TERM REPORT

CL - 304
CHEMICAL PROCESS TECHNOLOGY

TOPIC - EXTRACTION OF RARE EARTH METALS

GROUP NO. - 11

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INTRODUCTION

- The global demand for rare earth metals has surged due to the widespread adoption of clean energy technologies and the rapid growth of the power and transportation sectors.
- Elements like yttrium and scandium have become essential components in various applications, including clean energy technologies, phosphors, lasers, and magnets.
- Sustainability concerns have highlighted the need for technologies supporting materials recovery and recycling to conserve energy and natural resources in the utilization and disposal of inorganic materials.
- Despite recycling efforts, a significant portion of post-consumer metal scrap remains unrecovered, leading to increased reliance on primary metals production and escalating global energy consumption and greenhouse gas emissions.
- Rare earth elements, including 15 Lanthanides, scandium, and yttrium, have gained strategic importance due to scarcity and increasing demand worldwide.
- According to the United States Geological Survey, in 2020, the whole world has about 120 million tons of rare earth reserves, mainly concentrated in China, Brazil, Vietnam, India, Australia and other countries, but apart from China, other countries are mainly light rare earth resources.
- With the development of the rare earths separation industry, there have been multifarious methods including chemical separation (fractional crystallization, fractional precipitation) , REDOX , ion exchange and solvent extraction are used to obtain pure HREEs.
- Legislative measures like the Rare Earths and Critical Material Revitalization Act of 2010 underscore the strategic importance of rare earth elements, prompting initiatives to ensure a long-term supply.
- Criticality analyses have identified elements like Dysprosium, Neodymium, Terbium, Yttrium, and Europium as the most critical, known as heavy rare earth elements.
- Several current situations of the sources, distribution, and impurity removal of HREEs were also presented here. At last, these contents should provide a theoretical basis for the preparation of high-purity HREEs
- Various extraction methods, including selective oxidation, reduction, fractional crystallization, ion exchange, and solvent extraction, are

employed to produce rare earth oxides and metals, each offering unique advantages in separating and recovering these valuable elements.

Table 2
Summary of the HREEs and their common applications [41-46].

Elements	Applications
Gd	High refractive index glass or garnet, laser, X-ray tube, computer memory, neutron capture, NMR imaging contrast agent, magnetostrictive alloy
Tb (terbium)	Nd based magnets, green phosphors, lasers, fluorescent lamps, naval sonar systems, additives in fuel cell stabilizers
Dy (dysprosium)	Nd based magnet, laser, magnetostrictive alloy, additives in hard disk drive
Ho (holmium)	Wavelength calibration of laser optical spectrophotometer, magnet
Er (erbium)	Infrared laser, vanadium steel, optical fiber
Tm (thulium)	Portable X-ray machine, metal halide lamp, laser
Yb (ytterbium)	Infrared laser, chemical reducing agent, decoy flare, stainless steel, stress meter, nuclear medicine, earthquake monitoring
Lu	PET scanning detector, high refractive index glass, phosphor, catalyst, LED bulb
Y	Special glass, ceramic, catalyst, electric wire

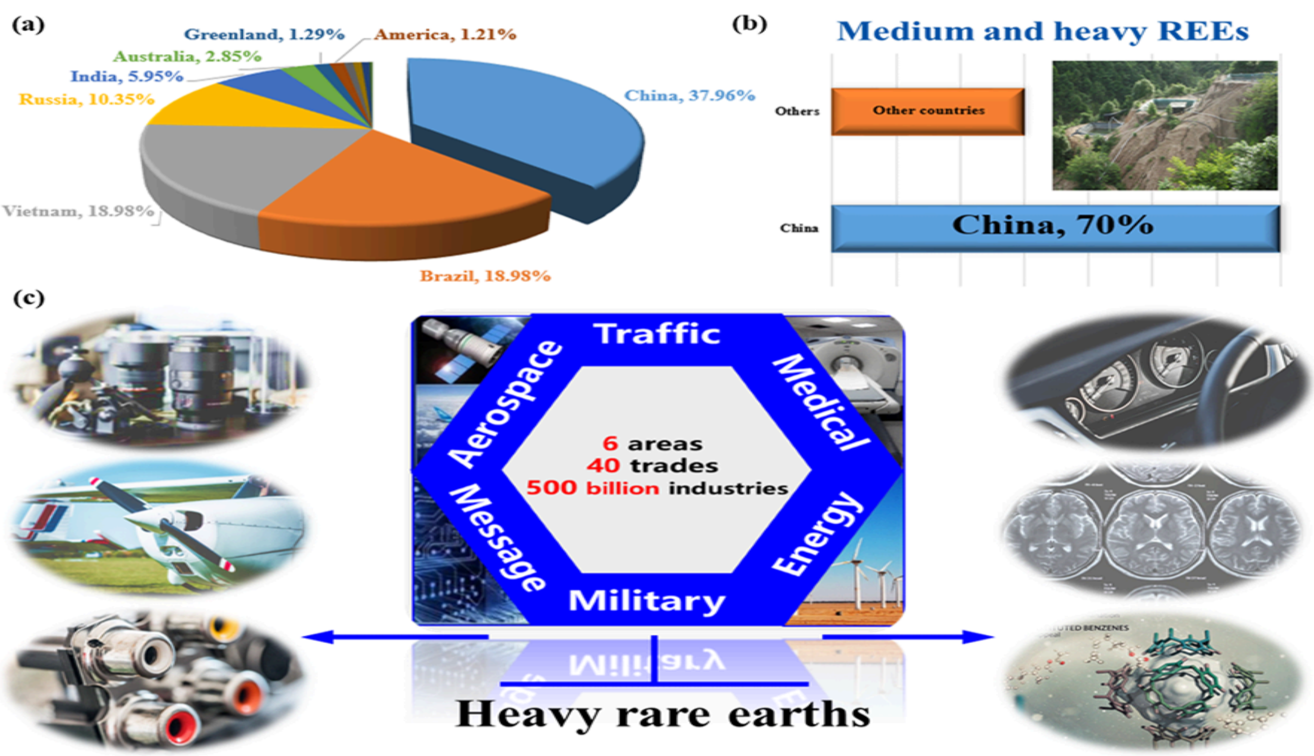


Fig. 1. (a) Global REEs reserves in 2020 (b) Global distribution of HREEs (c) Applications of HREEs.

METHODS OF EXTRACTION OF RARE EARTH METALS

In the extraction process, primarily the following methods are used:

- **Selective Oxidation:** The rare earth metal is oxidized selectively.
- **Selective Reduction:** Similarly, selective reduction is employed to obtain rare earth oxides.
- **Fractional Crystallization:** Technique used to separate rare earth elements based on their solubilities in a solution, allowing for the selective crystallization and separation of individual components through controlled heating and cooling processes.
- **Leaching of HREEs:** Techniques like in-situ leaching to dissolve and recover rare earths efficiently, aiming to reduce costs and environmental impact.
- **Ion Exchange:** Rare earth oxides are separated through ion exchange processes.
- **Liquid-liquid extraction of HREEs:** Liquid-liquid extraction of heavy rare earth elements (HREEs) utilizes the lanthanide contraction effect and complex formation to overcome similarities in electronic structure and atomic radius, enabling efficient separation.

There are other methods wherein rare earths are extracted using various methods from their abundantly available compounds.

- Reduction of Anhydrous Chlorides and Fluorides: Rare earth metals are obtained through the reduction of anhydrous chlorides and fluorides.
- Direct Reduction of Rare Earth Oxides: Direct reduction processes are employed to obtain pure rare earth metals.
- Fused Salt Electrolysis of Rare Earth Chlorides or Oxide Fluoride Mixtures: Rare earth metals can be extracted through fused salt electrolysis of rare earth chlorides or oxide fluoride mixtures.

These methods collectively enable the extraction and production of rare earth metals, playing a crucial role in various industrial applications and technological advancements.

SELECTIVE OXIDATION

- Selective oxidation is utilized to segregate rare earth metals such as cerium, praseodymium, and terbium by converting them from a trivalent state to a tetravalent state, facilitating their separation.
- Commonly employed oxidizing agents in selective oxidation reactions include persulfates, permanganate, and hypochlorite, while air or oxygen can also serve as oxidizing agents in these processes.
- In the selective oxidation process for praseodymium and terbium, their tetravalent states precipitate as rare earth oxides, settling due to their instability in aqueous solutions, thus aiding in their separation.
- Cerium's selective oxidation involves isolating tetravalent cerium from the rare earth mixture by either selectively dissolving trivalent elements in a dilute acid or completely dissolving all species in a concentrated acid followed by precipitation.
- Tetravalent cerium can be precipitated from the acidic solution by controlling the pH, facilitating the separation and recovery of cerium through selective oxidation methods.
- Selective oxidation plays a pivotal role in the production of rare earth oxides as it enables the segregation of specific rare earth metals based on their oxidation states, thereby contributing to the efficient recovery of these valuable elements.

SELECTIVE REDUCTION

- Selective reduction serves as a method for segregating rare earth metals like samarium, europium, and ytterbium by reducing them to a divalent state, thereby enabling their separation from other elements.
- In the process of selective reduction, samarium and europium can undergo reductive extraction into dilute sodium amalgam, while ytterbium can be separated using a method developed by Marsh specifically for selective reduction.
- McCoy devised a commercially utilized technique for the selective reduction of europium, wherein Eu (III) is reduced to Eu (II) by zinc in a chlorine solution, leading to the precipitation of divalent europium as a sulfate for subsequent processing.

- Unlike samarium and europium, zinc is not efficient in reducing ytterbium, prompting the use of an alternative method developed by Marsh for the selective reduction of ytterbium and samarium.
- Selective reduction presents an efficient approach for isolating particular rare earth metals based on their reduction states, thereby enhancing the effectiveness of recovery and purification processes.
- The process of selective reduction plays a pivotal role in rare earth metal production by facilitating the separation of specific elements through their reduction to a divalent state, streamlining their extraction and purification processes.

FRACTIONAL CRYSTALLIZATION

- Fractional crystallization serves as a technique for separating rare earth elements by exploiting their distinct solubilities in a solution, thereby facilitating the crystallization and subsequent separation of individual components.
- In this procedure, rare earth solutions are combined with a salt and then subjected to heating, followed by gradual cooling to induce the crystallization of rare earth oxides from the solution, thereby enabling their separation.
- For instance, ammonium nitrate salts are commonly employed in the separation of praseodymium and neodymium, while double magnesium nitrates are utilized for separating samarium, europium, gadolinium, and the ceric group during fractional crystallization.
- Bromates and ethyl sulfates find application in the separation of the yttric group in the fractional crystallization process, highlighting the versatility of this method in selectively separating various rare earth elements based on their characteristics.
- Fractional crystallization is particularly effective for lanthanides positioned at the lower end of the series, offering an efficient means of isolating specific rare earth metals from complex mixtures through controlled crystallization procedures.
- This method plays a pivotal role in rare earth oxide production by enabling the selective separation of specific rare earth elements based on their solubilities, thereby enhancing the efficiency of recovery and purification processes.

LEACHING OF HREEs

- Conventional methods for extracting rare earths from ion-adsorption ores are not efficient.
- In-situ leaching is a new technology that injects a solution underground to dissolve and recover rare earths, reducing costs and environmental impact.
- Researchers are working on optimizing leaching methods using techniques like controlled-rate leaching and new leaching agents.
- Ammonium salts are commonly used leaching agents, but new non-ammonia options are being explored to avoid pollution.
- Recovering rare earths from secondary resources is similar to primary resources, involving enrichment, leaching, separation, and purification steps.
- The text focuses on extraction and separation methods for high-purity rare earths, which is a critical step in the recovery process.

ION EXCHANGE METHOD

- Ion exchange entails the exchange of ions between an aqueous solution and an insoluble resin, involving absorption and elution stages for retrieving metals from the resin bed.
- This method finds utility in rare earth separation on a small scale due to its batch nature, with a commonly employed technique involving the retrieval of rare earth compounds using amberlite type resins and subsequent elution with completing agents such as citric acid, EDTA, and HEDTA.
- Neutral organic extractants like TBP are frequently utilized in ion exchange for recovering mixed rare earth oxides, whereas basic extractants are employed for retrieving anionic lanthanides, and acidic extractants like DEPHA are potent for separating most rare earth metals.
- Ion exchange reactions offer versatility in separating rare earth elements based on their properties, presenting an effective approach for selectively recovering specific rare earth metals from solutions through interactions with the resin.
- The method's capability to interchange ions between solution and resin enables the successful separation of various rare earth elements, thereby contributing to the efficient recovery and purification of these valuable metals.

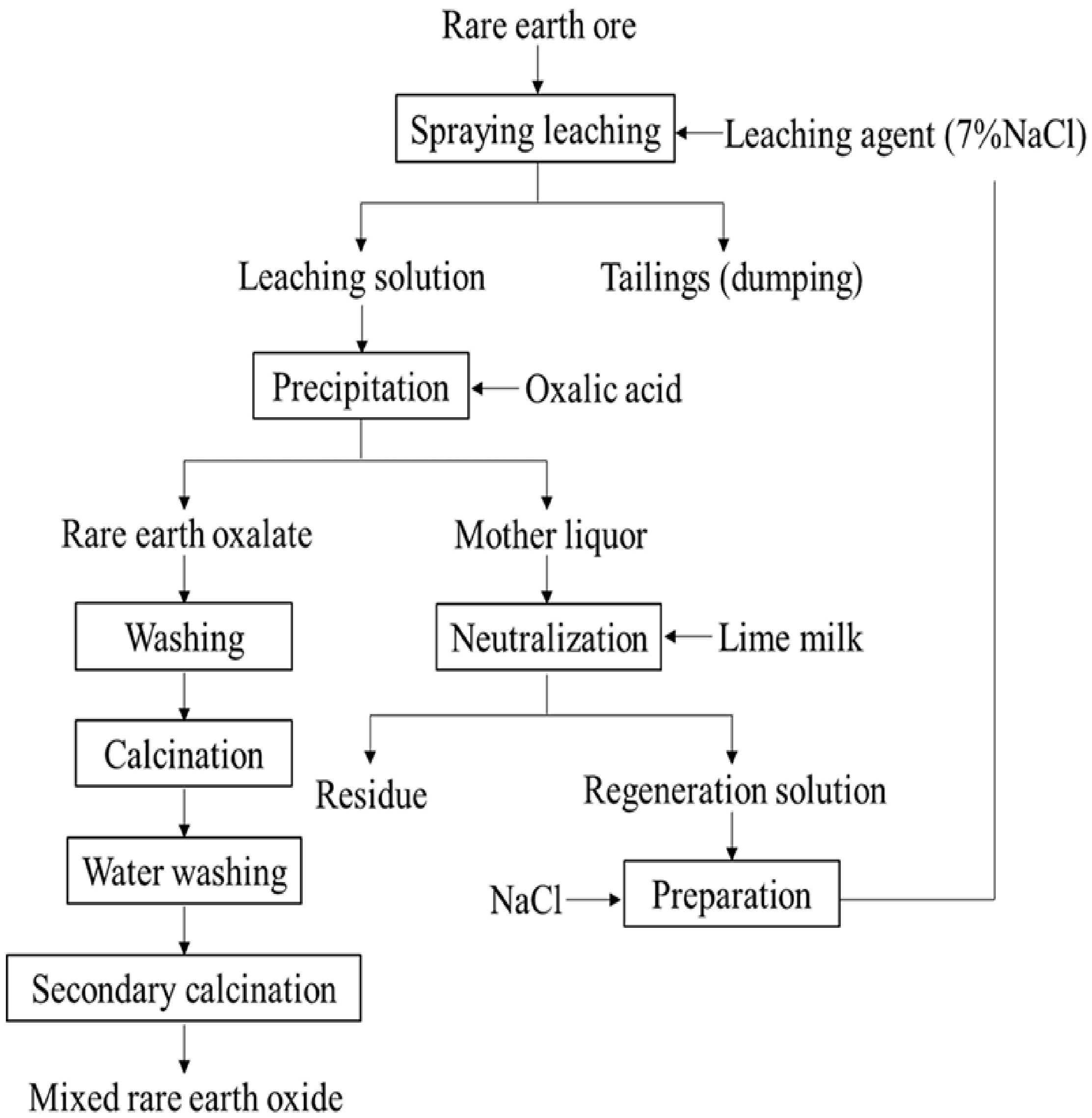
- Ion exchange plays a pivotal role in the production of rare earth metals by facilitating the selective recovery of specific elements through interactions with the resin, thereby enhancing the overall efficiency of rare earth element extraction and purification processes.

LIQUID-LIQUID EXTRACTION OF HREEs

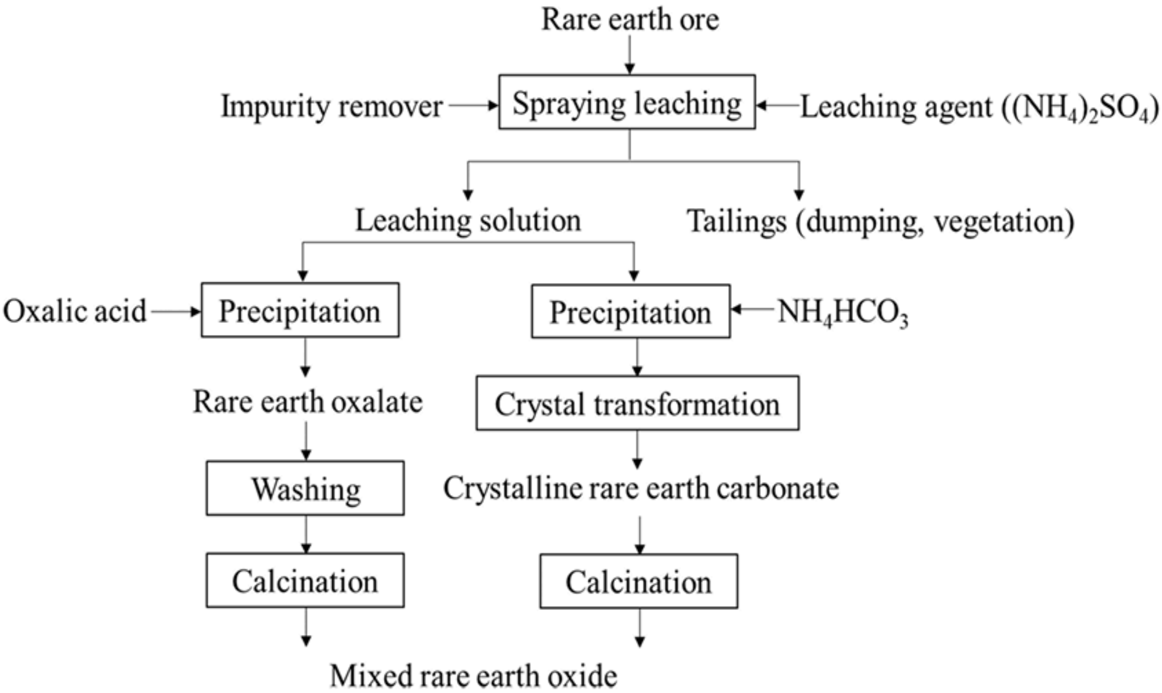
- Similar electronic structures, ion valence (mostly +3 with some exceptions), and atomic radii make it difficult to separate rare earth elements (REEs).
- As the atomic number of REEs increases, electrons fill an inner shell (4f) instead of the outer layer, leading to a high degree of similarity.
- Certain REEs have slightly unstable electron configurations, making them prone to losing or gaining an electron.
- The atomic radius of REEs generally shrinks with increasing atomic number due to incomplete shielding by electrons in a specific subshell (4f). However, there are exceptions for Eu and Yb.
- The size of an REE ion affects its ability to form complexes, which is a key factor used for separation techniques like solvent extraction.
- The lanthanide contraction effect allows separation of heavier rare earth elements (HREEs) from lighter ones (LREEs) due to their slight size variations.

FLOWCHARTS

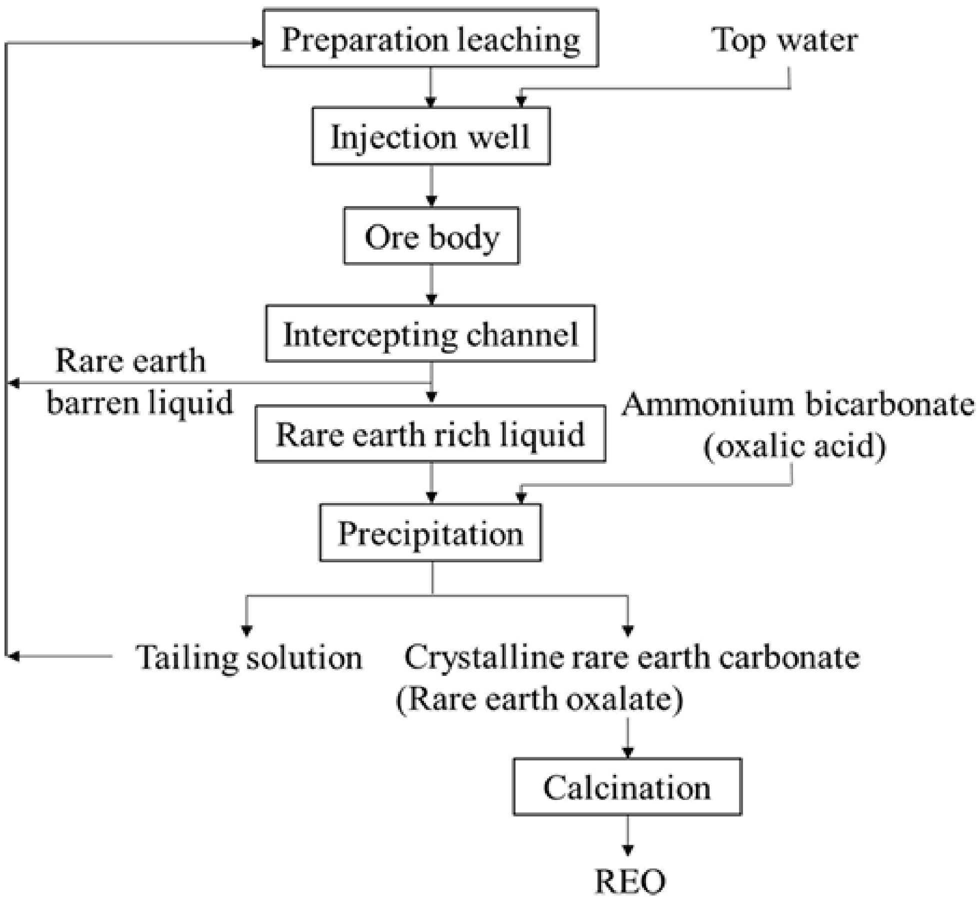
1. **The first-generation - sodium chloride pool leaching process of ion-type ore.**



2. **The second-generation - ammonium sulfate leaching process of ion-type ore**



3. **The third-generation - in-situ leaching process of ion-type ore**



Methods for Reduction Of Compounds Of Rare Earth Metals:

The following three methods help in extracting rare earth metals from their compounds found in nature.

DIRECT REDUCTION OF RARE EARTH OXIDES

- Direct reduction of rare earth oxides presents a method whereby rare earth oxides are reduced directly to metals without the prerequisite transformation into halides, offering a straightforward pathway to attain pure rare earth metals.
- Early endeavors in direct reduction by Winckler, Matignon, and Hirsch, employing magnesium or calcium as reducing agents, proved ineffective as the resultant mixture contained oxides and metals that were challenging to separate.
- A pivotal advancement in direct reduction was made by Daane in 1953 for reducing volatile rare earth metals. In this method, rare earth oxides were combined with lanthanum chips in a tantalum crucible under high temperature and vacuum conditions, leading to the sublimation and collection of rare earth metals as crystalline condensates.
- Further exploration into direct reduction by Onstatt involved the use of calcium instead of lanthanum. However, this approach necessitated multiple distillations to eliminate impurities and only yielded approximately 40% pure rare earth metals.
- General Motors introduced a molten salt process in 1988 for direct reduction, which entailed placing a rare earth oxide with calcium chloride and sodium chloride in a reaction vessel. In this process, calcium metal reduces the rare earth oxide to a rare earth metal at temperatures surpassing the melting point of the constituents but remaining below the vaporization temperature of sodium metal.
- The direct reduction of rare earth oxides represents a promising avenue to acquire pure rare earth metals, with diverse methods and techniques developed over the years to enhance efficiency and purity in the production process.

REDUCTION OF ANHYDROUS CHLORIDES AND FLUORIDES

- The reduction of anhydrous rare earth chlorides and fluorides serves as a method for generating pure rare earth metals by converting these compounds into metals through specific reduction processes.
- This technique entails the prior conversion of rare earth oxides into chlorides or fluorides before the reduction phase, enabling the utilization of various reducing agents due to the halides' comparatively lower stability compared to oxides.
- Metallothermic reduction of rare earth chlorides has undergone extensive research, with processes employing magnesium, calcium, lithium, and sodium as reducing agents to yield metals such as cerium, neodymium, gadolinium, and yttrium.
- Various techniques, including reduction with magnesium or calcium in dolomite-lined steel bombs, reduction with calcium in tantalum crucibles, and reduction with lithium vapor, have been developed to effectively produce rare earth metals from their chlorides.
- Although less prevalent than chlorides, metallothermic reduction of rare earth fluorides has also been investigated, with successful methods employing calcium as the reducing agent in high-temperature reactions conducted under argon atmospheres.
- Reduction via molten salt electrolysis presents an alternative approach for rare earth metal production, offering a less intricate and costly method compared to metallothermic reduction techniques. Commercial-scale production of lanthanum, cerium, praseodymium, and didymium has been accomplished through fused salt electrolysis of chlorides.

FUSED SALT ELECTROLYSIS OF RARE EARTH CHLORIDES OR OXIDE FLUORIDES MIXTURES

- Fused salt electrolysis emerges as a viable technique for rare earth metal production, presenting a simpler and more cost-effective alternative to metallothermic reduction methods. The method's feasibility is determined by assessing the theoretical decomposition potential.
- In this process, rare earth chloride mixtures undergo electrolysis at temperatures of up to 1100°C, as excessively high temperatures may cause electrolyte constituents to become volatile and lead to severe corrosion of cell wall materials by rare earth metals.
- Notably, lanthanum, cerium, praseodymium, and didymium (a neodymium alloy) have been successfully manufactured through commercial-scale fused salt electrolysis of chlorides, underscoring the efficacy of this method in rare earth metal production.
- To mitigate potential issues such as electrolyte volatility and damage to cell wall materials, the electrolysis cell operates within a temperature range of up to 1100°C.
- Fused salt electrolysis provides a controlled and efficient means of extracting rare earth metals from chloride or oxide fluoride mixtures, ensuring the production of high-quality metals suitable for diverse industrial applications.
- Through the application of fused salt electrolysis, essential rare earth metals like lanthanum, cerium, praseodymium, and didymium can be extracted and refined, bolstering the availability of these vital materials crucial for technological progress and industrial processes.

SUMMARY

- Yttrium and scandium, essential components in clean energy technologies, lasers, and magnets, are witnessing a surge in demand owing to global clean energy initiatives and technological progress.
- Securing stable supply chains for rare earth elements is paramount to fostering technological innovation and addressing supply-demand imbalances. This requires the implementation of intelligent processing, recycling, and reuse strategies for rare earth elements sourced from secondary outlets like post-consumer and manufacturing waste.
- The strategic significance of rare earth elements has escalated due to the limited availability of minable resources. Consequently, there has been a shift in production sources from traditional placer deposits to newer reserves such as monazite in South Africa and Bastnasite in Mountain Pass and China.
- Anticipated global demand for rare earths is poised for a significant increase, with China emerging as a dominant player in production. This trend has prompted strategic concerns and led to initiatives like the Rare Earths and Critical Material Revitalization Act of 2010 in the United States, aimed at ensuring a steady supply of these vital materials.
- A variety of methods are being explored for rare earth metal production, including the reduction of anhydrous chlorides and fluorides, direct reduction of rare earth oxides, and fused salt electrolysis of rare earth chlorides or oxide fluoride mixtures. Each method presents unique advantages and challenges in the production process.
- Effective techniques for preparing rare earth oxides, such as selective oxidation, selective reduction, fractional crystallization, ion exchange, and solvent extraction, are pivotal for obtaining pure rare earth metals from compounds. These methods significantly contribute to technological advancements and industrial processes.

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