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**RARE EARTH METALS AS A COMPONENT OF THE NATIONAL SAFETY IN MINERAL RESOURCES**

*In this article the analysis of use and extraction technologies of rear earth metals are presented. Examples of the impact of those metals on the world economy and politics are showed. In addition, the environmental impacts of the mining industry and question of the national safety of Ukraine in those raw materials were observed.*

*Key words: rare earth metals, environmental aspects, recycled materials, solution mining, pollution.*

*В статті проаналізовані використання та технології вилучення рідкісних земельних металів. Наведені приклади впливу цих металів на світову економіку та політику. Також розглянуті деякі аспекти впливу гірничодобувної промисловості на довкілля та питання забезпеченості України цією сировиною.*

*Ключові слова: рідкісні земельні метали, екологічні аспекти, матеріали вторинної переробки, вилуговування, забруднення.*

*В статье проанализированы использование и технологии извлечения редкостных земельных металлов. Представлены примеры влияния этих металлов на мировую экономику и политику. Также рассмотрены некоторые экологические аспекты влияния горной промышленности на окружающую среду и вопросы обеспечения Украины этим сырьем.*

*Ключевые слова: редкостные земельные металлы, экологические аспекты, сырье вторичной переработки, выщелачивание, загрязнение.*

*Statement of the problem and its relationship to important scientific and practical tasks. List of strategically significant minerals can vary depending on the military, political and economic priorities of the state system. Also,*

industrial production, global market conditions, state of foreign economic relations and other circumstances are very important for this issue. For Ukrainian economy the most important minerals are: iron and manganese ore, uranium, titanium, zircon, coal, various nonmetallic minerals [1], fuel and energy resources, noble metals, ores of nonferrous and rare metals, some nonmetals, which used for special alloys production (in the military and space technology, as well as the most important technological processes).

*Analysis of recent research and publications, which discuss current issues.* Today, rare earth metals are incorporated into many of the modern technological devices that we all use every day. For example, rare earth elements such as europium are implemented into cathode ray tubes and liquid crystal displays that are used in our television and computer monitors [2]. Cerium, one of the most abundant and least expensive rare earth elements, is used as a polishing agent for glasses and also in catalytic converters as a pollution inhibitor in all the vehicles in production today. Small, lightweight, rare earth element (REE) based magnets have allowed miniaturization of numerous electrical and electronic components used in appliances, audio and video equipment, computers, automobiles, communications systems, and military gear [2]. These permanent magnets have been completely revolutionized by alloys containing neodymium, samarium, gadolinium and dysprosium, which have allowed them to be manufactured smaller and lighter in order to keep up with the market for slimmer but yet more advanced electronic appliances such as iPod's, iPad's and cell phones. Neodymium based magnets are also known to be used in microphones, loudspeakers, headphones, computer hard drives and can be found in wind and tidal electricity turbine generators.

*Objective of this study* is to establish the value of rare earth metals for Ukrainian safety in the context of globalization.

*Statement of main research data with full justification of scientific results.* Environmental aspects of the technological applications of rare earth elements have also become increasingly important with the growing issues of green energy and the ongoing debate over global warming. For example, Rare earth elements within catalytic converters are pivotal in pollution control of automobiles while new energy-efficient fluorescent lamps implementing rare earth elements could also potentially reduce carbon dioxide emissions in equivalence to removing one-third of the automobiles currently on the road [2]. Batteries, which have become an important power source for just about every electronic device we use today, also pose a large challenge for our environment. But with lanthanum-nickel-hydride batteries replacing Ni-Cd batteries in computers and communications applications and possibly the lead acid batteries in automobiles, they would offer greater energy density, better charge-discharge characteristics and fewer environmental problems [2]. Lastly, with the increasing demand for possible solutions for electric automobiles, rare earth elements such as lanthanum are used as an intermetallic component of

Nickel-Metal-Hydride batteries which are the basis of electrically powered vehicles.

These are just a few of the many uses and implementations of rare earth elements in our world today and it is obvious that it would be impossible to have the advanced technological devices and applications that we currently employ without them. They prove to be incredibly important in the production of thousands of electronic gadgets, and have contributed to the ongoing push for greener and more efficient energy sources (fig. 1).

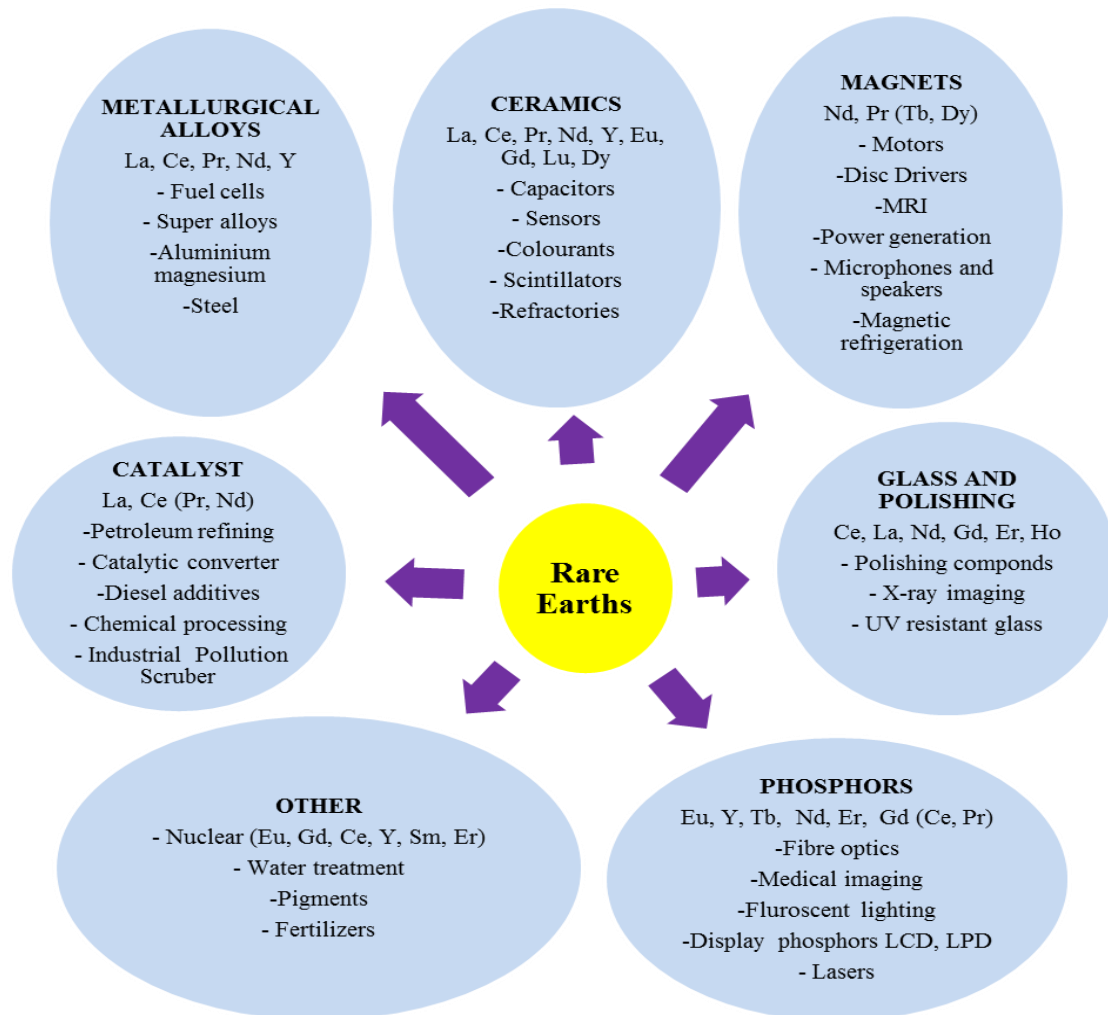


Fig.1. Application of rear earths

Until 1948, most of the world's rare earths were mined in India and Brazil. After 1950, South Africa became the world's main producer of REE and from 1960 to 1980, the Mountain Pass (REE mine in CA) was the biggest REE producer in a world (fig. 2). Today, some mines in India and South Africa still operate and produce some REE, but the percent of their production is very small compare to that of China (table 1). According to the latest data, China now produces over 97% of the world's REE supply (Inner Mongolia) [3] and it has 37% of proven world's reserves [4]. By comparison, in 2010, the USGS released a study which found that the United States had 13 million metric tons of rare earth elements available [5].

Table 2. World Mine Production and Reserves [6]

| World mine production and reserves |                       |        |                |
|------------------------------------|-----------------------|--------|----------------|
| Country                            | Mine production, tons |        | Reserves, tons |
|                                    | 2008                  | 2010   |                |
| USA                                | -                     | -      | 13000000       |
| Australia                          | -                     | -      | 54000000       |
| Brazil                             | 650                   | 650    | 48000          |
| China                              | 120000                | 120000 | 36000000       |
| Commonwealth of Independent States | NA                    | NA     | 19000000       |
| India                              | 2700                  | 2700   | 3100000        |
| Malaysia                           | 380                   | 380    | 30000          |
| Other countries                    | NA                    | NA     | 22000000       |
| World total (rounded)              | 124000                | 124000 | 99000000       |

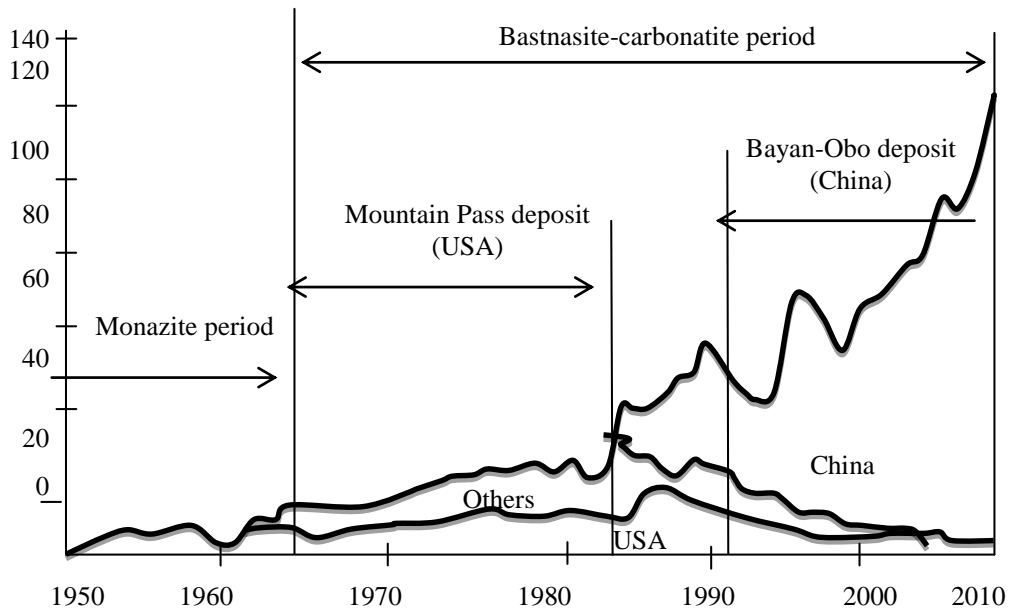


Fig. 2. Global production of rear earth oxides in thousand tons (Angerer et al, 2009)

Today though, there is growing concern that the world may soon face a shortage of the rare earth elements due to the extremely high appeal of REE (fig. 3). It is expected, that in several years, world's demand for REE will exceed supply by 40,000 tons annually.

These concerns have intensified due to the actions of China (main producer of REE's) on their export policy. Specifically, China has announced regulations on exports and a crackdown on smuggling [7]. "On September 1, 2009, China announced plans to reduce its export quota to 35,000 tons per year in 2010...2015, ostensibly to conserve scarce resources and protect the environment". On October 19, 2010 China reported that it will "further reduce quotas for rare earth exports by 30% at most next year to protect the precious

metals from over-exploitation" [8]. "At the end of 2010 China announced that the first round of export quotas in 2011 for rare earths would be 14,446 tons which was a 35% decrease from the previous first round of quotas in 2010" [9].

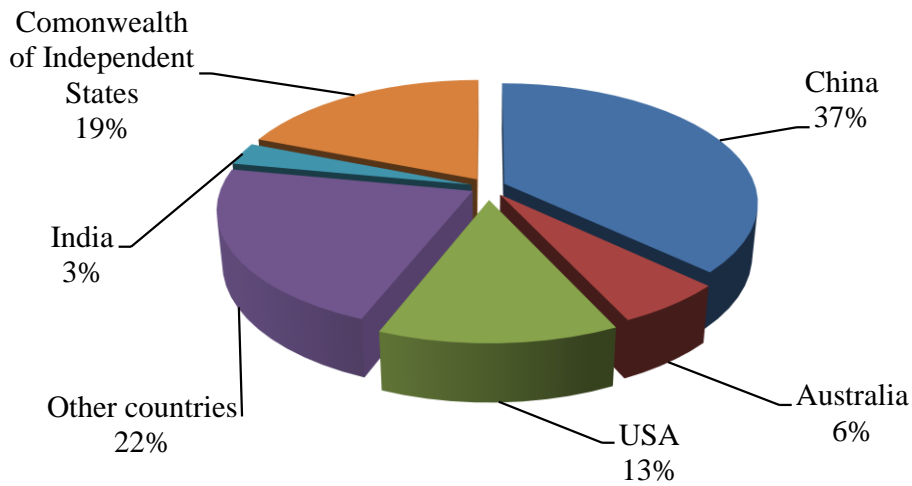


Fig. 3. Global Distribution of REE Reserves [7]

Due to the availability of a cheap working force in China, almost all REE mines around the world would be forced to lower production costs in order to remain competitive or be forced to close. Also, in the last decade, the consumption of REE has increased dramatically which has resulted with obvious price increases.

In past years the REE market has been in over-supply and has led to a lack of focus on recycling technologies, but due to fact that the price for some REEs have increased dramatically, and with some concerns about security of supply, pressure on primary production can be reduced by using secondary sources and recycling techniques. Today, only small quantities of REE-bearing scrap are recycled (table 2).

The most commonly recycled REE materials are magnets. In research articles, many researchers say that magnets made from recycled materials do not have the same performance as those prepared from primary raw materials. However, an advantage to REE magnets is that they can be reused; usually, the life of magnet is longer than that of the device in which it is used (i.e. disk driver). "Such companies as Honda and Toyota have developed effective return and refining programs for their hybrid vehicles which use nickel- metal-hydride batteries. Every consumer receives \$200 per battery returned at the end of its life".

Table 3. REE Price Trends 2002-2011 [10]

| REO  | Price (\$ per kg) |     |     |     |    |    |     |     |
|------|-------------------|-----|-----|-----|----|----|-----|-----|
|      | La                | Ce  | Nd  | Pr  | Sm | Dy | Eu  | Tb  |
| 2001 | 7                 | 4   | 11  | 6,2 | 9  | 35 | 310 | 135 |
| 2002 | 2,3               | 2,3 | 4,4 | 3,9 | 3  | 20 | 240 | 170 |

|      |      |      |        |        |       |       |       |      |
|------|------|------|--------|--------|-------|-------|-------|------|
| 2003 | 1,5  | 1,7  | 4,4    | 4,2    | 2,7   | 14,6  | 235,4 | 170  |
| 2004 | 1,6  | 1,6  | 5,8    | 8      | 2,7   | 30,3  | 310,5 | 398  |
| 2005 | 1,5  | 1,4  | 6,1    | 7,6    | 2,6   | 36,4  | 286,2 | 300  |
| 2006 | 2,2  | 1,7  | 11,1   | 10,7   | 2,4   | 70,4  | 240   | 434  |
| 2007 | 2,8  | 2,6  | 31,2   | 30,4   | 3,1   | 88,3  | 311   | 575  |
| 2008 | 8,8  | 4,4  | 32,9   | 32,6   | 4,8   | 120,8 | 491   | 740  |
| 2009 | 5,9  | 3,8  | 14,5   | 14,5   | 4,8   | 112   | 495   | 360  |
| 2010 | 6,4  | 5,0  | 30,8   | 30,3   | 4,5   | 193   | 525   | 580  |
| 2011 | 20,6 | 23,4 | 156,99 | 135,01 | 16,48 | 1459  | 2904  | 2119 |

Rare earth elements, a compilation of seventeen chemical elements such as cerium, lanthanum, neodymium and others, comprise what is known today, as one of the largest imported and exported products in the world. It would be hard to mention the rare earth metal market without mentioning China; the world's largest exporter of rare earths, responsible for supplying more than 97% of the global demand. As mentioned previously, China has begun to cut back on the amount of rare earth metals that it produces and has started enforcing embargoes on the export of rare earth metals to certain countries. China has also adopted a series of policies this year to balance environmental protection needs and industrial demands, including stricter emission limits on miners, and an imposed recourse tax. In conjunction with these imposed policies along with stricter controls over exporting rare earth metals, it is believed that it will increase operational costs, leading to higher prices of rare earth metals all together. In addition to being the largest producer of rare earths, China is also one of the largest consumers, using extreme amounts of rare earth metals in their enormous electronics markets.

Rare earth elements are extremely important to the electronics industry, where they are used in manufacturing car batteries, cell phones, computer memory chips, motherboards, plasma televisions, and many other electronic devices that we all use every day. The military and defense department also use rare earth elements as a primary component in anti-missile defense, precision-guided weapons and other rare earth based technologies. Recently, with the increased demand for other forms of cleaner and more renewable energy, rare earth elements have been widely used in the production of hybrid and electric automobiles. The demand for rare earth elements is expected to increase each year, as the push for more electronics and green technologies grow, increasing the market for China. A report released in 2010 by the U.S Government Accountability Office, estimated that building a rare earth metal supply chain in the United States could take up fifteen years and would involve a series of complications including the creation of new technologies and obtaining patents that are currently held by international companies.

*Resources in Ukraine.* The REE resources of the Commonwealth of Independent States (CIS) are dominated by loparite deposits. Russia has significant REE resources in the apatite-nepheline of the Kola Peninsula but REE are not currently being extracted during the processing of these ores. Total

reserves of the CIS are estimated at 19 million tones. Kyrgyzstan has significant reserves of REE estimated at 51500 tons (table 3).

Extractions of radioactive elements, such as uranium and thorium, are often associated with the discovery of other REEs. Uranium mining is similar to REE mining, and is consistent of three major mining practices: surface (open pit), underground, and solution mining. As an example of open pit mining in the U.S, Molcorp’s Mountain Pass extracts REE ore in an open pit mine, measuring 100 m deep [11]. Solution mining, or beneficiation, is in-situ mining and involves “leaving the ore ... in the ground ... [and] dissolving them and pumping the pregnant solution to the surface” [12].

Other methods focus on extracting the heavy mineral sands in surface placer deposits, followed by wet and dry processing methods. Extraction is typically done by floating cutterhead or bucket wheel dredges, in which minerals are concentrated and tailings are discharged to the disturbed areas . The mineral concentrate is then sent to a wet milling process (i.e. screens, hydrocyclones, spirals, etc.) and then to dry milling process (i.e. scrubbing, drying, screening, electrostatic, electromagnetic, magnetic, and gravity processes).

Table 3. Rare Earth resources in Ukraine [13]

| Deposit Type    | Deposit name                          | Location |           |                          | REE minerals  | Age               | Host Rocks  |
|-----------------|---------------------------------------|----------|-----------|--------------------------|---|-------------------|---|
|                 |                                       | Latitude | Longitude | Source                   |   |                   |   |
| Carbonite       | Chernigovskii (Novopoltavskii)        | 47-14N   | 36-15E    | Kogarko and others, 1995 | monazite, allanite, ancylite, cerium fergusonite                          | 1820-2190Ma       | beforsite, alvikite, carbonatite breccia, syenite, peroxenite |
| Alkalic igneous | Azov sea Coast Dikes                  | 47-11N   | 36-34E    |                          | niobium, phosphorus, titanium   | Early Proterozoic | Alkaline pyroxenites, jacupirangite                           |
| Alkalic igneous | Korsun-novomirgorodskii Pluton margin | 48-14N   | 31-17E    |                          | <u>allanite</u> , <u>chevkinite</u>                                       | Late Archean      | Monzosyenit, syenite, rapakivi granite, gabbro, granite       |
| Alkalic igneous | Malotersyanskii                       | 48-20N   | 35-39E    |                          | <u>pyrochlore</u> , <u>bastnäsite</u> , <u>allanite</u>                   | 1740 Ma           | Syenites, foyaite   |
| -               | Yastrebits                            | 51-14N   | 28-51E    |                          | <u>bastnäsite</u> , <u>parisite</u> , <u>allanite</u> , <u>britholite</u> | 1720 to 1740 Ma   | Syenite, foyaite  |
| -               | Azovske                               | 45-35N   | 34-34E    | NIMA, 2001               | -   | -                 | -   |
| -               | Mazurivske                            | -        | -         | O’Driscoll, 1998         | -   | -                 | -   |
| Phosphorite     | Dniprodzerzhinsk                      | -        | -         | Will and others, 1995    | -   | -                 | -   |

Once the material has been concentrated, acid digestion usually follows. As mentioned above, two main minerals ores containing REEs are monazite and bastnasite. Sulfuric acid and hydrochloric acid are used in each of the concentrated slurries, respectively. The EPA provides outlines of processing the ores. In monazite ores, the REE- and thorium-sulfates in the slurry concentrate react with sulfuric acid between 180-200°C and are recovered through filtration as REE-oxides. The waste solids from the ore are then discarded. For bastnasite ore, the slurry is filtered, and the filter cake is digested with NaOH, producing REE-hydroxide cakes. The cakes are then chlorinated with HCl, filtrated, and evaporated, producing REE-chloride products. The waste contains sodium fluoride, which is further processed and the subsequent cake is discarded.

Mining of REE causes significant amounts of pollution. In China, reports have shown that 1 ton of REE's mined produce 60,000 m<sup>3</sup> of waste gas, 300 m<sup>3</sup> of acidic water, and 1.4 tons of radioactive waste. Reports of diseases, water pollution, and farmland destruction exist, even for well-regulated mine areas [14]. The EPA outlines different waste streams for each unit operation in the extraction and processing of REEs. In the extraction/beneficiation step, the tailings and any magnetic fractions are considered waste streams. When the concentrate is processed with acid digestion, the waste solvent and solids are considered ignitable while wasted filter cakes contain lead and mercury [10].

For each of the different REE metals processed, varying wastes result. According to the EPA, for lanthanide production, a corrosive ammonium nitrate solution is produced; in cerium production, process wastewater contains lead and ammonium, which are corrosive. In mischemetal (an alloy of REE) production, the spent liquor produced is corrosive, while air pollution control devices have corrosive wastewater containing chromium and lead, with the resulting waste sludge found to be corrosive.

In Protano, et. al. (2002), reasons for REE concentrations in natural streams resulting from naturally leached mine waste piles are explored. The high oxidation numbers and high ionic radii properties of REE dominate the aqueous geochemistry. Often, the REE metals have an oxidation state of 3<sup>+</sup>, and in oxidant conditions, become 4<sup>+</sup>. The change in oxidation state decreases the ionic radii, resulting in an enhanced surface reactivity and strong complexes with hydroxides, fluorides, sulfides, carbonates, and phosphates [15].

*Conclusion.* The demand for rare earth metals is expected to increase each year, as more electronics and green technologies depend on these important chemical elements. China, as the world's leading producer of rare earth metals and related electronics, is currently in the driver's seat. Today, many papers estimate that building a rare earth metal supply chain could take up to 15 years. As China continues to protect its supply of rare earth metals, other countries around the world will be forced to develop their own production capabilities in order to meet the growing demands for rare earth metals.

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