

CRITICAL METALS – THEIR CURRENT STATUS AND INDIAN CONTEXT

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ABSTRACT

In geological parlance a large number of Rare Elements are in the forefront for use in most modern and future technologies in the world. These are classified into five genetic groups as follows: Group1- Rare Alkaline Elements(Li,Rb,Cs), Group2-Light Element(Be),Group3- Rare high melting elements(Nb,Ta,Zr,Hf),Group4-Rare Earth Elements(La to Lu,Sc,Y) and Group5- Dispersed elements- Ge, Re, Tl, Cd, Ga, In, Se, Te, . Some of these metals are classed as “critical metals” due to their geological scarcity and supply risk. These scarce metals that are not mined as such, but are now obtained exclusively, or mostly, as by-products of the major industrial metals. The list includes gallium (from bauxite); arsenic, cobalt, molybdenum, rhenium, selenium, tellurium (from copper ore), cadmium, germanium and indium (from zinc); cobalt (from nickel) and rhodium and ruthenium (from platinum and palladium). To this, 17 Rare Earth Elements (REE) are included. These critical metals are important for future sustainable (“green”) technologies. China and USA are major producers of primary REE in the world. The former dominates the world scenario. India does produce REE from beach and inland monazite sand. The future demands for the critical metals rest on their use as (i) Dopants in Semiconductors ,(ii) Catalysts,(iii) Electrical storage,(iv) Alloying elements,(v) Additives and (vi) Abrasives. India has the geological potential to search for many of the critical metals.

I .INTRODUCTION

The United Nations Environment Program (UNEP) identified Critical Metals (CM) for future sustainable (“green”) technologies and their recycling potential. The technologies selected were electronic and electrical equipment (EEE), photovoltaic technologies, batteries and catalysts. The metals considered to be critical were tantalum, indium and ruthenium for EEE; gallium, tellurium and germanium for photovoltaic technologies; cobalt and lithium for batteries; platinum group metals (PGM) for catalysts and rare earth elements (REE) in general. These metals are classed as “critical metals” due to their geological scarcity and supply risk. Concern about the future need for these metals in most developed economies has resulted in a number of reports discussing sources of supply and their criticality. India is endowed with diverse and significant mineral resources. It is the leading producer of some of the minerals. India produces 89 minerals out of which 4 are fuel minerals, 11 metallic, 52 non-metallic and 22 minor minerals. In India, 80% of mining is in coal and the balance 20% is in various metals and other raw materials such as gold, copper, iron, lead, bauxite, zinc and uranium. However shortage of indigenous supply of CM has been felt for long. Ministry of Mines, Govt.of India had stressed the need to intensify exploration & process R&D for creating indigenous production capacities. To achieve this, a high level Steering Committee has been constituted to look into the current availability of Rare Earths and to suggest short, medium and long term strategies for exploration, production and processing, to ensure long term availability of the raw material (C-TEMPO, 2011).

II. RARE ELEMENTS

In geological parlance these CMs` are classified into 5 groups under a broad term as Rare Elements. These are lithophile, rare and are difficult to extract. These were discovered relatively late than other elements of the periodic table due mainly to absence of demand.

GROUP-1) Rare Alkaline Element- Li, Rb, Cs

GROUP-2) Light element- Be

GROUP-3) Rare high melting elements- Nb, Ta, Zr, Hf.

GROUP-4) Rare Earth Elements(REE)- La,Ce,Pr,Nd, Sm,Eu,Gd,TB, Dy,Ho,Er,Tm,Yb,Lu,Pm(15th element which has been artificially produced). The trace elements Sc and Y are also classed within REE because of geochemical similarity.

GROUP-5) Dispersed elements- Ge, Re, Tl, Cd, Ga, In, Se, Te,

III. RESOURCES

GROUP-1) Rare alkaline elements are found in Peraluminous S and I type or mixed S+I type pegmatites, granites emplaced in supracrustal rocks and basement gneisses. These are genetically known as LCT type with Ta>Nb.

GROUP-2) Beryllium is also associated with LCT type acid rocks.

GROUP-3) Rare high melting elements are found in subaluminous to metaluminous pegmatites and granites. They may represent undepleted juvenile granitoids or may be of crustal source. These are genetically known as NYF type with Nb>Ta.

GROUP-4) Rare earth elements are found throughout the world and some REEs are more common than many known elements. The problem is a lack of rare earth deposits that have sufficient concentrations of REEs to make mining them economical. The rare earth elements consist of seventeen metal elements – 15 elements from the lanthanide series of elements (atomic numbers 57 to 71) plus scandium (atomic number 21) and yttrium (atomic number 39). Scandium and yttrium are included in the rare earths since they are chemically similar to the lanthanide elements and are found with the lanthanide elements in nature. The 17 rare earth elements comprise the largest chemically coherent group of elements in the periodic table. Rare Earth Elements (REE) are used extensively in almost every conceivable advanced technology product (cell phones, televisions, DVDs, electric vehicles) and as well in many low-technology products (oil refining, cigarette lighters, incandescent lighting). Rare earths are relatively abundant in the Earth's crust, but discovered minable concentrations are less common than for most other ores. U.S. and world resources are contained primarily in bastnaesite and monazite. Bastnaesite deposits in China and the United States constitute the largest percentage of the world's rare-earth economic resources, while monazite deposits constitute the second largest segment. Apatite, cheralite, eudialyte, loparite, phosphorites, rare-earth-bearing (ion adsorption) clays, secondary monazite, spent uranium solutions, and xenotime make up most of the

remaining resources. Undiscovered resources are thought to be very large relative to expected demand (USGS, 2013).

Carbonatite, a magmatic rock rich in carbonates, is an important host for REE along with Fe, F, Mn, P, Sr and Nb. Primary REE is obtained from the following sources.

- (i) Mountain Pass, USA. - Carbonatite (Calcite, barite, bastnaesite [5-15%]. Apatite, allanite, galena, hematite-magnetite and pyrite occur as accessories. The ore grade is 8.9% REO (5% cut-off).
- (ii) Bayan Obo, China- Fe- 35%, REO- 1% to 6.19%.
- (iii) Apatite ore- 0.4 to 1% REO. - No production record.

As on date there are only 2 deposits as above which have been contributing to REO production in the world.

Secondary REE sources are:

- (iv) Monazite- Beach Placer
- (v) Xenotime- Beach Placer
- (vi) Residual deposit- Capping Carbonatite
- (vii) Ionic Adsorption type – recorded in some soils capping granite.

Only IV and V had contributed to byproduct REE production.

GROUP-5) These elements are associated with some sulphides and oxide deposits of important metals and are won as byproducts only.

IV. RARE ELEMENTS BYPRODUCTS FROM MAJOR METAL ORES

IV.1 COPPER ORE BY-PRODUCT METALS: COBALT, RHENIUM, MOLYBDENUM, TELLURIUM AND SELENIUM.

Cobalt is a by-product of copper and nickel ores. Cobalt is contained in sedimentary copper deposits which are mainly composed by copper oxides and carbonates. In 2010, the total global production of cobalt was 88,000 tonnes, of which 35% was produced from copper and 50% from nickel.

Rhenium and molybdenum are recovered as by-products of the roasting of copper-porphyry ores (copper sulfides). These ores contain an average of 0.3% to 1.6% of copper, depending on the mine, plus 0.01% to 0.05% of molybdenum and a minimum of 0.001% of rhenium . Porphyry ores account for 55% of world copper production, and the average potential output of 281,000 tonnes of molybdenum and 9,370 tonnes of rhenium can be estimated. But from actual production it appears molybdenum is being extracted rather efficiently, but rhenium is not. India's Malanjkhand copper porphyry deposit has no reported byproduct of Rhenium and molybdenum.

Tellurium and selenium are co-products of copper refining from various copper ores. For each tonne of copper refined there are 65 grams of tellurium. In 2010, with total world copper

production of 16.2 million tonnes, it appears that 1,050 tonnes of tellurium were potentially available for recovery but not recovered. Selenium is produced entirely as a by-product of copper refining although coal is by far the most abundant source. Production data shows that world actual production of selenium was 3,250 tonnes. This implies that recovery efficiency is quite good.

IV.2 ZINC BY-PRODUCTS: GERMANIUM AND INDIUM.

Currently germanium and indium are co-produced with zinc from sphalerite (ZnS), a zinc sulfide that contains up to 0.05% germanium and indium along with 67% zinc. The actual output of germanium and indium were 574 and 120 tonnes respectively in 2010. The recovery is far less than the actual contents. In India byproduct germanium and indium from the Rajasthan lead-zinc ores are not reported. Although not exploited at present, sphalerite is also an important resource of gallium.

IV.3 NICKEL BY-PRODUCTS: COBALT AND PGMS.

The vast majority of cobalt resources are in nickel-bearing laterite deposits (nickel oxides and silicates) and sedimentary copper deposits of Congo and Zambia. Laterite deposits contain an average of 1.3% of nickel and 0.1% of cobalt and supply about 40% of nickel production. In 2010, the production of 580,000 tonnes of nickel from laterite could have yielded 58,000 tonnes of cobalt. Overall, the potential production of cobalt as by-product of nickel and cobalt is estimated in 467,000 tonnes.

In 2010, the total production of PGM (Platinum Group Metals) was almost 690 tonnes out of which 456 tonnes were mined as such, 11 tonnes were a by-product of nickel and 222 tonnes were recycled. The mine production of platinum and palladium was 192 and 202 tonnes respectively. The total production of the PGM by-products metals was 73 tonnes: 29 tonnes of rhodium, 35 tonnes of ruthenium, 7 tonnes of iridium and 2 tonnes of osmium. PGM produced as by-products of nickel were mainly in Botswana, Canada and Australia.

PGM can be additionally recovered from pyrrhotite, an iron sulfide mineral associated with nickel sulfide ores. The ore mineral contains up to 30 and over 5 g/t of rhodium and ruthenium and iridium, respectively.

Recycling is a significant source of PGMs, unlike the other metals, as it provides 222 tonnes mainly from auto-catalyst (37%), electronics (51%) and jewelry (12%). The highest amount of PGM recycled is palladium (158 tonnes) followed by platinum (57 tonnes) and rhodium (7 tonnes). The major amount of palladium, 114 tonnes, is recovered from electronic products. Platinum and rhodium are mostly recycled from three way catalyst in internal combustion vehicles. There is no published information about the recycling of ruthenium, iridium and osmium. These metals could especially recycle from electronic devices where they are used in small quantities for electric contact, printed resistors and in alloys for spark plug contacts in airplane and automobile engines.

IV.4 IRON BY-PRODUCT METALS: RARE EARTHS.

In 2010, about 48% of rare earth oxides were produced as by-product of iron ores, mainly in Bayan Obo mines (China). Iron mineral ores in that mine contain 350 kg of iron, 60 kg of rare earth oxides and 1.3 kg of niobium. In 2010, 54,000 tonnes of rare earth metals were produced from Bayan Obo. Baosteel, the company operating the mine aims to produce 24 million tonnes of iron, which means a potential future production of 3.5 million tonnes of rare earth oxides and 89,100 tonnes of niobium.

IV.5 ALUMINUM BY-PRODUCT METALS: GALLIUM.

Bauxite contains an average of 42.5% of aluminum and 0.0065% of gallium. In 2010, world mine production of aluminum was 28.15 million tones, yielding 106 tonnes of gallium. Based on the average content of gallium in bauxite however, theoretically about 4,000 tonnes of gallium could have been recovered already. Since there is a lot of bauxite in the world, future gallium production may be quite significant.

IV.6 TIN BY-PRODUCTS: NIOBIUM AND TANTALUM

Niobium and tantalum are mainly mined from pyrochlore and tantalite respectively. They are also obtained from tin slag. Cassiterite (tin) ore contains about 0.03% of niobium and 0.01% of tantalum, which leads to a potential production of 780 and 260 tonnes respectively. In 2010, their production from tin was 2 tonnes and 106 tonnes, respectively.

V. FUNCTIONS OF RARE ELEMENTS

There are a number of functions that are especially relevant to **future demand for critical metals**.

- A) Dopants in Semiconductors: These are minor amount of trace metals that change the semiconductors.
 - i) Printed circuit board (PCB): INDIUM, GALLIUM AND GERMANIUM.
 - ii) Phosphors: STRONTIUM ALUMINATE ACTIVATED BY EUROPIUM AND DYSPROSIUM, YTTRIUM, EUROPIUM AND GADOLINIUM, LANTHANUM, CERIUM, EUROPIUM OXIDE, INDIUM, GALLIUM
 - iii) Photovoltaic cells: CADMIUM-TELLURIDE (CDTE), COPPER INDIUM GALLIUM SELENIDE (CIGS) AND TRIPLE-JUNCTION CELLS MADE OF GALLIUM ARSENIDE (GAAS), GERMANIUM AND INDIUM GALLIUM PHOSPHIDE (GAINP2).
 - iv) Detectors: INDIUM AND TELLURIUM.
 - v) Optical fibers: GERMANIUM
- B) Catalysts: Catalysts are substances that slow (negative catalyst) or speed up (positive catalyst) the rate of chemical reactions. They are not consumed and can be reused over and over in subsequent reactions.
 - i) Automobile: PLATINUM-PALLADIUM-RHODIUM AND RARE EARTH OXIDES.

ii) Petroleum refining: CERIUM AND LANTHANUM, RHENIUM, PLATINUM-PALLADIUM

iii) Industrial chemicals: COBALT, GERMANIUM, MOLYBDENUM, TELLURIUM, PLATINUM- RHODIUM-IRIDIUM- RUTHENIUM - OSMIUM, CERIUM,

C) Electrical storage: Storage of electrical energy makes it possible to balance intermittent supply and demand. The major methods to store electrical energy are batteries (electrochemical) and capacitors (electric charge). In the distant future electrical energy may be stored in superconducting magnets.

i) Storage batteries: NICKEL, LITHIUM, MISCHMETAL (A MIX OF LANTHANUM, CERIUM, NEODYMIUM AND PRASEODYMIUM), COBALT, PGM

ii) Capacitors: TANTALUM

D) Alloying elements:

An alloy is a mixture of two or more metals to get better characteristics than either metal alone. The characteristics of alloys vary depending on their composition.

i) Permanent magnets: SAMARIUM-COBALT AND NEODYMIUM-IRON-BORON.

ii) Other metal alloys: COBALT, INDIUM, NIOBIUM, TELLURIUM, TANTALUM, TUNGSTEN AND REES (SCANDIUM, YTTRIUM AND CERIUM).

iii) Cemented carbides: COBALT AND TUNGSTEN

E) Additives: Additives are substances added to preserve the quality and appearance of coatings, and for coloring.

i) Glass pigments: SELENIUM AND RE METALS

ii) Ceramic pigment: REE

F) Abrasives:

Rare earth elements are excellent abrasives for glass polishing in the manufacture of LCD, optical glass, mirrors, photo-masks, plate glass, lenses and cut glass.

All REE`s are used.

VI. RARE ELEMENTS IN INDIA

Though India is a major producer of many important metals and other industrial minerals, the status of Rare Element production is rather dismal. India has been progressively emerging as a major industrialized and economically advancing country in the world. In keeping with such growth it is imperative that she develops Rare Element resources which are used extensively in almost every conceivable advanced technology product and as well in many low-technology products. China has a near-monopoly on mining and processing rare earth elements but is itself expected to become a net importer of REEs in the near future. The reliance on rare earth elements for much of the world's future growth, particularly for alternative energy development, is well known and needs not be overstated. The status is tabulated in the following table.

Major Metal Deposits	India Mine	Associated byproduct Rare	Status of
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	Production	Elements	byproduct in India
Copper	Rajasthan, M.P., Jharkhand	Molybdenum	ICC, Ghatsila
		Selenium	ICC, Ghatsila
		Tellurium	ICC, Ghatsila
		Rhenium	
		Cobalt	1560tpy refining capacity only.
Zinc	Rajasthan	Germanium	NA
		Indium	NA
		Gallium	NA
Nickel	Nil	Cobalt	Nil
		PGM	Nil
Iron Ore (Carbonatite type)	Nil	REE	Nil
		Niobium	Nil
Aluminium	Orissa,	Gallium	55kg/y- UP, 950kg/y at Orissa(P)
Tin	60tpy, Chhattisgarh	Niobium	Nil
		Tantalum	Nil

TABLE I - Status of Rare Element production in India. NA- Not available.

India has recognized the following metals as strategic: Tin, Cobalt, Lithium, Germanium, Gallium, Indium, Niobium, Beryllium, Tantalum, Tungsten, Bismuth and Selenium (Planning Commission, Govt.of India, 2012). The basis for labeling these as strategic was reported to be ; a) rapid increase in demand in high technology , b) limited substitutes, c) many are produced as byproducts of base metals thereby restricting the raw material availability, d) spatial limitations, e) difficult economic extraction , f) Unstable / inconsistent political systems, mining regulations, legislative regimes and environmental risks for many of these minerals ,g) time lag between exploration and extraction and h) increasing state controls impose restrictions of free market availability. India is dependent on imports to a large extent and is thus vulnerable to supply/price fluctuations. The global market for rare earth elements is expected to reach USD 10.96 billion by 2020, according to a new study by Grand View Research, Inc (Grand View Research, 2014). Growing demand for metal catalysts such as Cerium and Lanthanum is expected to drive the market over the next six years. Depleting reserves, stringent regulatory framework, complex extraction and capital intensive nature of the extraction process are expected to be key challenges for market participants over the next six years. Recycling of Rare metals from e-waste does not appear to be feasible in view of tiny contents in complex circuits of such gadgets, labour-incentive and slow extraction from wastes. Some authorities still believe that recycling of these elements from waste could prove to be a key opportunity for the market in the near future. The following are the key points for India`s immediate concern on the subject.

1. Growing industrialization of India would be increasingly dependent upon the use of high technology and use of Rare metals.

2. Several important industries, critical to India's national security, renewable energy mission, electronics, consumer durables, clean technology etc. is dependent on Rare metals.
3. The current understanding and knowledge of the Rare Metal hosting minerals is limited and thereby India's response to search and exploration is slow. Necessary training and preparedness are necessary to organize and develop expertise in the field including extraction.

The Group-4 Rare Earth Elements is sourced from monazite beach sand placers. The resource estimates of monazite in the beach and inland placer deposits have been enhanced from 7.90 million tonnes in 2002 to 10.21 million tonnes in 2005 by Atomic Minerals Division. The production of rare earth in India in 2008 was only 35 tonnes. Monazite ore of rare earth metals is naturally radioactive. Because of environmental problems during mining its exploitation was restricted. India possesses a combined capacity of 6240 tpy treatment of monazite to separate rare earths. R.E. oxides, like oxides of Y, Ce, Nd, Pr and La in adequate purities are produced from Kerala. India is the second-largest supplier of yttrium in the world. Both Uranium and Thorium are also separated for indigenous use.

VII. WORLD DEMAND

Global production of REE was around 133,600 tons in 2010 (Humphries, 2013). World demand for rare earth elements were estimated at 136,000 tons per year, with the difference was covered by previously mined aboveground stocks. World demand is projected to rise to at least 160,000 tons annually by 2016 according to the Industrial Minerals Company of Australia. In addition to the 2 well known primary deposits and byproduct REE from beach sand, some mine capacity at Mt. Weld Australia has come on-stream in 2012, but far below the projected 11,000 metric tons of capacity. Other new mining projects could easily take as long as 5-10 years to reach production. In the long run, however, the U.S. Geological Survey expects that global reserves and undiscovered resources are large enough to meet demand. China began producing notable amounts of rare earth oxides in the early 1980s and became the world's leading producer in the early 1990s. Through the 1990s and early 2000s, China steadily strengthened its hold on the world's rare earth oxide market. They were selling rare earths at such low prices that the Mountain Pass Mine and many others throughout the world were unable to compete and stopped operation.

China had dominated the production of Rare Earth Elements, tungsten and molybdenum till about 2010. China's share of the global production of rare earths is now down to as low as 80%, from 95% in 2010. China has also restricted export of these critical metals on ground of domestic consumption and environmental protection. This had contributed to growth of their local industries. New supplies for most rare earths are coming online as uncertainty over China's supply reliability and a period of higher prices stimulated investment in new mining projects elsewhere. Greenland and Russia both opened new tracts to rare-earths exploration in the past years.

The US Administration announced the filing of a World Trade Organization (WTO) case against China, citing unfair trade practices in rare earths in March 2012 (Humphries, 2013).

Subsequently the WTO confirmed that China had lost a case on rare-earth metals, the latest setback for Beijing in a dispute marked by price spikes and widespread concern among technology firms and defense-related users of the critical materials. China's export duties on rare-earth metals, molybdenum and tungsten were found inconsistent with its obligations in the WTO. It also ruled against Beijing's export quotas on the materials and its move to restrict their trade.

VIII. MAJOR USES

Some of the major end uses for rare earth elements include use in automotive catalytic converters, fluid cracking catalysts in petroleum refining, phosphors in color television and flat panel displays (cell phones, portable DVDs, and laptops), permanent magnets and rechargeable batteries for hybrid and electric vehicles, generators for wind turbines, and numerous medical devices. There are important defense applications, such as jet fighter engines, missile guidance systems, antimissile defense, space-based satellites and communication systems.

Concluding Remarks

- a) Within the context of energy policy, the Chinese government has been encouraging "green energy technology" alongside the European Union. This support has led to an increase in the usage of solar and wind power as well as the production of wind-powered electrical generation, hybrid electric vehicles, and permanent magnet generators. Since rare earths are the main inputs for production of these green technologies, it is expected that the domestic consumption of rare earths will ascend drastically in the future.
- b) China's bid to flex its monopoly muscles on REE have caused quite a concern in the global market and possibly it is time for the developed and some developing countries to consolidate their own resources and shed dependence on China.
- c) The new National Mineral Policy of the country states on production of high purity materials- "Research will be directed towards raw materials required for production of materials of high purity for use in advanced technology applications such as semi-conductors, photo-voltaic, lasers, special sensors, high temperature new ceramics, hard and high temperature materials, superconductors, insulators, very thin films, glasses and liquid crystals and metal and mineral fibers". This is a clear indication on thrust for development of Rare metals.
- d) Recycling of Rare metals from e-waste is claimed as viable. In Umicore, Hoboken, Belgium, the company annually recycles about 350,000 tons of e-waste, including photovoltaic cells and computer circuit boards, to recover metals including tellurium. When it comes to recycling, anything is possible. It's a question of whether it's economic. Despite the relatively high concentrations of rare earths in electronic equipment waste it's actually **chemically easier to separate them from the surrounding material in simple rocks than in complicated phones.**
- e) India possesses the capacity to extract Rare Earth oxides from Monazite beach sand. But primary deposit of REE and other Rare Elements of critical nature have to be discovered. Additionally, recovery of byproducts from her base metal mine ores would call for

developments in technology. All these Rare metal resources are the future targets for consolidation and stock piling in view global uncertainty in supply.

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