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Alternative Resources of Rare Earth Elements in Pakistan †

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Abstract: Rare earth elements (REEs) have emerged as strategic elements. Due to their unique electronic and magnetic properties, REEs have extensive applications in modern-day technologies. Two aspects make the supply chain of REEs very critical: first, more than ~85% of the global rare earth elements are processed by China alone; second, presently, hardly any substitute materials exist for these elements. The supply chain of these elements is vulnerable because of the Chinese monopoly on rare earth resources. These circumstances drove researchers to explore alternative resources for these elements. This article reviews the prospective alternative resources of REEs. Based on the available resources and technical experience, a road map has also been suggested.

Keywords: rare earth elements; alternative resources; waste management and utilization; green engineering; sustainability and circular economy; Pakistan

1. Introduction

Rare earth elements (REEs) include 'Lanthanides' (atomic number 57–71) and two elements of Group IIIA of the Periodic table, i.e., ^{27}Sc and ^{39}Y. The REEs are further subdivided into light rare earth elements (LREEs), i.e., elements from ^{57}La to ^{64}Gd, and heavy rare earth elements (HREEs), including ^{65}Tb through ^{71}Lu. The unique electronic properties of REEs help them find applications in emerging technologies, catalysts, special alloys, and high-performance magnets. The high-performance permanent magnets are vital for clean energy technology and many defense applications. The major reserves of REEs are found in China, the USA, Australia, and Myanmar. Other viable ore bodies are found in Thailand, Vietnam, and India. China is the world's largest producer of REEs by a wide margin [1].

2. Alternate Resources

Because of the ever-increasing REE applications in innovative products and green technologies, a growth rate of ~10% per year has been witnessed in the last decade. The limited reserves, Chinese monopoly, increased demand, and high value of REEs are the driving forces behind exploring alternative sources and recycling rare earths. Promising secondary sources with significant concentrations of REEs include marine sediments, ore tailings, and the recycling and processing of wastes like mine tailings, coal ash, and electronic-waste (e-waste).

2.1. Deep-Sea Mining

Depleting terrestrial deposits and widening the gap between the demand and supply of REEs have provided an impetus for exploratory research in deep-sea mining. Apart from base and precious metals, including Cu, Zn, Pb, Ag, and Au, the seabed can provide a new resource for REEs. Studies show that deep-sea mud contains high concentrations of rare earth elements (>5000 ppm) and yttrium at numerous sites in the Pacific Ocean. Because of the enormous available volume and promising mineralogical features, the mud reserves of REEs have great potential for REEs. Presently, our experience with the deepest oil rigs is

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limited to ~3500 m, whereas REE-rich muds are found at depths of more than 5000 m. New technologies will, therefore, be investigated to exploit these reserves. In addition, extensive studies are needed to better understand the deep-sea ecosystems [2].

2.2. Wastes

REEs can be recycled from scrap metal and end-of-life products, e.g., magnets, phosphors, and catalysts. Relatively large amounts of REEs are found by recycling rechargeable nickel–metal hydride batteries (as $LaNi_5$) and permanent magnets (as $SmCo_5$- and $Nd_2Fe_{14}B$-based alloys). In addition to recycling, other resources of REEs include mine tailing, carbon fly ash, and e-waste.

2.2.1. Mine Tailings

Apart from other options, the recovery of REEs as a by-product from ores of other metals and REE-rich mine tailings is an area of active investigation. The extraction of the target materials leaves behind a mass that has a relatively high percentage of REEs compared to its initial concentration in the virgin ore. In addition, recovery from metal tailings is simpler in many respects. The tailing process precludes many pre-extraction steps. In tailings, REEs are pre-concentrated, homogenized, and close to the surface. This reduces the capital and operating costs of REE extraction, thus making it an attractive option. Mine tailings are potentially a major secondary resource of REEs. The mine tailings with significant potential for REEs are discussed below.

Bauxite: Besides iron and titanium, bauxite residues contain REEs. The concentrations of REEs in the bauxite residue may range from 500 to 1700 ppm. The annual global production of bauxite residue exceeds 150 million tons. This makes bauxite residues a significant source of REEs. Research efforts are underway to efficiently recover REEs from bauxite residue [3].

Gold: HREEs have been reported in residues from alluvial gold mine tailings in the Columbia and Olympic Dam Cu-Au-Ag deposits in Australia [4,5]. Gold rush-era mines in the western United States are presumed to be a good resource for REEs. The large amounts of REEs are believed to have been initially discarded in the old gold mines, either because they formerly had no value or the ores were analyzed only for the target material.

Iron: The iron–niobium–REE deposit of the Bayan Obo Inner-Mongolia Mine (China) has been mainly extracting iron since 1927. The ore deposit, in addition to Fe (~35%), contains up to 6% rare earth oxides. The tailings from iron ore mines in Kiruna, Sweden, have been reported to contain a substantial amount of REEs with a concentration of 1200–1500 ppm [6].

Zircon: REEs are often found side-by-side with zirconium. Studies aiming at the optimization of REE extraction from zircon tailings have been initiated in China and Indonesia [7,8].

Uranium: Various studies have been conducted to recover REEs from uranium tailings. The primary study on the Mary Kathleen mine in Queensland (Australia) suggests that a combination of hydrometallurgical, bioleaching, and phyto-extraction processes provides the best results [5].

2.2.2. Fly Ash

Coal accounts for more than 39% of the world's energy production. Coal is also used in various other industrial processes, e.g., cement production and gasification. These processes generate enormous volumes of coal ash. Coal ash is classified into slag, bottom ash, and fly ash. Fly ash is composed of fine particles from the combustion of coal that are carried by flue gases. Most of the REEs end up in the fly ash. Detailed economic feasibility and environmental impact analyses have been undertaken that will determine the suitability of fly ash for REE extraction. Nevertheless, the large volume of coal fly ash makes it a potential secondary resource for REEs [9].

2.2.3. E-Waste

E-waste is the fastest-growing component of solid waste. Each year, nearly 40 million tons of e-waste is produced globally. The e-waste contains valuable elements like precious metals, Cd, Co, Cu, Ni, Pb, Zn, and REEs. Breakthrough in the recovery of these metals from e-waste can be a sustainable resource for many metals because of the ever-increasing volume of e-waste. The new ultrafast Flash Joule Heating (FJH) process for the evaporative separation of metals from e-waste is a very promising technique because of its high yield and environmental friendliness [10].

3. Separation Chemistry

In nature, REEs have mineralized together and are found in mixtures with other REEs. Individual rare earth elements must be separated and refined from the neighboring lanthanides for use in target applications. The similarity of the chemical properties of REEs makes them nearly indistinguishable, thus making the task of separation extremely complex and cost-intensive. Various technologies have been developed for separating and recovering individual rare earth elements. Solvent extraction is the most widely used separation technology for REEs. This newly reported self-assembly route holds great promise for REE separations [11].

4. Options for Pakistan

There is a consensus among the professionals that Pakistan remains the least geologically explored country. The exploratory work conducted in most cases is unscientific, random, insufficient, and sketchy. The lack of reliable data makes any planning effort futile. REE deposits have been claimed at various sites in Khyber-Pakhtunkhwa, Gilgit-Baltistan, and Balochistan. These claims, however, remain invalidated. The occurrence of carbonatites in Gilgit-Baltistan and Neelam implies the significant potential for LREE deposits.

As a result, the potential resources of REEs in Pakistan are confined to alternate resources. The option of deep-sea mining is ruled out because of the lack of technological capability. Bauxite is mined in Pakistan, but the fact that the raw ore is exported without processing undermines this situation. The drilling work on the new Chiniot-Rajao iron ore project is in progress. The potential of REEs in these reserves, however, is yet to be explored.

Due to the nuclear material program of the country, data on many uranium sites are available. This includes data on the abandoned uranium mines and sites not mined due to the low grade of uranium reserves. Zircon tailings are another resource worth considering.

The poor economic conditions have made Pakistan a dumping ground for e-waste. In the context of REEs, this curse provides an opportunity for alternative resources of many valuable metals, including REEs. The addition of coal-fired power plants to the national energy sector will generate an ever-increasing volume of fly ash, which is another potential resource for REEs.

The established affinity of REEs with alluvial and ocean clays makes a sound case for the exploration of REE-enriched alluvial sands and scanning the vast beach line of the country.

As mentioned earlier, the extraction and separation of REEs is a very complex process. Fortunately, the vast experience acquired from the separation processes of nuclear materials, particularly solvent extraction, can provide a good head start for extraction of REEs from the alternative resources mentioned here.

5. Conclusions

1. The limited proven reserves and increasing demand have driven countries to explore alternative resources and innovative processes, e.g., deep-sea mining and the recovery of REEs from wastes.
2. Recent developments in separation chemistry (self-assembly) and e-waste processing (FJH) are expected to provide breakthroughs in the recovery and separation of REEs.

3. Since the concentration levels of REEs in the wastes are quite low, only the co-production of rare earth elements with other associated valuable elements makes waste an economically viable resource.

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References

1. Liu, S.; Fan, H.; Liu, X.; Meng, J.; Butcher, A.R.; Yann, L.; Yang, K.; Li, X. Global rare earth elements projects: New developments and supply chains. *Ore Geol. Rev.* **2023**, *157*, 105428. [CrossRef]
2. Kato, Y.; Fujinaga, K.; Nakamura, K.; Takaya, Y.; Kitamura, K.; Ohta, J.; Toda, R.; Nakashima, T.; Iwamori, H. Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. *Nat. Geosci.* **2011**, *4*, 535–539. [CrossRef]
3. Borra, C.; Blanpain, B.; Pontikes, Y.; Binnemans, K.; Gerven, T.V. Recovery of Rare Earths and Major Metals from Bauxite Residue (Red Mud) by Alkali Roasting, Smelting, and Leaching. *J. Sustain. Metall.* **2017**, *3*, 393–404. [CrossRef]
4. Echeverry-Vargas, L.; Ocampo-Carmona, L.M. Recovery of rare earth elements from mining tailings: A case study for generating wealth from waste. *Minerals* **2022**, *12*, 948. [CrossRef]
5. SKrneta; Ciobanu, C.L.; Cook, N.J.; Ehrig, K.; Kontonikas-Charos, A. Rare Earth Element Behaviour in Apatite from the Olympic Dam Cu–U–Au–Ag Deposit, South Australia. *Minerals* **2017**, *7*, 135. [CrossRef]
6. Abaka-Wood, G.B.; Ehrig, K.; Addai-Mensah, J.; Skinner, W. Recovery of Rare Earth Elements Minerals from Iron-Oxide-Silicate-Rich Tailings. *Eng* **2022**, *3*, 259–275. [CrossRef]
7. Liu, H. Investigation on joint mining of Rare earth elements and zircons from the Yangtze River, China. *J. Phys. Conf. Ser.* **2021**, *2021*, 012055. [CrossRef]
8. Trisnawati, I.; Prameswara, G.; Mulyono, P.; Prasetya, A.; Petrus, H.T.B.M. Sulfuric Acid Leaching of Heavy Rare Earth Elements (HREEs) from Indonesian Zircon Tailing. *Int. J. Technol.* **2020**, *11*, 804–816. [CrossRef]
9. Dodbiba, G.; Fujita, T. Trends in Extraction of Rare Earth Elements from Coal Ashes: A Review. *Recycling* **2023**, *8*, 17. [CrossRef]
10. Deng, B.; Luong, D.X.; Wang, Z.; Kittrell, C.; McHugh, E.A.; Tour, J.M. Urban mining by flash Joule heating. *Nat. Commun.* **2021**, *12*, 5794. [CrossRef] [PubMed]
11. O'Connell-Danes, J.G.; Ngwenya, B.T.; Morrison, C.A.; Love, J.B. Selective separation of light rare-earth elements by supramolecular encapsulation and precipitation. *Nat. Commun.* **2022**, *13*, 4497. [CrossRef] [PubMed]