do open pit mining.
- The ore body is of a high quality that it will cover the cost.
- It has lower impacts on the ground surface. Because open pit mining may leave permanent damage on the earth surface.

We use following mining methods:

1. Narrow Vein Stopping

Vein is a sheet like structure containing minerals. In this method we mine the underground vein and minerals are removed. We must make excavations for pump chambers, engine rooms or for access purposes.

2. Large Scale mechanized Mining

• Long-wall Mining

A long wall of ore body is mined in a single slice. They require large machine.

• Sub-level caving

Explosives are used to blast levels of ores.

• Block Caving

This method utilizes gravity to extract the ores after being blasted by explosives.

1) In-Situ Leaching

In-Situ leaching is a mining process that utilize dissolving a solid deposit and recovering it in the form of solution. The first step is drilling bore holes that can be done with the help of explosives or hydraulic fracturing to create pathways to reach the deposit. The leaching solution is pumped into the ore body which dissolves the solid ore body and this ore bearing solution is extracted back to the surface. This method can be used to extract salts and minerals without employing traditional mining methods.

It should be noted that lixiviant is pumped into the ore body through a borehole that circulates and dissolves the ore from porous media and is recovered from a secondary borehole. Lixiviant is dependent on the rock body and varies accordingly [30].

3. Beneficiation

The process involves physical separation of valuable constituents of the ore. This method decreases the impurities and increases the concentration of the ore material. It contains a sizing unit, separator unit, and dewatering of the minerals.

The first step of the process is scrubbing which utilizes water to make the ore ready for crushing and grinding. What follows crushing and grinding is gravity separation [31].

A. Gravity Separation

Gravity separation is often the first technique when there is a huge difference between the specific gravities of the main and the gangue minerals. The reason for it being cheap is it is quite cheap and highly efficient [32].

The reasons for employing gravity separation process are as follows:

- As a pre-concentration increase, it reduces the waste material.
- To recover heavy mineral after crushing and grinding which otherwise are quite difficult to recover.
- To decrease the downstream processing cost by increasing heavy metals concentration
- It decreases tailings.
- It can sometimes create commercial products that can be profitable without requiring further processing.

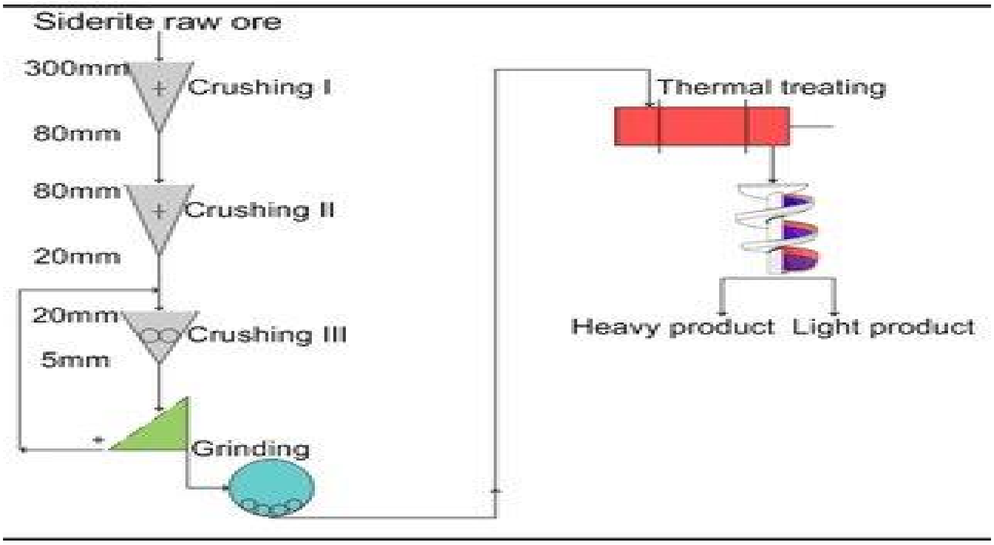

Figure 7 Gravity Separation process Flowsheet

The process is performed with air and water. It utilizes the difference of densities between two minerals to separate them. The method utilizes the relative movement of the particle in response to the gravity mainly because of the specific gravity. There is also an effect of the force of resistance to the motion due to viscous fluid. Therefore, specific gravity plays an important role in the separation. It should also be noted that the density difference between the gangue and mineral is important for effective separation. Because of the density difference, the separation much better with water. But dry dressing also offers an advantage that it does not require dehydration at the end of the process [33].

B. Magnetic Separators

There are two general usage categories of magnetic separators that are the refinement of feeds containing magnetic minerals and the concentration of magnetic minerals. The aim in the first process is to remove magnetic minerals as they are undesirable whereas in the second case magnetic minerals are separated as the prime product.

Magnetic separation techniques have been used quite commonly in rare earth bearing minerals such as xenotime or monazite. Scientific research on the minerals shows that they exhibit a 4f sub shell electronic configuration which means that they exhibit electromagnetism. There is a specific research to calculate magnetic capabilities of individual rare earth element depending upon their chemical compositions. The results suggest that xenotime has more magnetic susceptibility as compared to monazite.

It is commonly used alongside magnetic separators for the beneficiation of monazite from beach sands. It can be used to separate nonmagnetic waste minerals such as rutile and zircon from the paramagnetic monazite. It can also be utilized to separate monazite just before the more selective separation methods. Since xenotime is more magnetically susceptible than monazite, it can be easily separated using this technique. However, if the grain size is less than 100µm than flotation is the only option [33].

Bastnasite rare earth ores originating from China are beneficiated using magnetic separators. It separates Fe containing minerals before further processing steps. It is stated that the Chinese have been successfully utilizing magnetic separation by combining it with gravity separation and are achieving up to 60% of bastansite from their second greatest deposit without requiring flotation. The grain size also had a significant effect on the magnetic susceptibility and therefore on the magnetic separation. The results suggest that when 80% of the grains in the feed had a size of 74µm, there was 78% recovery with grade improvement from 49g/t to 315g/t.

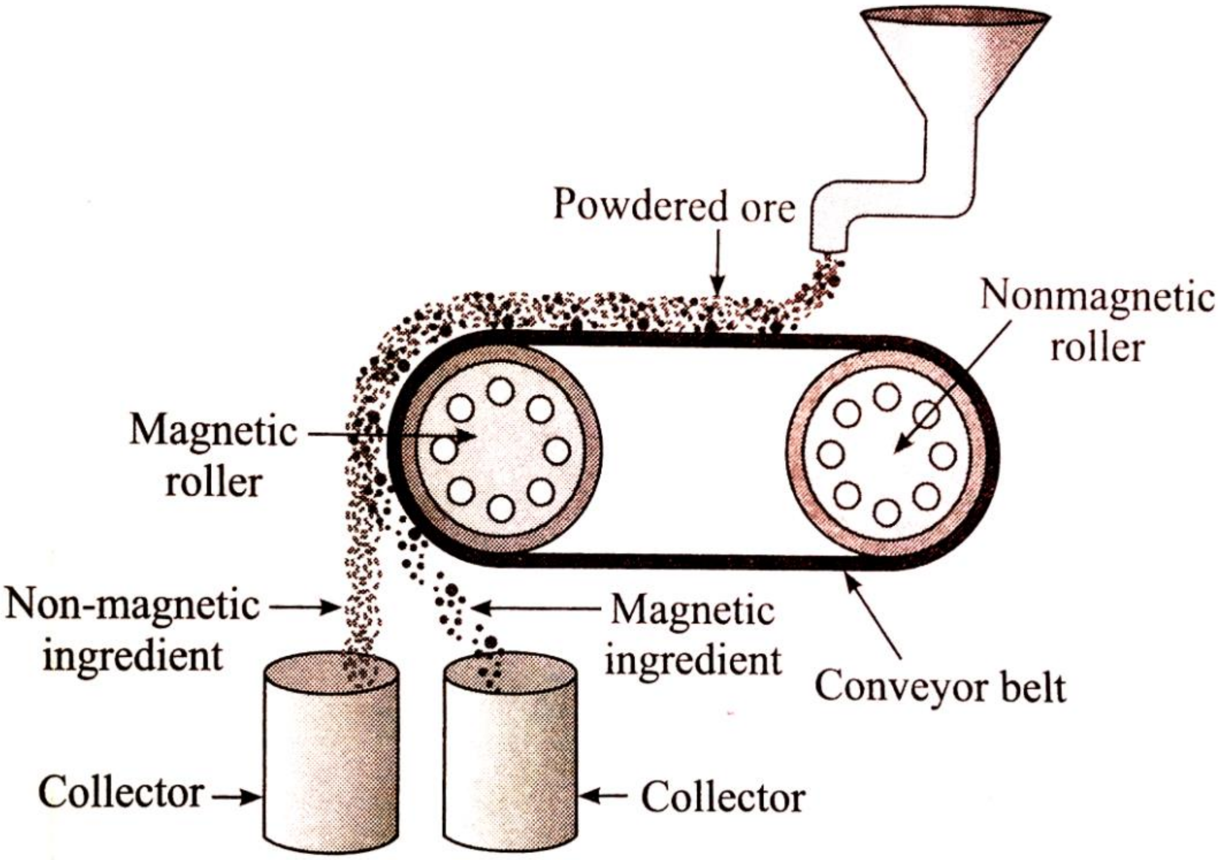

Figure 8 Magnetic Separation Process

C. Electrostatic Separation

It is employed only in case when the other techniques are not beneficial because the other process require wet feed and for electrostatic separation the feed should be moisture free. It is extremely costly to remove the moisture from the feed, therefore, it is used in special cases. This technique employs the difference in the conductivity to obtain separation. In REE mineral processing, it is used to in the separation of xenotime and monazite from gangue minerals. A more specific example is the separation of xenotime from ilmenite because ilmenite is conductive, and xenotime is not.

This can be particularly good technique for the separation of heavy mineral sand. It can also reduce losses of REE as the ultra-fine coal particles containing REE which are discarded can be recovered using this technique. The major problem that this technique presents is the condition that all feeds must be dry. Except for heavy mineral sand deposits, all feeds are required to be in the form of slurries and the energy and cost requirement for drying a particular feed is too that this technique cannot be used on the industrial scale [34].

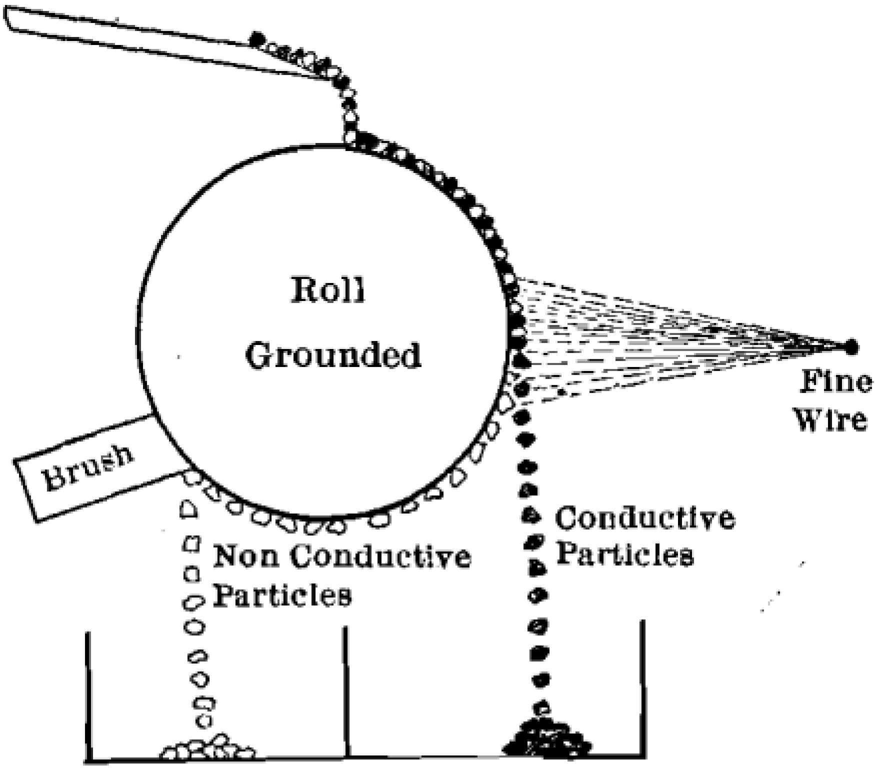

Figure 9 Simplest Electrostatic Separation Process

D. Froth Flotation

This process is quite common because of the facts that it can be applied on a wide range of particles and that it can be processed in accordance with the unique minerology of the deposit. There has been significant research related to froth flotation used for the beneficiation of batnasite and monazite.

Two of the world’s largest deposits are using froth flotation to beneficiate bastnaesite. Fatty acids, dicarboxylic acids, hydroxamates and organic phosphorus acids are used as collectors whereas lignin sulfonate, sodium carbonate, sodium hexafluoro silicate and sodium silicate are used as depressants in these situations. Fatty acids are commonly used as collectors in froth flotation of bastnasite mainly because of the availability and traditional usage of them. The problem associated with their usage is that they require significantly large volume of depressant and high temperatures to achieve separation. Chemisorption is the mechanism considered responsible for the adsorption of fatty acids on the bastnaesite minerals. The flotation is improved with the usage of hydroxamates as they form chelates that are stable on the mineral cations present on the surface. Hydroxyamide and hydroxyoxime are the two possible forms of hydroxamic acids. For the purpose of froth flotation hydroxyamide is the only acceptable form. Another advantage of hydroxamic acids is that when they are in solution, they interact with rare earth ions which can create additional sites by absorbing on to the mineral surface. hydroxamic acids effectiveness has been proved with the water hardness and decreasing pH, because a large amount of collector and hydrogen ions are consumed by Ca^{+2} and Mg^{+2} ions.

The solubility of the fatty acids increases with increase in temperature. This increase in temperature results in increasing of cation solubility and therefore increased adsorption of collector on the surface of bastanite in comparison of gangue minerals. This increase in adsorption can be explained by the fact that only bastnaesite can make transition from physical to chemical adsorption with temperature increase. To increase the efficiency of fatty acid in froth flotation process phosphoric and hydroxamic acids, petroleum sulfonate, and a secondary amine fatty acid, oil fatty acids containing high rosin, high molecular weight primary amine and petroleum sulfonate are used. These schemes have been found to reduce minimizing reagent use and reduce the cost because it avoids the processing steps necessary for heating the flotation pulp before starting the process.

The flotation process for monazite is different than that of bastansite because of the difference in the minerology of the deposits. The gangue associated with monazite minerals are rutile, quartz, ilmenite, and zircon and therefore require different flotation reagent as compared to bastansite in order to achieve a rather improved separation. Same fatty acids are used as collectors as in the case of bastansite. Therefore, adsorption of the hydroxamates and fatty acids on the mineral surface is chemical as well. Zircon and rutile are two main types of gangue minerals, and they require a depressant for the flotation process to begin with. Sodium sulfide, sodium oxalate, and sodium silicate are commonly used depressant for this purpose. Sodium sulfide and sodium oxalate can also be used to activate monazite. Sodium sulfide can be used to depress and activate zircon if added more than 10mg/l. The depression of zircon from sodium sulfide is justified by the adsorption of SH^- and S^{2-} Ions onto the mineral surfaces which reduces the metal cations and in terms reduces the potential sites for adsorption of collector.

There is very less literature data available for other REE minerals because their surface chemistry does not support the condition required for froth flotation and therefore froth flotation process is avoided for them [35].

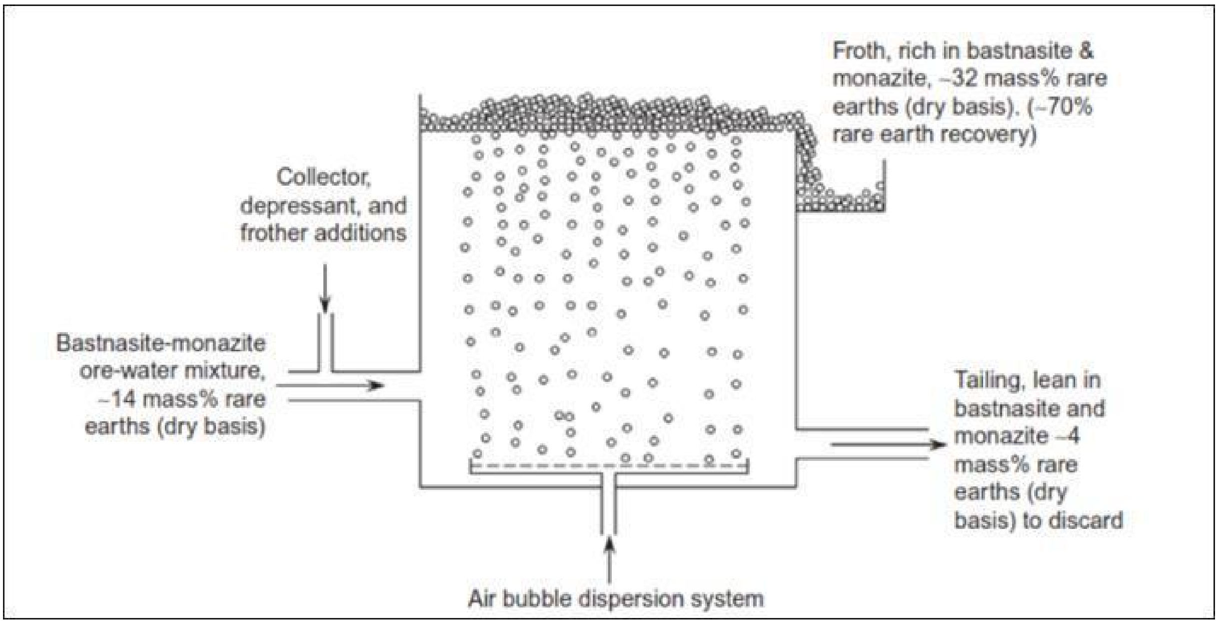

Figure 10 Froth Flotation Process

The following process represents beneficiation routes for Bayan Obo REE ores

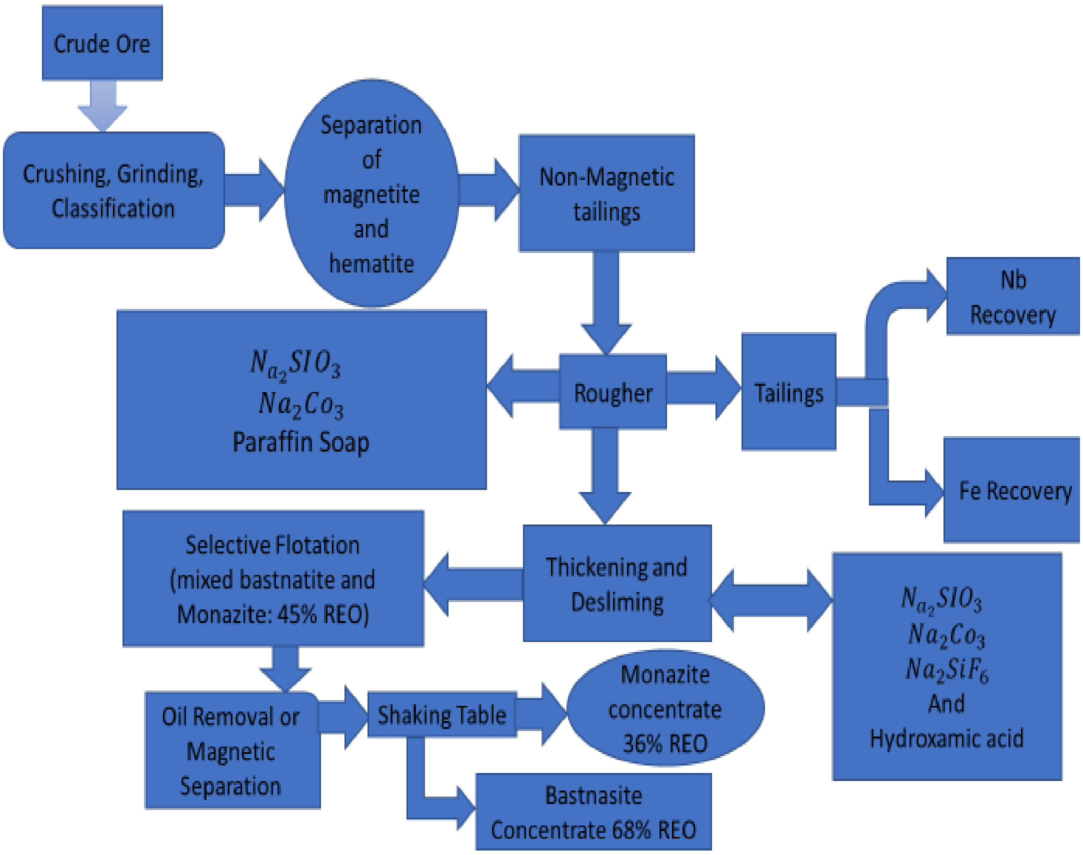

Figure 11 Beneficiation routes for Bayan Obo China [36].

4. Chemical Treatment

This is the next process which is also referred to as Cracking process. There are two main streams of the process which are alkaline and acid treatment. Both streams remove impurities and enhance the concentration of REE bearing minerals. Acidic treatment employs use of inorganic acids such as Nitric acids, Hydrochloric acids and, Sulfuric acids whereas alkaline treatment are performed using Sodium Hydroxide and Sodium Carbonate. Researchers claim that this technique is most utilized for monazite and bastansite processing because of the chemical composition of the two minerals. Chinese have been using sulfuric acid at elevated temperature to remove sulfur dioxide, sulfur trioxide, hydrogen fluoride, and silicon tetrafluoride. Two Scrubbers are used to extract dangerous gasses and are later discharged into the atmosphere. The scrubbers utilize sodium carbonate to treat the dangerous gases as it is evolved into the atmosphere.

Monazite can be treated by alkaline as well as acidic treatment. Three other elements are present in the leach solution that are ferum, thorium, and uranium. There are three additional treatments required during acid treatment which are as follows:

- Precipitation by sodium double sulphate
- Ammonia hydroxide-based neutralization
- Sodium oxalate-based neutralization

After removal of impurities and radioactive elements, four treatments can be performed in order to achieve purification by alkaline treatment which also include dissolution by nitric, sulfuric or hydrochloric acid [36].

5. Separation Process

This process is used to enhance the individual concentration of the minerals. There are mainly five separation process which are as follows[37][38]:

- Supercritical Fluid
- Biosorption
- Electro-winning
- Solvent extraction
- Ion exchange

But this process is very complicated due to the similarity of their chemical properties. One method that can be employed is fractional crystallization. It involves change of salt concentration through temperature control and evaporation. A precipitating agent is added to solution that helps in removing the metal.

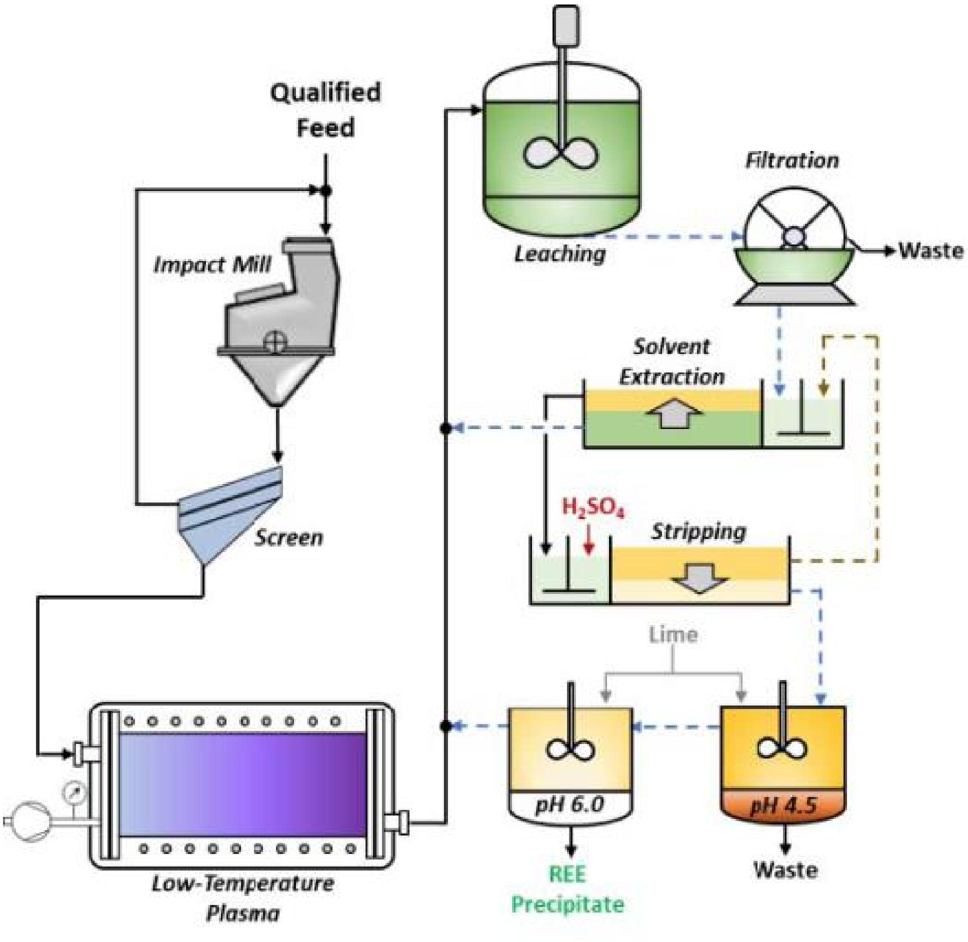

Figure 12 Separation Process of Rare Earth Minerals

Ion Exchange method produces highly pure REE but it cannot produce large quantities of it, so it is employed under special circumstances. Solvent extraction is used more extensively amongst all processes. In this process, stable complexes of metals are formed which are separated later by gravity. The first phase is organic phase which during the process is transformed to water phase. Distribution coefficient defines the liquid-liquid separation which can vary from element to element. The equation for it is the following [39][40]:

$$D_A = \frac{C_{A1}}{C_{A2}}$$

6. Refining

After separation process, the product obtained is in the form of salts that are turned into metals. The process used are metallo-thermic reduction and molten salt electrolysis. The process of refining requires large amount of electricity and time. However, it is suspected that Chinese companies can achieve 98% of purity.

The process involves REO treatment with hydrofluoric acid to form fluoride. This fluoride is treated with calcium and the liquid fluoride formed is separated from the metal. Highest quality of purity is then achieved by vaporizing the calcium residues through temperature vacuum process. Some REE have very low boiling point therefore this vaporization process cannot be used for their refining instead it is achieved by reducing the with metallic La which has very low vaporizing pressure. In some cases, barium can be used for high boiling point REE and mishmetal (an REE alloy composed of La and Ce with traces of Nd, Pr and other REE iron) can be used for low boiling point REE. Mishmetal s produced from batch process electrolysis using a graphite anode [40][41][38].

Here is full description of the production process from a plant located in Kyrgyz Republic owned by Stans Energy Corp which had a conflict with local govt and had to revise the plan [42].

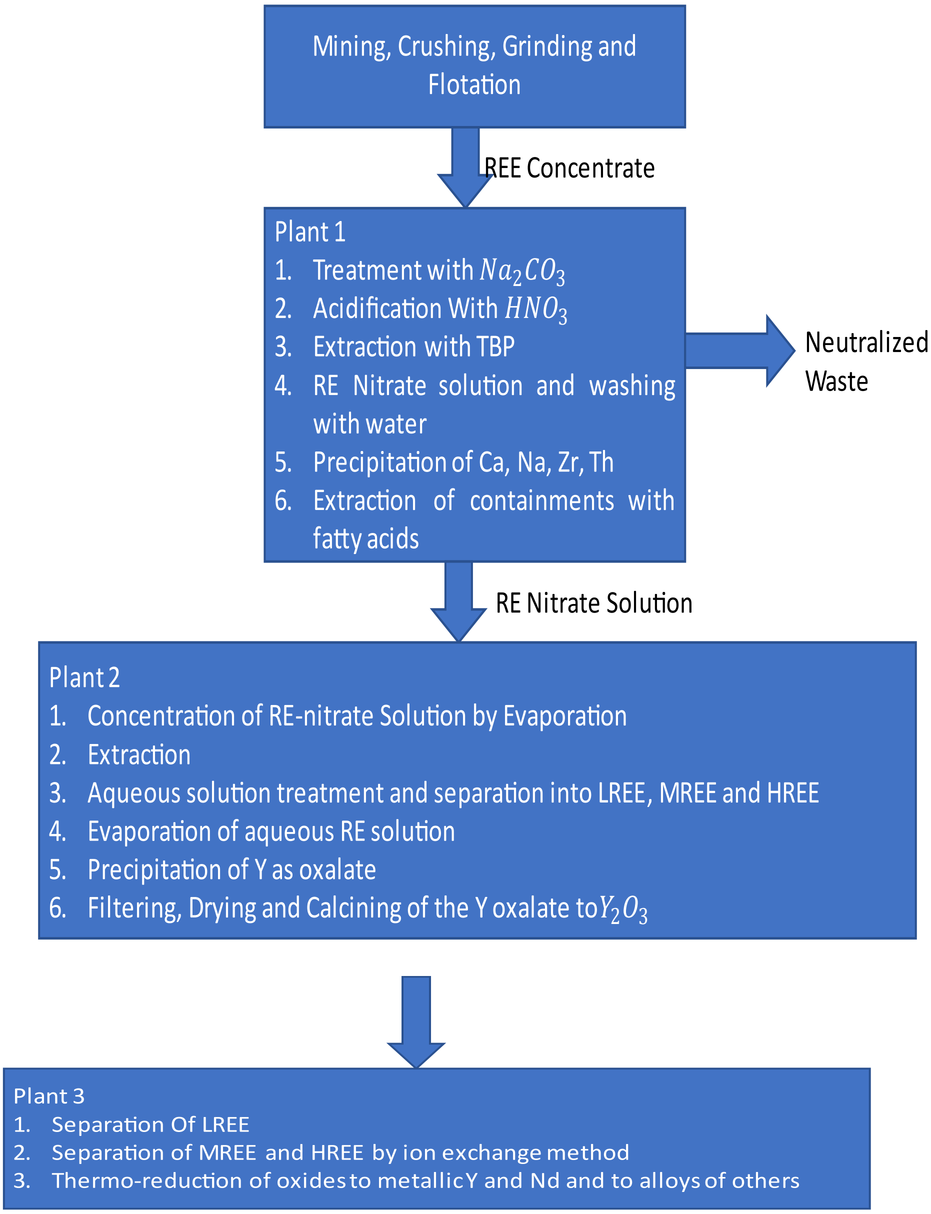

Figure 13 Production scheme from a plant located in Kyrgyzstan [40]

Energy Requirement

As rare earth elements are considered critical, they are given special attention. Generally, the resource is considered critical when it is either scarce or there is a potential supply constraint and the replacement to the material is considered inferior. REMs are distributed as trace elements, regarded as “hitch hikers” and when they are abundant in certain metallic ores, they are termed as “attractors”. Hitch hikers and attractors are physically and chemically very similar therefore their separation is given the most importance. The ores containing REEs are separated using standard methods as in mining, extraction and refining. The difference lies in beneficiation and the separation. Despite the flowsheets process, there is only limited data available on the material and energy requirement for the processing of the REEs [43][44].

The processing of ore includes mining, beneficiation and separation of rare earth. Despite being mined through open pit mining, the energy requirements vary for crushing grinding depending upon the hardness and the gangue associated with the mineral. The separation of REEs is dependent the chemical form in which they are extracted. Here we try to explain energy and material requirement for each step.

1. Mining and Grinding

About 95% of REMs are discovered in three minerals. They are bastnasite, monazite, and xenotime. The hard rocks are extracted from the surface using open pit mining. They are then blasted and transported to the mills. After, they are subjected to crushing and grinding until 90% of the material is no bigger than 0.15mm. The crushed material is subjected to a classifier and is passed through four agitators. The first three heats the feed slurry to 90°C whereas the last agitator cools the slurry down to 60°C and are passed on to flotation [45].

According to Gupta, the energy of 0.35-0.45 GJ/Tonne of mined ore is required during open pit mining, crushing and grinding. Depending upon the hardness of the rock, fine grinding is the most energy intensive process with a requirement of 0.11 to 0.28 GJ/Tonne of ore. Energy required can be estimated based on the hardness, for example, Bastnasite has hardness of 4-5 Mohs which is like that of apatite. Therefore, the energy required for bastnasite crushing is also like that of apatite. This gives us a required energy of about 0.06 GJ/tonne of primary ore. This value is in line with that of US bureau of mines, which has estimated the value to be 0.1 GJ/tonne and claimed that about two-third of the energy is spent only for grinding. The energy required during processing of the ores is also dependent upon the concentration of primary ores. The ore mined at the Mountain Pass contains an average of 7.7% of REO and the recovery of REO is as high as 90% due to very fine grinding. Therefore, 17 tonns of mineral ores and 1.75 GJ energy are required to extract 1 tonne of REM [46].

Xenotime and monazite have hardness values of 5 Mohs which are quite close to apatite. An advantage that it offers is that the primary ore has already undergone weathering and transportation due to which it does not require crushing and grinding operations. According to Gupta, the energy required for placers is around 0.02 GJ to 0.07 GJ/tonne of ore, mostly for physical concentration. According to US bureau of mines, energy of 0.45 GJ/tonne of REM is required. To obtain 1 tonne of REM, 160 tonns of mineral ores and 6.4 GJ energy are needed [47].

2. Beneficiation

The beneficiation of Bayan obo mineral requires flotation and chemical beneficiation of REM roasting with sulfuric acid. From the primary ore 72% is the rare earth elements and 28% is gangue. In order to obtain 1 tonne of REM, 2.46 tonns of bastnasite concentrate and 3.72 tonnes of monazite concentrates are required to undergo further treatment. 0.40 tonne of REM is lost per ton REE concentrate obtained. REMs recovered from bastnasite are roasted at 500°C in the rotary kiln with 98% sulfuric acid[48]. This roasting is the most important and the most complex process which requires sulfides being heated in air or in oxygen. This roasting is carried out for following reasons:

- Oxidation of sulfur content
- Sulfation roasting
- Convert sulfur to oxides for its complete removal.

The energy balance equation described below can be used to measure the theoretical heat required to roast 1 tonne of bastnasite at 500°C:

$$Q = m \cdot C_p \cdot \Delta T$$

Whereas,

m= mass of bastnasite

C_p= heat capacity at constant pressure

ΔT= change in temperature

The energy required during this process is estimated to be 0.20-0.27 GJ/tonne of bastnasite. Since, 2.46 tonnes of bastnasite concentrate are needed to generate 1 tonne of REMs, the required energy for roasting would be 0.49-0.66 GJ/tonne of REMs. Realistic estimate is given by lime rotary kiln heat data as it reaches the same temperature during the roasting to that of bastnasite. To roast 1 tonne of lime, 6-9.2 GJ of heat and 0.06-0.09 GJ of electrical power is required. If that is true for REMS, total energy for roasting 1 tonnes energy required is between 6.06 GJ and 9.29 GJ. In ideal cases, only 20% of RE input are lost but if we consider the yield reactions are not 100% and the unreacted materials that are lost permanently, 60% of the input is lost during the process [49].

The following tables describes the input and output required during several extraction process in the beneficiation stages.

Mass balance of ore extracted from Bayan Obo China mine[50]

	Input (Tonnes)	Output (Tonnes)
Bastnasite	6	1.2
Sulfuric Acid	4.5	1
Sodium Chloride	13	12
Sodium Hydroxide	2	0.5
Hydrochloric Acid	1.3	0.3
Water	2	3.5
Hydrofluoric Acid		0.5
Sodium sulfate		3
RE sulfate		1.4
RE disulfate		1.5
RE hydroxide		0.5
RE chlorides		2.7
Total	27.41	27.41

Table 6 Mass balance of ore extracted from Bayan Obo China mine

Mass Balance of the 1 tonne extraction of REMs using Molycorp Method[51]

	Input (tonnes)	Output (tonnes)
Bastnasite	2	0.2
Hydrochloric Acid	1.5	0.5
Sodium Hydroxide	0.4	0.04
RE flouride		0.07
RE hydroxide		0.04
Water		0.3
Sodium Fluoride		0.34
Carbon dioxide		0.50
RE chlorides		1.90
Total	3.7	3.7

Table 7 Mass Balance of the 1 tonne extraction of REMs using Molycorp Method.

Mass Balance of the 1 tonne extraction of REMs using Goldschmidt Method[25]

	Input (tonnes)	Output (Tonnes)
Bastnasite	2.6	0.07
Chlorine	2.5	1.6
RE fluorides		0.8
RE chlorides		1.9
Oxygen		0.3
Carbon dioxide		0.6
Total	5.5	5.5

Table 8 Mass Balance of the 1 tonne extraction of REMs using Goldschmidt Method.

Mass Balance of the 1 tonne extraction of REMs using Chlorination [52]

	Input (tonnes)	Output (tonnes)
Bastnasite	2.7	0.30
Chlorine	1.61	0.69
RE Fluoride		0.80
RE Chlorides		1.90
Oxygen		0.25
Carbon Dioxide		0.60
Total	4.4	4.4

Table 9 Mass Balance of the 1 tonne extraction of REMs using Chlorination.

Mass Balance of the 1 tonne extraction of REMs using Akali treatment[25]

	Input (tonnes)	**Output (tonnes)**
RE phosphate	2.19	0.20
Sodium Hydroxide	1.30	0.15
Nitric Acid	2	0.4
RE hydroxides		0.2
Trisodium phosphate		1.6
RE Nitrate		2.6
Water		0.5
Total	5.5	5.5

Table 10 Mass Balance of the 1 tonne extraction of REMs using Akali treatment.

Mass Balance of the 1 tonne extraction of REMs using acid treatment[25]

	Input (Tonnes)	**Output (Tonnes)**
RE phophate	3	0.5
Sulfuric Acid	7.60	7.50
Oxalic Acid	2	0.50
Phosphoric Acid		1.20
RE sulfate		0.50
RE oxalate		0.40
RE Oxides		1.30
Carbon Dioxide		0.60
Carbon Monoxide		0.5
Total	12.50	12.50

Table 11 Mass Balance of the 1 tonne extraction of REMs using acid treatment.

3. Separation of RE elements

The separation of REE elements is quite difficult because of the similarity in their chemical properties. Separation process such as fractional crystallization, fractional precipitation, ion exchange and solvent extraction can be used for the purpose. Solvent extraction provides information about the required amount of solvent but does not provide solvent to feed ratio required. Because the actual practice by industry remains secret, we can only provide a rough estimation about the amount of the electricity and the material required for the process. The solvent to feed ratio is 3:1. If we assume a recovery of about 90-95%, 7.02-7.41 tonnes of TBP dissolved kerosene are required for the extraction of 1 tonne of REM. To extract 1 tonne of yttrium oxide, 7.04 tonnes of kerosene containing TBP.

REMs are extracted using settlers which mixes the phases. Gravity allows the phases to separate, and, in the end, metals are stripped out. The required energy is for pumping. 1 tonne of Yttrium oxide and uranium requires the same amount of energy to obtain the same amount of REMs. 22 GJ for solvent extraction and 0.07 GJ for stripping are required to produce 1 tonne of yttrium oxide. The stripping and extraction of 1 tonne of uranium requires 0.01 GJ and 0.3 GJ per stage, with at least 50 stages required. The total electricity required for two processes would be 0.36 GJ and 15.25 GJ respectively. Therefore, 15.60-22.7 GJ are required to extract 1 tonnes an individual REM [53].

4. Reduction of Individual REMs

Electrolysis and metallothermic reduction are used to obtain pure REM. High purity REMs are produced by metallothermic reduction of RE oxides, anhydrous RE chlorides and flourides. Metallothermic reduction can be used where temperatures are high and fused salt electrolysis cannot be used. Following equation can be used to represent reaction of reduction:

$$MX\mathrm{n} + \mathrm{iR} \rightarrow \mathrm{M} + \mathrm{iR}X^{n}/_{i}$$

Whereas

M= metal to be recovered

X= Oxygen, fluorine, or Chlorine

R= Reducing agent that can be carbon, hydrogen or metals like calcium, aluminum and potassium

During the electrolysis of rare earth chlorides, the valence of the ion deposited is usually 3. The theoretical voltage is calculated to be about 4V even though the original losses make the voltage a bit higher than the theoretical value. It also depends upon efficiency of the cell. According to Shedd et al. the average voltage is 8.5V and the efficiency of the current is 37%. 38-48 GJ of energy is required to obtain 1 tonne of REM except for the case scandium and yttrium which require 148 GJ and 75 GJ/tonne. Mischmetal can be produced with electrolysis. Mischmetal contain neodymium, cerium, lanthanum and praseodymium. Energy consumed to produce a mixture of RE from bastnasite is 55.45 GJ/tonne. This value is in line with value estimated by many authors which is in the range of 48.96-57.60GJ/tonne. These values are supported by the calculations and analysis of thermodynamic data required to recover 1 tonne of REE by reduction and electrolysis [54].

The following table provides an extensive overview of the material and energy required for the production of 1 tonne REE[25]

	Rate of Recovery (%)	**Material input (tonnes)**	**Energy input (GJ)**
Mineral Processing Mining			
Bayan Obo Bastnasite	50	60.3 mined ore	6.2
Mountain pass Bastnasite	88	17.8 mined ore	1.8
Monazite/Xenotime	77	160.4 mined ore	6.5
Beneficiation Extraction 1: Bayan Obo Mineral	70	6 Bastnasite 4.5 sulfuric acid 12 sodium chloride 1.5 sodium hydroxide 1 hydrochloric acid 2 water	6-9
Extraction 2: Bastnasite by Kruesi and Duker	90	2 Bastnasite 1.5 hydrochloric acid 0.30 sodium hydroxide	0.04-0.05
Extraction 3: Bastnasite by Goldschmidt process	95	2.56 Bastnasite 2.5 Chlorine	4.5-6.5
Extraction 4: Baotau Concentrates	89	2.8 Bastnasite 1.7 chlorine	7
Extraction 5: Monazite by Rhone-Poulenc	92	2.5 Monazite 1.5 Sodium hydroxide 2 Nitric Acid	1
Extraction 6: Xenotime	85-90	3 Xenotime 8 Sulfuric Acid 2 oxalic acid	0.2-0.25
Separation			
Solvent Extraction	90%	7-7.5 TBP	15-22
Reduction			
Metallothermic Reduction		-	0.30
Electrolysis		-	40-50

Table 12 an extensive overview of the material and energy required for the production of 1 tonne REE.

Uses Of REE

Rare earth elements find usage in several industrial technologies and products. Their presence in the products enhance their stability, strength and several other properties. They are used in ceramics, glass, alloys and oxide compounds and add to their properties. An increase in thermal stability and strength is observed when alloying with rare earth elements. In petroleum industry, they are used as catalysts. They increase the number of small hydrocarbons in the mixture. In glass industry they are mainly involved within the process that involves high temperature like coating, coloring and glass additives. They are also used as permanent magnets, in technological applications as televisions and other electronic devices.

There are two main categories according to the purity of the REE:

- Mischmetal
- Pure REE compounds

Mischmetal is a mixture of rare earth elements and their oxides whereas the pure REE compounds as the name implies that they are highly pure and contains at least 90% of any rare earth element. Yittrium is the most widely used REE because of its special properties. There are four main industrial uses off REE:

1. Metallurgy
2. Catalysts
3. Ceramics and glass
4. Electronics and other uses

The following chart represents REE usage of different industries by percentage [55][56]:

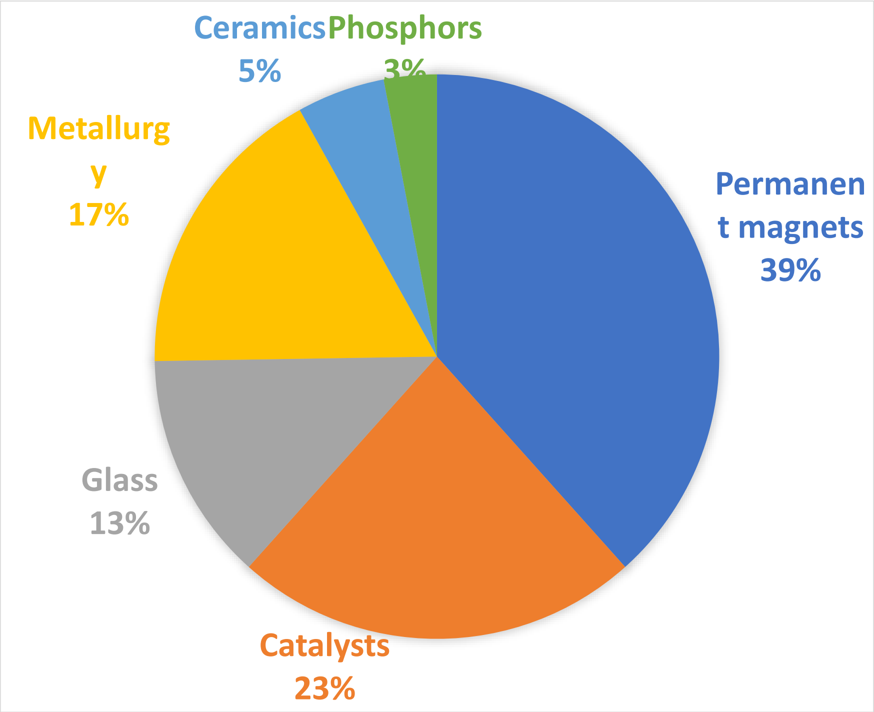

Figure 14 Uses of REE in different Industries [53]

Here is a detailed description of each category.[48]

1. Metallurgy

Aerospace engineering uses magnesium-based alloys, the addition of mischmetal enhances its strength. Addition of Ce and mischmetal increase the fluidity thereby reducing the shrinkage of the material. This alloy finds it application in high temperature environment. Addition of REE to aluminum and magnesium conducting wire used as a high voltage transmission lines, increases tensile strength, resistance to corrosion, vibration and heat.

1.1.Steel

REE are used mainly in steel industry for desulfurization and deoxidation. For this purpose, mischmetal or rare earth silicides are added into the steel. Added elements offers the benefit of controlling graphite and sulfide shape thereby allowing the modification of remains and increasing the strength of the steel.

1.1.1. High strength low alloy steel

The uniform strength in longitudinal and transverse directions is increased which in terms increases the resistance to cracking of steel under high stresses. HSLA steel being high strength is used in motor mounting brackets, foundations of offshore installations and power stations, road tunnels and concrete bridges.

1.1.2. Fecralloy Steel

Fecralloy steel are highly resistant to extreme temperatures of up to 1300 °C. It is stainless steel which is formed by adding 5% yttrium, 5-7% aluminum and 15-20% chromium oxide precipitate to the surface of fecralloy steel. It is used in exhaust system of combustion engine, electrical and laboratory furnaces and automobile emission control catalysts.

1.1.3. Other Steels

Oxidation resistivity can be improved by addition of mischmetal to cast steel. When added to free machining steels reduces the carbon content to 0.9% which reduces release of hazardous gases during the production process. This type of steel is used to produce agricultural tools.

1.2. Cast Iron

Mischmetal bearing Ce is used in ductile cast iron to control tramp elements. This addition enhances the ductility, fatigue resistance and weldability of the cast iron. This iron is used in transmission housings, motor exhaust pipes, eccentric gears and brake drums. This cast iron is of importance to pipes for drinking water supplies as well as for automobiles and agricultural industry.

1.3. Pyrophoric Flints

This is probably the first application REE on industrial scale. This alloy consists of a small amount of Mg and Cu, 23% of iron and 74% of mischmetal.

2. Catalysts

It is one the main application of rare earth elements. The catalysts are used in petroleum and automobile exhaust catalyst. They are becoming popular as automobile exhaust catalysts as they are lighter than ceramics catalysts. [4]

2.1. Petroleum Cracking Catalysts

This catalyst consists of three parts:

1. Silica-Alumina refractory binder
2. An inert filler
3. A rare earth element containing zeoloite

Na-zeolites are the most used which contains a mixture of La, Nd and Pr. The addition of REE increases structural stability and cracking capacity of the catalyst as well as reduces coke production. An additional benefit is the retaining of acidic properties under high temperature which increases the thermal stability in stripping process.

2.2.Exhaust Emission Catalyst

REE are used as three-way honeycomb coatings in the catalysts which are used to control the exhaust emission by increasing the oxidation of harmful gases produced in the process. REE based anti-knock agents are readily replacing lead-based agents as they are more environmentally friendly thereby decreasing the environmental pollution and catalyst poisoning. CeO_2 reduces carbon monoxide and unburnt fuel emission in the exhaust pipe.

2.3.Other applications as a Catalyst

Ce is used as a catalyst in several applications like production of tyre rubber, photovoltaic devices, self-cleaning ovens and ammonia synthesis. Polyethylene production utilizes La as a hydride catalyst. Mixture of REE is used for the removal of sulfur dioxide from gas streams, in the nitrogen oxide reduction and recovering chlorine from hydrochloric acid.

3. Ceramics

Ceramics are used in electronics industry, as dyes and as refractories [5].

3.1.Electronics Industry

Ceramics capacitors use REE oxides which changes certain features such as permeability, di-electricity, and temperature compensation. LREE when added can increase formation of stable dielectric constants. REE oxides increases the life of the capacitors. The main usage is in the multilayer capacitors which are readily replacing the electrolytic capacitors. Thermistors contains small amounts of Y and La to dope barium titanate. La-chromite increases the thermal resistivity which improves resistivity in high temperature and corrosion and enhances electric conductivity.

3.2.Dyes

A small number of REE-oxides or mixture when added to dyes can strongly intensify the colors in ceramic dyes for example a brilliant yellow color is produced when Pr-oxide is added to zirconia-silica mixture. Similarly, orange color is resulted from addition of Y-oxide and purple color from Nd-oxide. To give color to porcelain Ce-oxide is used and the process is named double firing. 100-150g/m^2 of REE are added in the mixture.

For applications that require high temperature, Y_2O_3 is used. These applications could be vacuum melting of reactive materials, molten material study for microscope lenses and furnace windows. Metallic crucibles are used for temperatures higher than 1800 °C, Ce-sulfide is one of the important crucibles.

One of the strongest ceramics is a sialon which is based on silicon nitride with Y_2O_3 as sintering agent. It is used as a coating on nozzles for high temperature technology, turbo-engines, in cutting tool tips and in adiabatic engines.

4. Glass

Glass industry regards REE as an important material both due to its use as mixed compound and in separating impurities [58].

4.1. Glass Polishing

Due to its mechanical abrasion and chemical dissolution, Ce-oxide is highly effective in polishing of glass. REE polished glasses have numerous applications such as camera lenses, cathode ray tubes, television screens, glass plates, ornaments, mirrors, precision optics, and ophthalmic glass. Other REE based oxides can be used for polishing, but Ce-oxide benefits are unmatched.

4.2. Optical Glass

This is the most common, important, and largely utilized application of REE oxides in glasses. Highly pure La-oxides (99.5-99.9%) can be utilized up to 40% of the content in the glass. The main usage of this type of glass is inside fibre optics which require qualities such as light transmission, high degree of transparency and high refractive index. Successful experiments with the addition of La-oxide, Y and Gd have been performed showing up promising results.

4.3. Glass Decoloring

Decoloring of glass is required if there is a need to increase the dispersion and refraction of light. For decolorizing, La and Ce-Oxides are used. Ce-oxide can remove arsenic which is a toxin from the lead glass crystal. Such a glass is used in applications where low colorizing and strong light transmission is required as in the case of camera lenses. Additional treatments with Nd, Pr, Er, or Ho-oxides have resulted in enhanced benefits.

4.4. Glass Coloring

Main applications of REE in glass coloring is for the glass art. Nd-oxide is added to the glasses that are used during the wielding process to protect the eyes from yellow flare that is emitted due to sodium vapors. Glasses are tinted pink when melted with 1-5% of rare earth oxides especially Nd-oxide. X-ray fluoroscopy material uses Er-oxide in crystal and photothermic glasses resulting in the required pale pink color. Ce-oxide is used with different coloring oxides to give colorful tints to glass used in ophthalmic and tableware glass, and absorptive glass.

4.5. Radiation Control Glass

REE have a benefit that they can absorb electron and ultraviolet light from both natural and technical sources, due to which they can be used in the glass to control radiation. Most used REE oxide for the purpose is Ce-oxide. This type of glass is used where high frequency radiation could occur such as medical devices, space instruments, microwave and nuclear devices, fluorescent lamps and screens of Tv. REE altered glass can also be used as a container for light sensitive food, museum pans, wielding glass, and protection glass in nuclear and radiochemical laboratories.

4.6. Fluorescence and Glass Coatings

Fluorescence is resulted when atoms are excited due to absorption of light. Fluorescent glass when doped with highly pure Nd-oxide is used as high-powered laser. Glass coating for scientific equipment's is a rather rare use of pure REE compounds. However, La-oxide, Ce-flouride and Nd-flouride without even the traces of iron content are required for the coating process.

5. Permanent Magnets

There are two types of REE based permanent magnets [7].

5.1. Samarium-Cobalt Magnets (Sm-Co)

Since the beginning, REE are being used as permanent magnets because of being stronger magnets then the non-REE based magnets which are Pt-co and Al-Ni-Co magnets. REE used as a permanent magnet also benefits being small and lighter in weight. This permanent magnet is used in wrist watches, radar missile guiding system, television and computer devices.

5.2.Neodymium-Iron-Boron Magnets (Nd-Fe-B)

Currently this the strongest magnet material. Therefore, they even reduce the size of the magnets then Sm-Co. It also enhances the strength of the magnets thereby strengthening against demagnetizing. They are also cheaper than the other REE based magnets. They are used in brushless motors, computers peripheral and other electronic devices. Automobiles industry uses this magnet as it considerably reduces the weight.

REE and its compounds are used in a lot of other fields. Some of them are mentioned below [56]:

- Bubble memory Systems
- Oxygen Sensors
- Metal hydrides
- Nuclear Industry (Uses involve burnable poison, neutron absorbers and radiography)
- Lasers
- Fluorescent lamps
- Xray Screens
- Cathode ray Tubes

Recycling of REE

As the name implies, REE are not rare but quite abundant in the earth crust. Yttrium, neodymium, lanthanum and cerium are more abundant than lead whereas each of the 17 rare earth elements are abundant than silver. REE are relatively well distributed throughout the world, but their production is dominated by China. China recently imposed quotas on export of REE which resulted in the price hike and supply issues around the world. Taking into consideration, their usage in the clean energy, United States Department of Energy, due to the risk of supply and their importance in clean energy, has listed 8 REE as critical and 5 others as medium in short and long term, respectively. REE is also in the list of critical material for the future development of European Union [59].

Consequently, more and more efforts are being put into examining the feasibility of recycling of REE from the scrap and end of life used components. Although recycling of REE is still at around 1%. Experts believe that the recycling of REE could reduce the ecological footprints of mining, but the cost of recycling makes it less competitive. Binnemans et al. have provided an extensive closed-loop prospect for RE products. This is defined in the figure below:

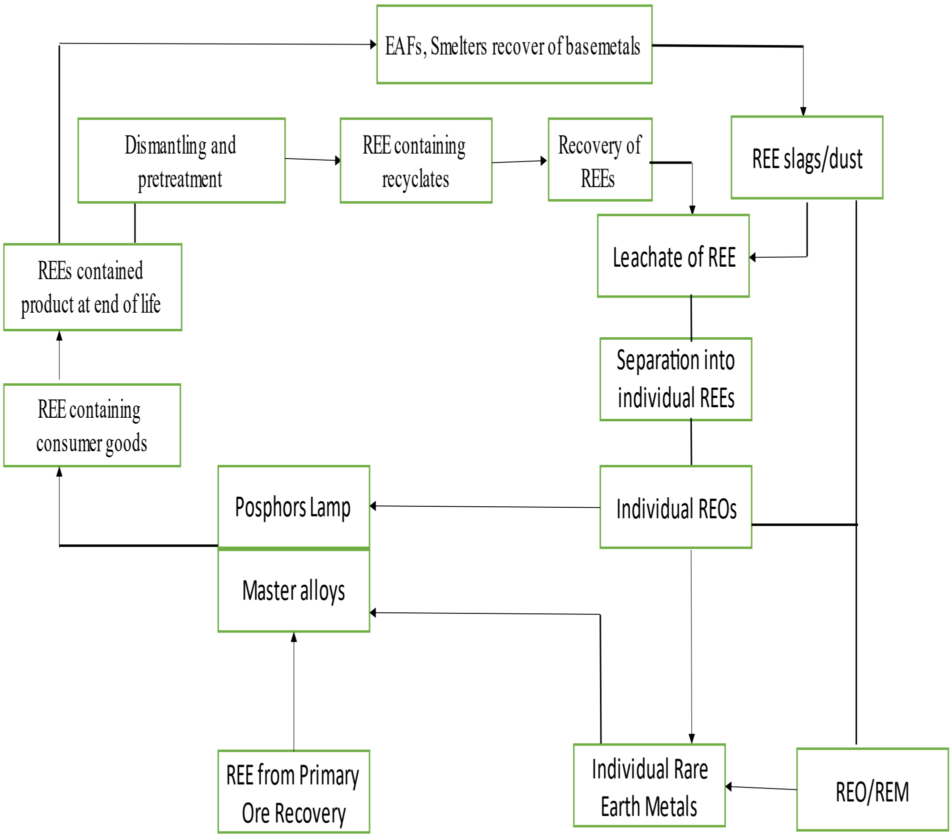

Figure 15 Recycling of REE[60]

1. Recycling of Rare Earth Catalysts

There are three main groups of catalysts:

- Fluid cracking Catalyst
- Automobile Converter Catalyst
- Styrene Catalyst

1.1. Fluid Cracking Catalysts

They are used in refineries to convert heavy hydrocarbon fraction into lighter ones in petroleum refineries. The catalyst becomes contaminated with carbon during the operation. This catalyst is mixed with the fresh one until it is deemed spent. This catalyst is a hazardous waste now. According to experiments, the REO content of this waste is considered unrecoverable.

1.2. Automobile Catalytic converter

This is the application, in which REOs are used to protect the actual catalysts. The actual catalysts have intrinsic values higher than 20% than those of the REOs, are platinum group metals. These automobiles catalytic converter can be recycled to their original platinum group metal values. The recycling can sometimes fail because of the involvement of smelting operation as the REOs are slagged off and not recovered at all.

1.3. Styrene catalysts

In this case, REO content is not recovered [61].

2. Recycling of Rare earth Permanent Magnets

Over the last few years, studies have been conducted on the recycling of permanent magnets. Important thing to keep in mind is that the magnet could contain additional material such as organics or metals. The objective of recycling should be predefined such as if the final product is intended to be separate or a blend. The figure below, defines a different process that can be used to recycle permanent magnets.

Both routes have advantages and disadvantages. If REEs are recovered as metals, the most significant advantage offered is that they do not need to be reduced to metal and therefore energy intensive steps are avoided. The disadvantage is that the recovered could be used for the same purpose as the original material from which they were recovered. If REEs are recovered as salts, they must undergo an oxidation step which evaporates them. This oxidation is followed by a reduction step to produce metals. This final step is already persistent in the industry and can easily be employed for recycling.

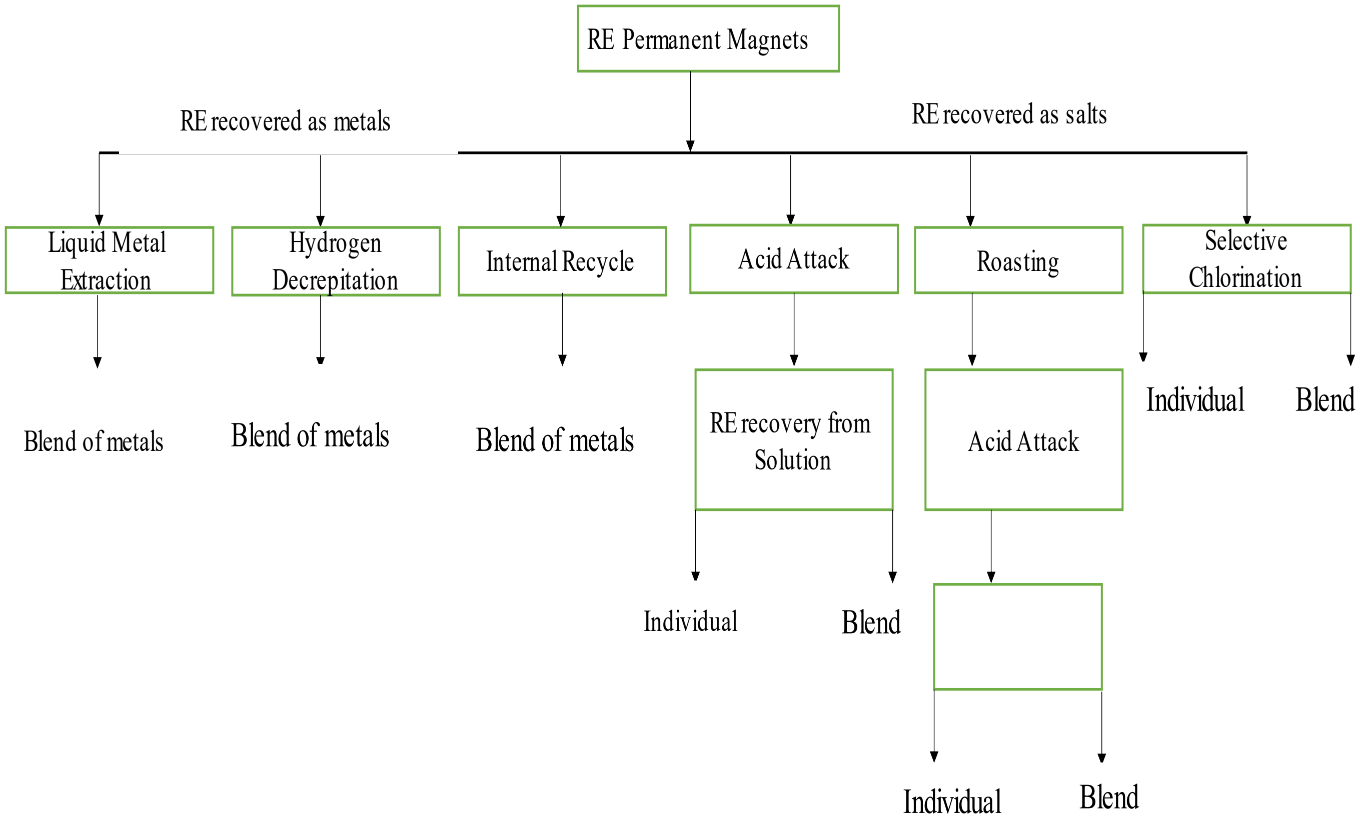

Figure 16 Flow chart of the various recycling options of rare earth magnets [60].

2.1. Recycled as salts

2.1.1. Acid dissolution

It is a relatively straight forward method that employs inorganic acids to dissolve the magnet. During the leach, large amount of hydrogen is produced. Non-selective and concentrated leach solutions are also produced that contains large amount of iron. Moreover, organics presence can cause several problems. However, the dissolved and filtered magnets result in a concentrated solution could contain 100-120g/L Fe, 40-60g/L REE, and 4-6g/L Co.

There are number of processes that could be used to recover REEs from magnet leach solution with difference being the separation of iron from the REE. The processes are:

- Double salt selective precipitation of REEs, oxalic acid or HF, followed by iron removal.

- Solvent extraction of iron using a commercial extractant N 503.

Japanese researchers have been successful in separating rare earth metals and iron by a two-stage electrodeposition process from ionic liquids (Choline-Based). These processes are described in the following figures:

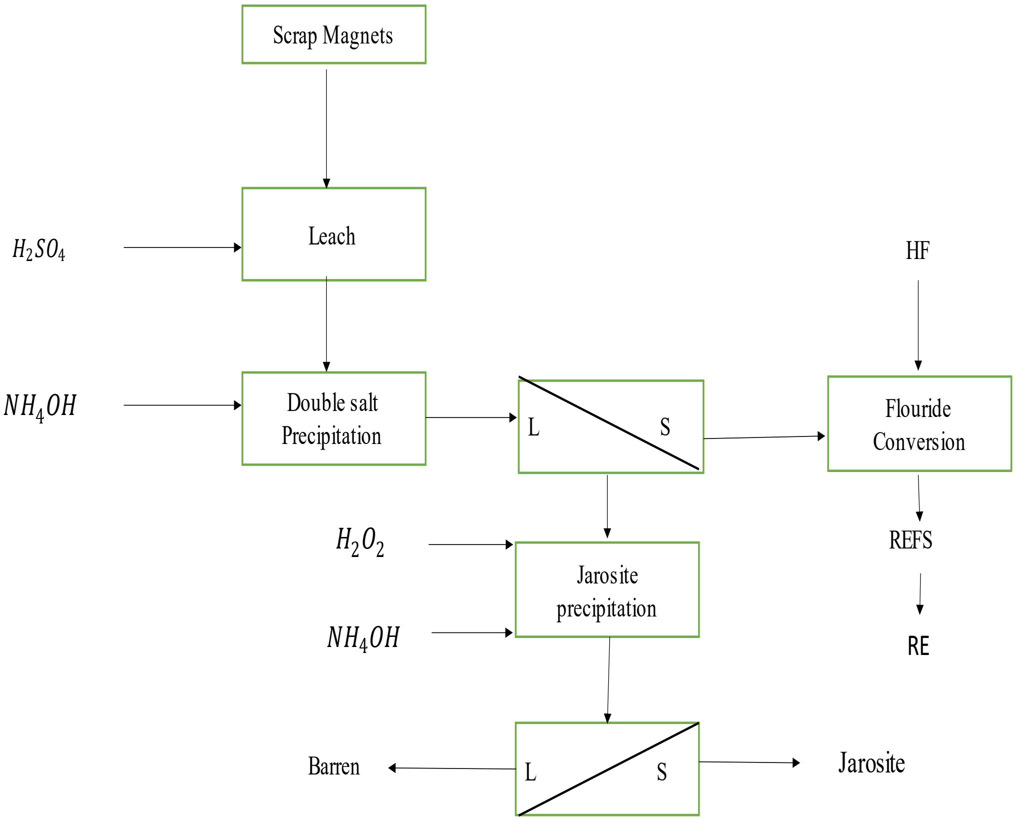

Figure 17 Process flow sheet to recycle Scrap magnets [61].

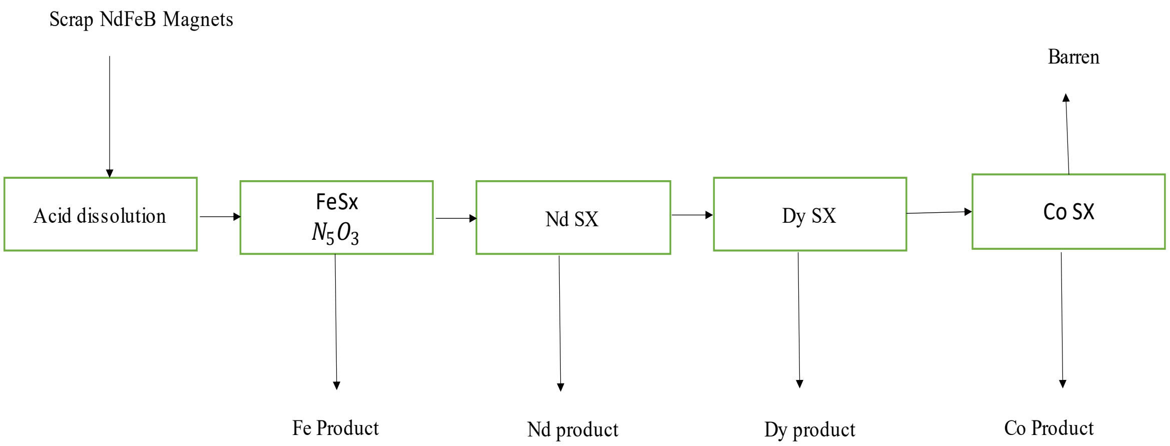

Figure 18 Simplified process flowsheet to recycle Scrap NdFeCo magnet [62].

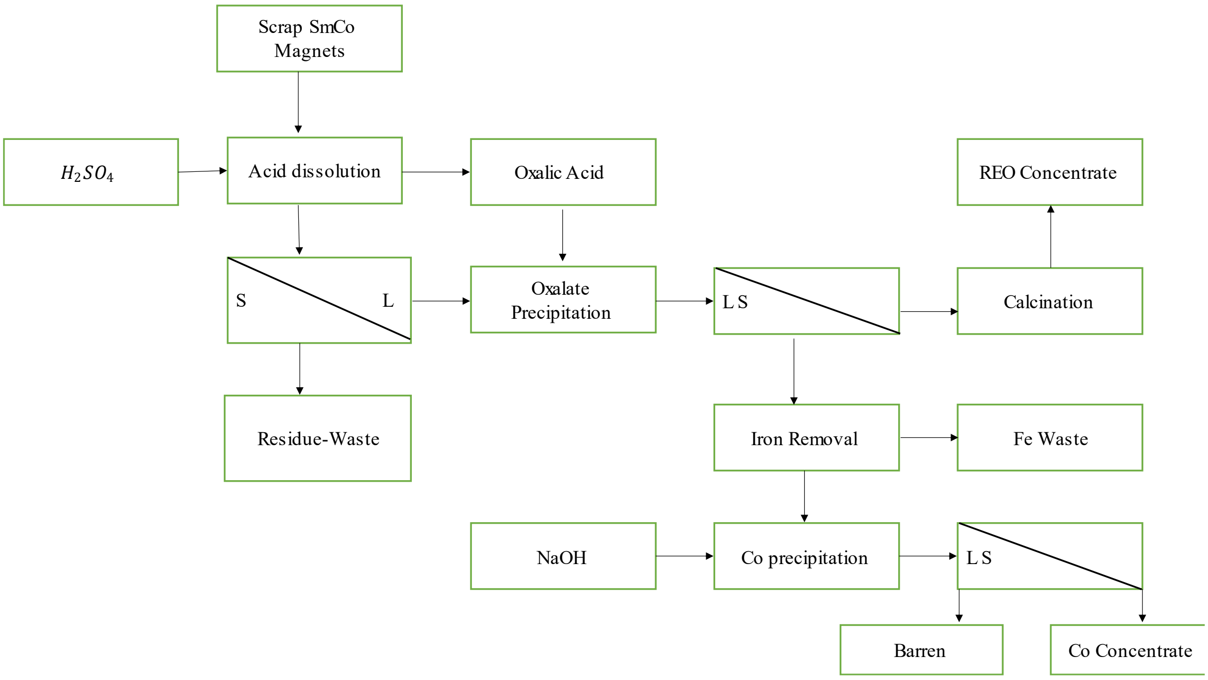

Figure 19 Simplified process flowsheet to recycle Scrap SmCo Magnets [63].

To improve the quantities of iron extracted from the REE, it is recommended to perform oxidative roasting of the magnet scrap before acid dissolution as it minimizes the amount of iron dissolved during the acid leach thereby simplifying the process.

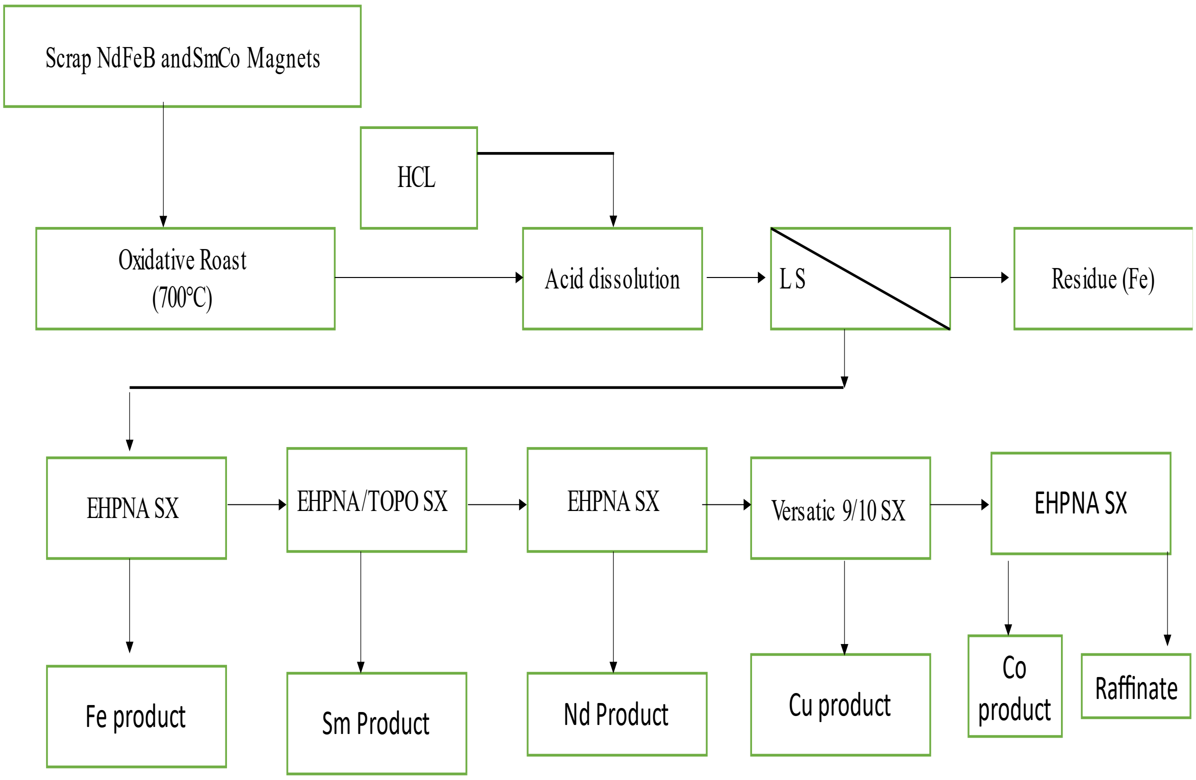

Figure 20 Simplified process flowsheet to recycle NdFeB and SmCo scrap Magnets [64].

2.1.2. Selective Chlorination

Scrap magnets can be recycled using selective chlorination. Ferrous chloride added to NdFeB scrap at elevated temperature of 800-1000°C results in rare earth chloride mixture. Similarly, highly pure cobalt and samarium chlorides can be recovered separately, from aluminum chloride added to SmCo scrap [62].

2.2. Recycling of REEs as Metals

This process although seems to be most attractive as it involves direct recycling of the spent magnet. This process involves re-melting with possible removal of impurities, thereby allowing the change of composition by adding some fresh components. Unfortunately, this process is not possible most of the times and alternates are preferred.

2.2.1. Recycling through Liquid Metal Extraction

Liquid Pb-Zn metals is used to separate La from Ni. This process is now extended to separate Fe+C0 from Nd+Dy+Pr in NdFeB magnets. The base metal is not soluble in the molten metal which allows selective distribution of REEs with in the molten metal (Mg). The laboratory results have indicated that the recycled metals exhibit similar functions and properties to that of the fresh metal.

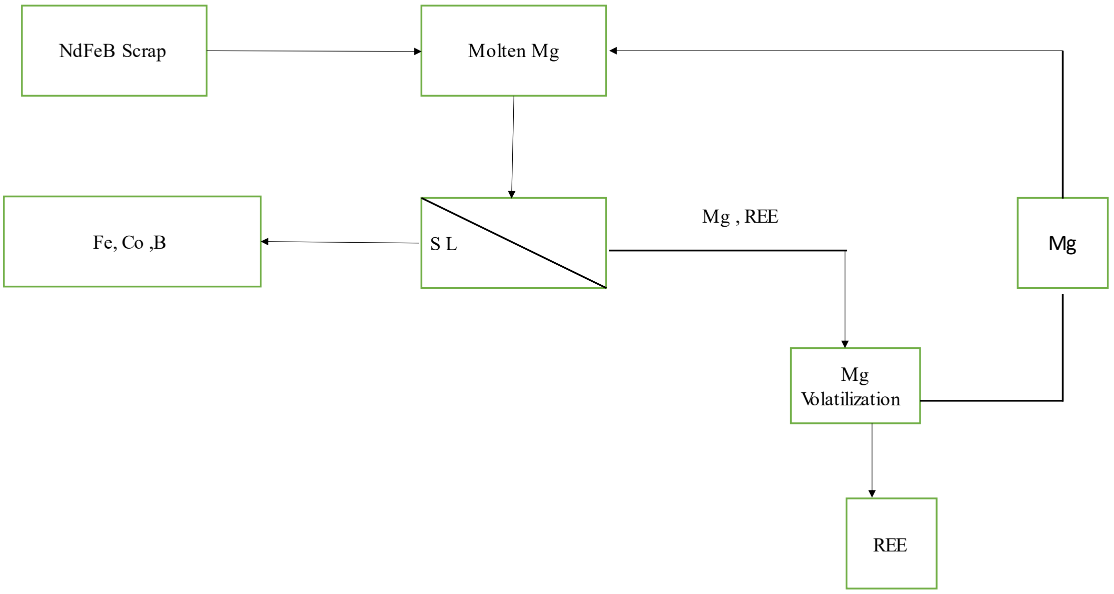

Figure 21 Simplified process flowsheet to recycle rare earth elements through liquid metal extraction [58].

2.2.2. Recycling through Hydrogen decrepitation

Recycling of REE metals from SmCo and NdFeB permanent magnets could be achieved with hydrogen decrepitation developed by the University of Birmingham (UK). This process involves breaking RE alloys into powder. There is preferential penetration of hydrogen into RE-rich grain boundaries with an increase in the volume of the material. The grains are broken away from the material automatically, within few hours, which are then separated by screening. Results have indicated that the magnetic properties of magnet have been maintained by blending decrepitated material with Nd hydride [63].

2.2.3. Recycling of Rare Earth from alloys (Ni-MH batteries)

This area has seen much development due to development of rechargeable batteries for electric and hybrid cars and other consumer goods. Therefore, public announcements have been made by large automobile companies in this regard such as Honda, Mitsubishi, Hitachi, Dowa and Rhodia/Solvay in partnership and Umicore. The Umicore Battery Recycling division can process up to 7000 t/a of batteries through their ultra-high temperature patented process.

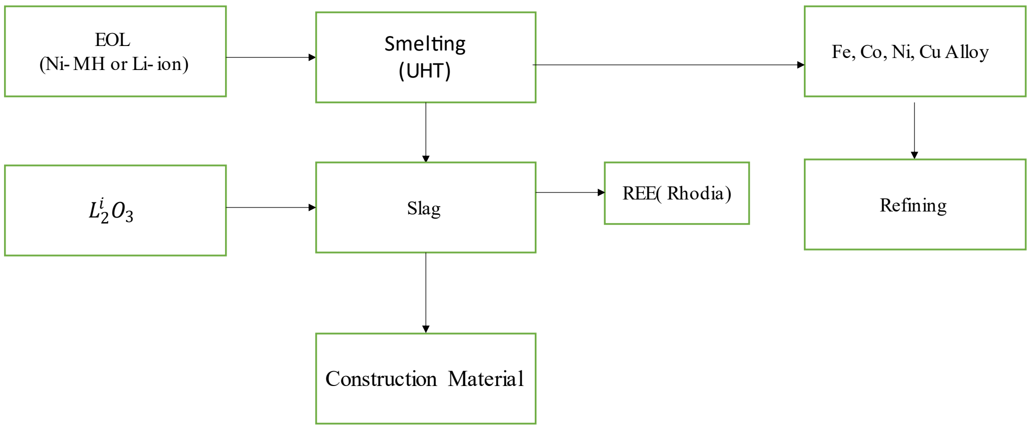

Figure 22 Simplified process flowsheet of Umicore battery Recycling UBR Plant [67].

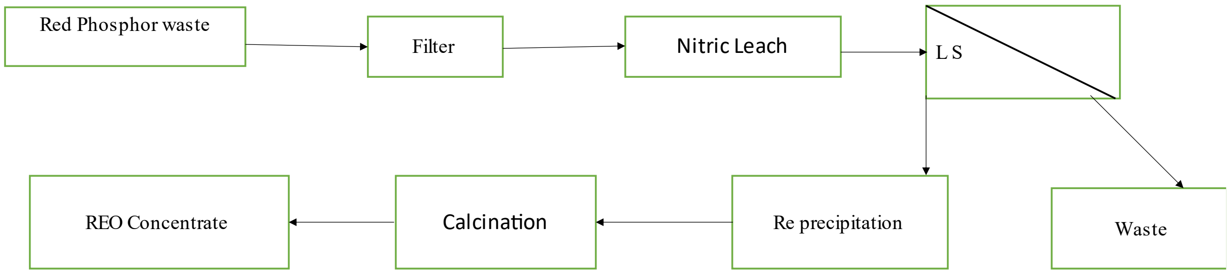

Figure 23 Simplified process developed by Matsushita Electronics Corp (Osaka, Japan) [68]

2.2.4. Recycle of REE from phosphors

Liquid crystal display, cathode ray tubes, tri-phosphor fluorescent lamps utilize rare earth-based phosphors. Rare earth used in these applications are important and several recycling processes have been developed.

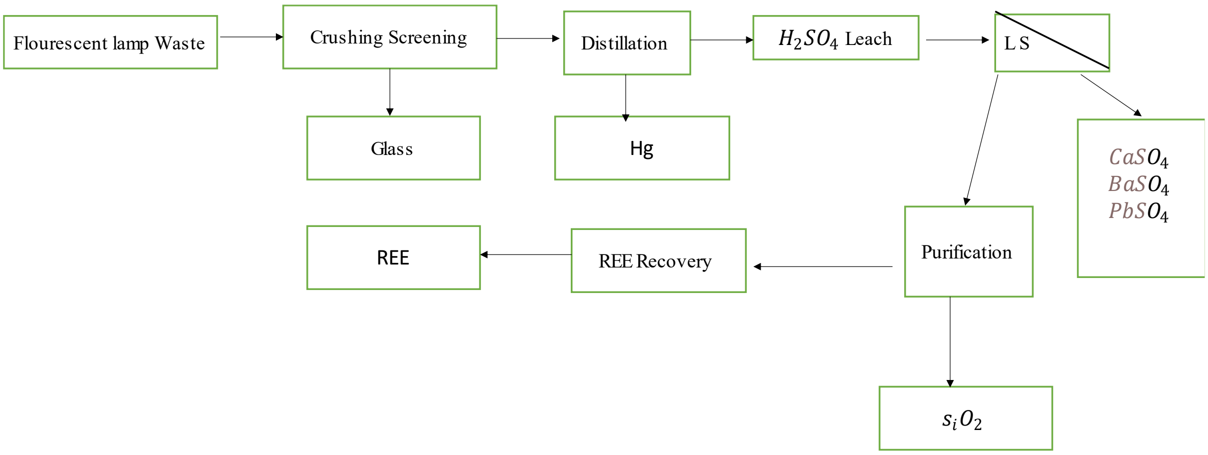

Figure 24 Simplified process to recover rare earth elements from flourescent lamp waste [69].

Environmental Impacts of REE

1. Introduction

In recent years, the rare earth processing and extraction phases have come under a lot of scrutiny from public and political factors based on natural resource extraction and environmental narratives. There are two main objections to rare earth industry despite REE being important to several industries. The main objections being that they are extracted through a mining process that leaves permanent marks on the earth surface thereby affecting the social and ecological life of peoples living in the vicinity. Some of REEs have been linked with radioactive material thereby increasing radioactive pollution. Some researches conducted on the processes in the past have resulted in the distrust amongst the general population.

An example is the Australian Mount Weld mine whose concentrate was shipped to Malaysia for processing because its processing was not allowed in Australia due to environmental concerns. There has been a significant movement against this project in Malaysia which also highlights the fact that underdeveloped countries are being used for processing the product for a developed country. This case also highlights the need of circular economy approach which means that a positive trade of goods must be established there by decreasing the need of export of environmentally harmful externalities [64].

The Malaysian case can be traced back to 20 years ago, when Mitsubishi operated The Asian Rare earth site at Bukit Merah. Environmentalists claims that there were serious mismanagements at the site which resulted in the leakage of the radioactive material. These allegations were upheld by the courts but later acquitted by the highest court of Malaysia which resulted in serious mistrust from the general public. Although, experts claim that with the advancement in the technologies the current processing and mining of REE is safe, there are still concerns that we may experience the past given the negative history of minimal engagement of the general public in the area [65].

Here we have a breakdown of the possible sources of environmental pollution associated with each step of REE processing.

2. Mining Of REE

Since REE are produced associated with some ore therefore the process of REE mining is dependent upon the accompanying element being extracted. The prime example is the Chinese Bayan Obo mine which was discovered in 1927 as an Iron mine and is the world's largest extraction site for fluorite [66]. There are large footprints of mines still present in the area and will never be removed thereby destroying the ecology of the area permanently. The experts claimed that the quota was enforced by the Chinese authorities which resulted in the reduced productions were meant for environmental rehabilitation of the region. Although Chinese authorities claim otherwise despite questions being raised from the Japan, United States and Europe [67].

A French newspaper Le Monde conducted an independent research which included documented interviews of the farmers and residents of the village of Xinguang Sancum. The research was later published in The Guardian in year 2012, claimed that the agricultural activities were stopped by the farmers in the village and the local population decreased from 2000 to 300 within a decade. Municipal environmental protection agency later conducted the study in the region and claims that the increased pollution along with dozens of new factories and other industrial process were responsible for the migration of the people from the region. Su Bo, the vice minister for industry and information technology expressed publicly in 2012, that the Chinese Government is not willing to trade the growth of REE industry with the environment. Some reports claim that the Chinese Government has committed to clean up the damage caused by REE industry in the area and have allotted 4 billion Yuan, but the experts believe that some of the damages caused by the mining process is permanent and cannot be reversed [68][69].

A similar case of Mountain pass REE mine in the United States was forced to close due to environmental concerns. The mine was forced to shut down in 1990 due to the leakage of a pipe system that carried wastewater to an evaporation system. An investigation later revealed that 600,000 gallons of wastewater flowed into the natural water reservoir due to 60 spills over the period of 4 years in between 1984-1988. San Bernardino County sued the management of the site. The matter was resolved by payment of $1.4 million, in terms of fine and settlements. The management has since changed the piping system of the site which means that the tailings will be handled along with wastewater on the site thanks to some advancement in the technologies. In 2013, an independent team of experts visited the site and were satisfied that the mine can operate within environmental regulations. The site can be opened now with minimal environmental concern.

LAMP site in Malaysia is dependent on the concentrate from the Mount Weld mine in western Australia. This mine has a smaller impact than the above discussed mines located in China and United States mostly because of the remoteness of the field and its smaller footprint. The ore mined may result in higher thorium content than the other mines but is still far below radiation concerns in comparison to the uranium operations. The point here is that we should keep in mind the ecological and geological difference before making a comparison between two mines. Connections between mining, processing and generation of various types of wastes must be addressed [8].

3. Processing of REE

The processing of ores is achieved through multiple facilities and is a very complex process. Flotation and solvent extraction processes along with electrolytic process may be required for the purpose. There is hardly any research on the damage caused by REE processing to the environment. A limited or no qualitative set of data is available on the energy requirement for the process.

Following is the result of a research conducted on how much of the ore results in a useful product and how much is disregarded as waste material. This study shows the original raw material and the resulting products, by-products, and gangue [70].

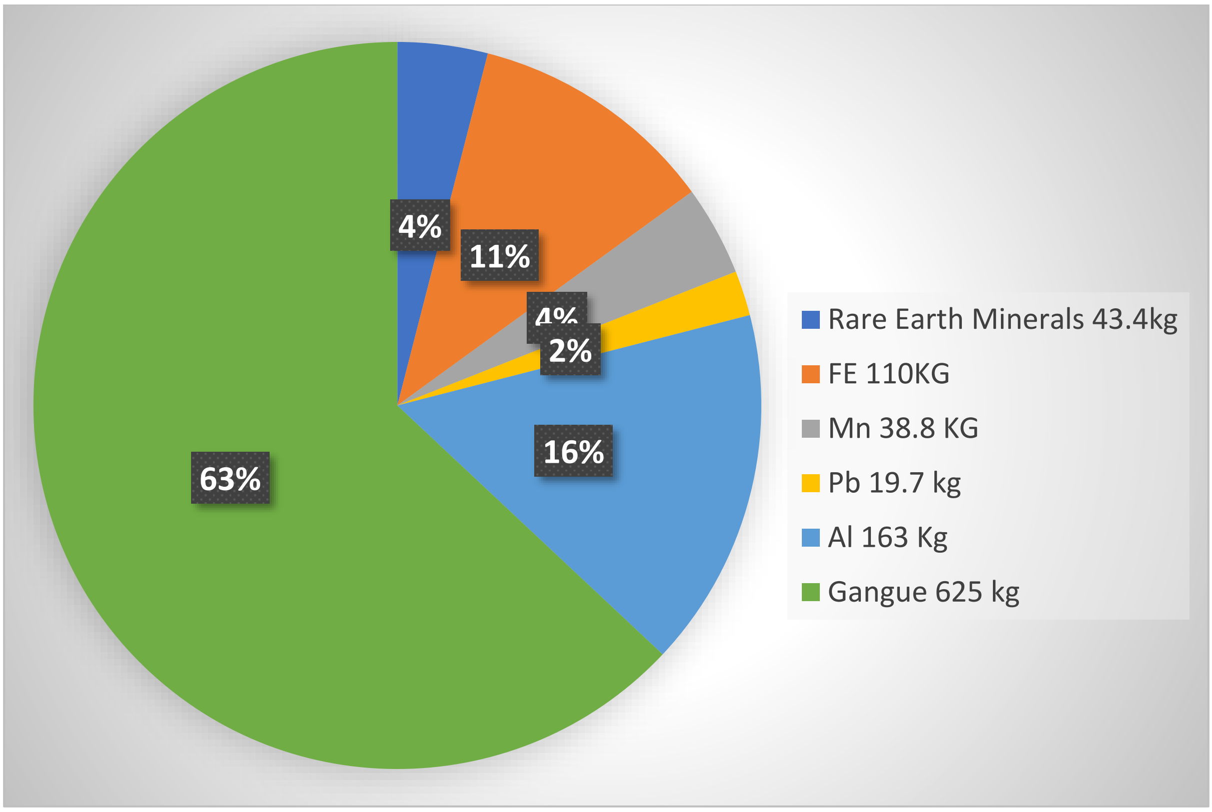

Figure 25 Extracted Raw Material from the ground[70]

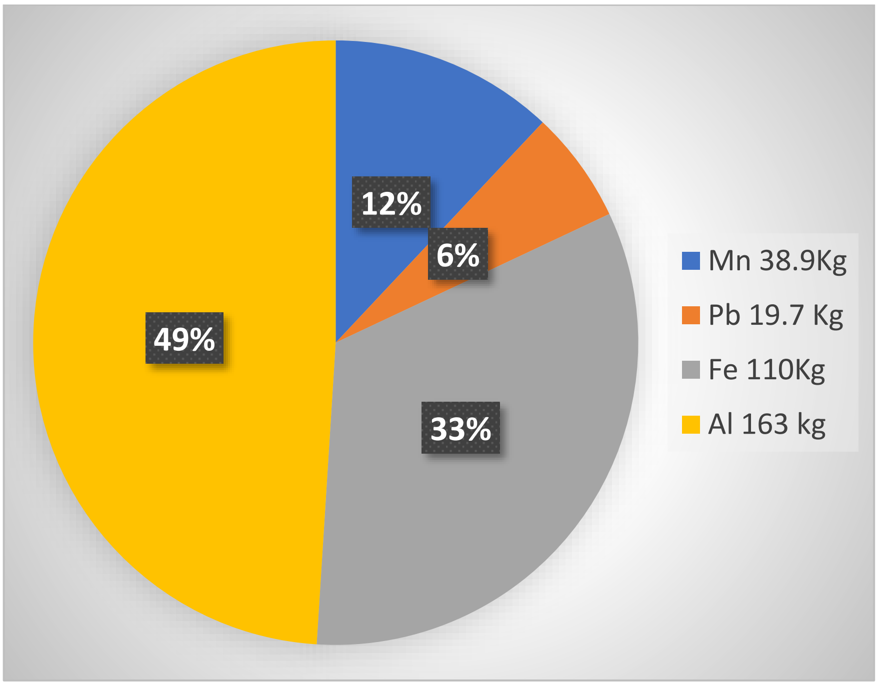

Figure 26 Mineral Recovery from the extracted raw material (33.1%)[70]

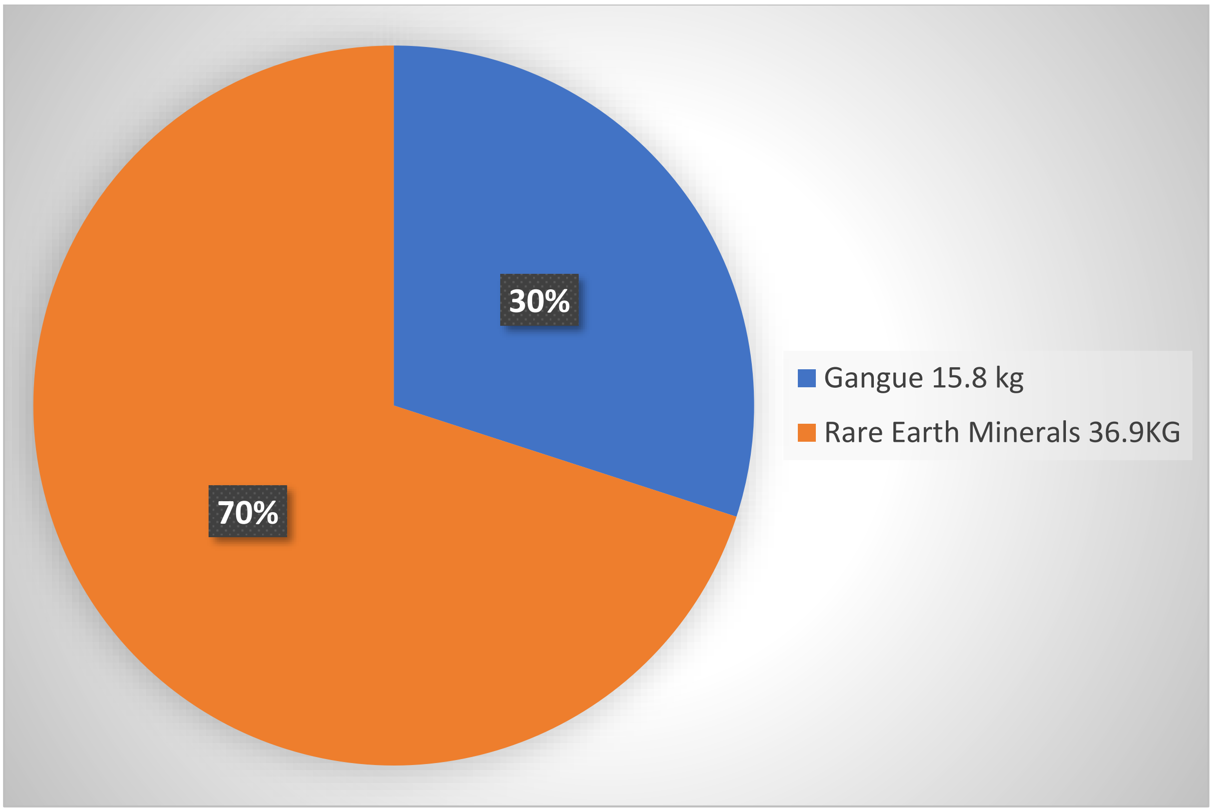

Figure 27 Extracted Rare Earth Concentrate from the original Raw material (5.3%)[70]

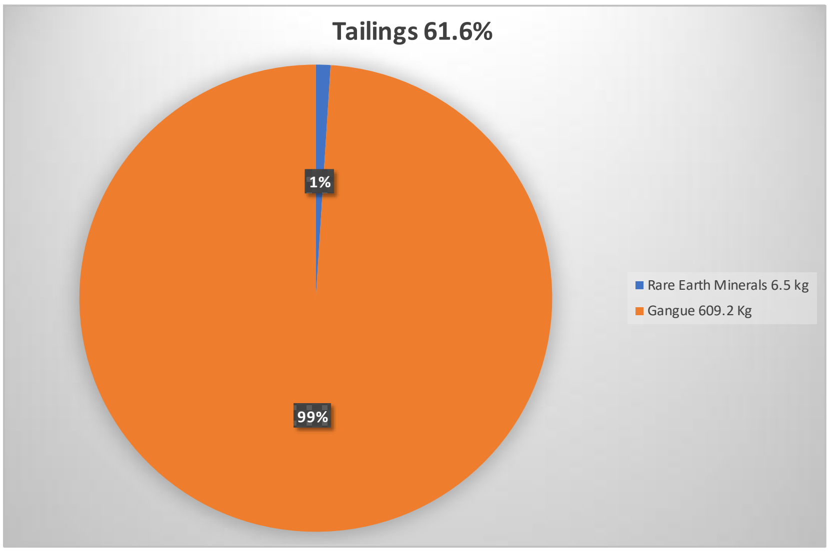

Figure 28 Tailings from the original Raw material[70]

The **gangue** is defined as the amount of waste material mixed with the desired material. This is the waste that is of much concern to the public. However, the industry claims that this material is not waste. It contains considerable amount of thorium and can be used to extract usable products. But the problem is that it requires regulatory compliance because if the material is termed as waste, it must be disposed immediately whereas only if the material is termed useful it can be stored in compliance to the regulations set by authorities. The waste associated with each ore differs from one another and therefore the technologies and materials required also vary. But the general wastes are considered the same for compliance reasons [70][71].

4. Refining

This is the chemical process that is required after the initial processing of REE. This is to extract specific metals from REE that can be used in different industries. The steps involved in processing of the ores are quite like each other with extraction precision required in some cases.

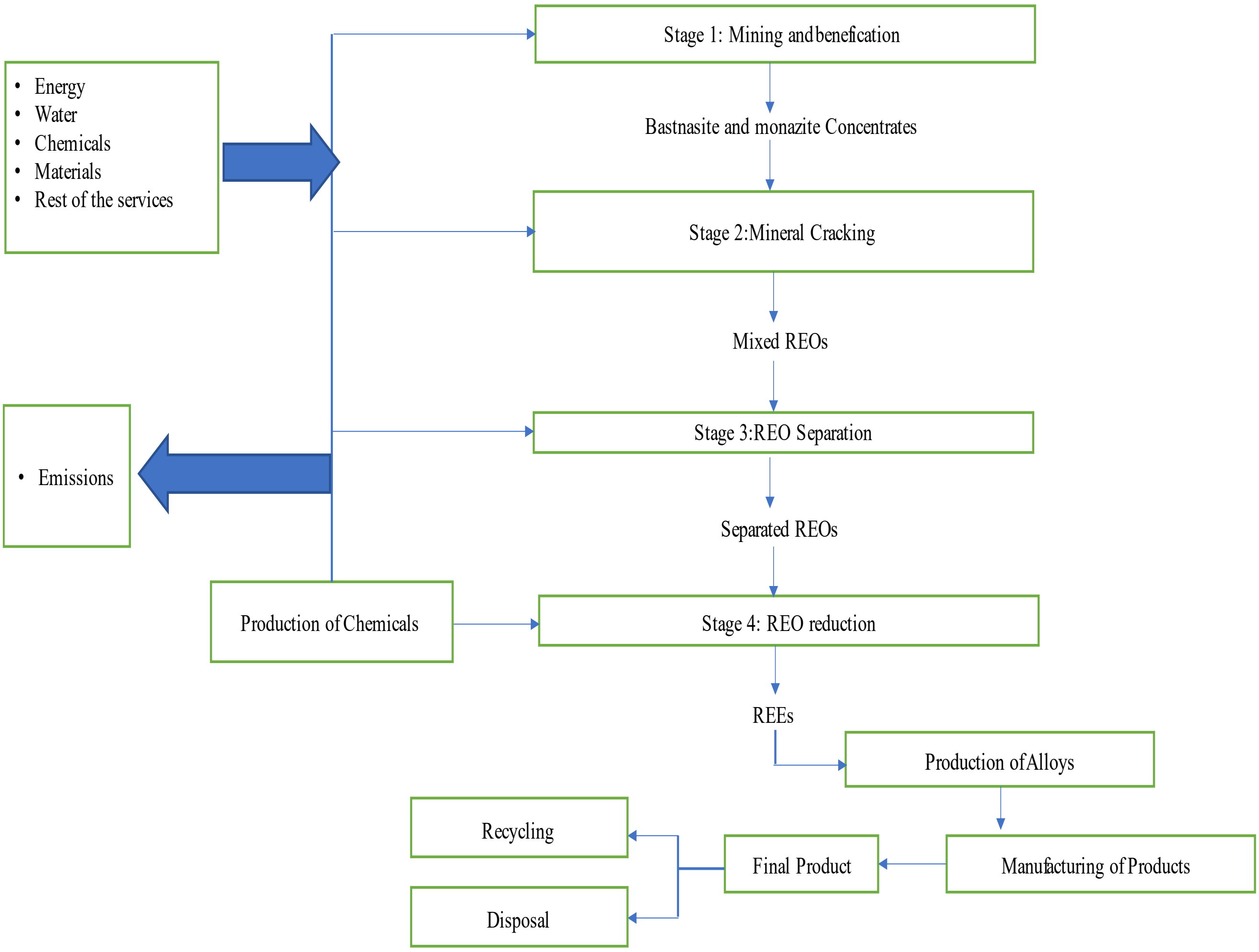

Figure 29 Standard Mineral processing practice[72]

Oxide is used in the rare earth sector as reference unit regardless of the actual form of the product such as oxide, carbonate, oxalate and chlorate etc [72].

5. Radiation Monitoring

The radioactive isotopes are present in the rare earth elements which needs to be monitored based on the ore grade. The experts have been monitoring the ore from uranium mines for more than a decade and have now concluded that for the betterment of the environment it should be monitored very closely. The study was conducted on the high-grade Athabascan deposits of Uranium in Saskatchewan, Canada [63].

The processing of the ore generates thorium which is the major concern because the decay process for thorium involves alpha particle emissions. Although, alpha particles do not travel far but have known to cause severe damage to humans when inhaled. This fact was revealed when studying the air pollution in the basements of the homes in North America. The study found Radon gas which contains alpha emissions and experts after several verification concluded it to be harmful for people living in the vicinity.

6. Air, Water and Soil

As is in the case of most industries, REE require strong environmental monitoring. For example, the processing of ores requires both organic and inorganic reagents which are then mixed with water. Now, this wastewater needs to handle with utmost care or else it can result in the serious damages to the water quality of the area as seen in the case of LAMP facility in Malaysia and Molycorp expansions at Mount pass, California.

Us Environmental Protection Agency claimed in a report in 2011 that the extraction of the ore from earth which results in the damage to the earth crust results in only a small portion of the process. Refining the rare earth metals into marketable products is a major part of the operation. For example, Hyperacidity can result due to acidic leaching process during refinement. Although carbonate rare earth minerals provide a natural immunity against acidity, excessive carbonate can lead to alkalinity and therefore require pH monitoring [63].

7. Safety of the Workers on Site

Safety considerations required for processing Plants of REE are like those required in normal chemical industries involving solvent extraction, piping for high intensity chemicals and electrolyte process. Although, most of the sites are locate remotely due to safety concerns but some can be near populated areas if they comply with the regulations. For example, there is site in France in a small village which is a strong economy for tourism. There has been no public objection to this site thanks to environmental surveillance by Installations Classées pour la Protection de l'Environnement (ICPE), They have a lot of experience in monitoring safety of the Nuclear sites as France is dependent on the nuclear power [73].

8. Health Concern

The health Concern is mainly related to RE emanate from thorium containing wastes as it is a source of radiation. In China, since most of the processing has nor recorded data and is nor recorded publicly, so epidemiological evidence of REE is missing. However, there was a study related to health and toxicity conducted by Suzuki and Hirano in 1990 and the data provided are like that of toxicity due to metals. Similarly, thorium related effects are also unknown due to the facts that either there were no studies or if there were, the sample size was not large to cause a significant Causation. There are however defined safe levels of radiations that can be used as reference in rendering a site as safe. By making the data public will enhance the trust of the general public and may result in growing the industry even further [74].

Conclusions

Due to recent price hikes and their extensive usage in the emerging green technologies, it is expected that the growth and demand for the REE will see a sharp rise soon. We need to look for the REE reserves in the ocean bottom sediments. This deep-sea mining will be a feasible option for the cost-effective recovery of REE. The development of a sustainable exploitation scheme is the need of the hour as it will help prevent the environmental damage as it requires a lot of time and money to restore the environment.

It is recommended to exploit red-mud, coal fired ash and electronic recycling scheme for future supply rather than opening new mine projects. REE usage is increasing by the day which will result in the increase in their concentration in the environment and the aquatic system which will have implications on the human health. A strict monitoring is needed for soils that can allow the mobility and uptake of REE and at the REE dump site where runoffs could cause local environment contamination.

Recycling of REE has not taken off yet. With the advancement of technology, various commercial plants to recycle the rare earth from the scrap are now running. The recycling rate can be improved by providing the transportation facilities for bringing the RE scrap to the processing center. In addition to economics, sustainability, stewardship and strategic factors must be considered whereas these additional factors cannot be quantified economically but should be a part of overall equation. Moreover, environmental effects of recycling and life cycle assessment must be considered. Research shows that the recycling can be an alternative source of REE.

There has been no breakthrough in finding the alternative to the REE so far and their applications and dependency are increasing at an alarming rate. The emphasize is needed on the development on the REE extraction and processing from unconventional sources which ensures environment and human safety. It is essential to determine the individual REE content in different material in both liquid and solid forms. There are high-sensitive and selective analytical techniques useful for this determination and can prove to be helpful for the future exploration of REE.

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