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RARE METALS EXTRACTION FROM NON-FERROUS RESOURCES IN INDIA : PRESENT STATUS AND PROSPECTS OF R&D

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ABSTRACT

Rare metals comprise of those naturally occurring elements with relatively lesser abundance in the earth's crust which are difficult to extract by normal metallurgical processes. The present paper summarizes the ore / mineral resource base including the secondary resources, current usage and extraction technology of rare metals in India. The R&D in India has resulted in the exploitation of such processes or poised for gainful utilization. As the technologies for extraction of rare metals follow a different methodology than those applicable to the normal base metals and were not readily available at the early stage of development during 1950-1990s, indigenous developments matured and were put to use; a few such technologies are described. Mention may be made of the applications of special processing options such as: halide metallurgy, strong acid / alkali treatment for breaking down the refractory minerals –HF/ alkali fusion; solvent extraction/ ion exchange for metal separation, and vacuum melting/ electron beam melting/ refining etc for melting/ refining, to meet the stringent specifications of the rare metals. In most cases, extraction is carried out using primary resources, but for metals not present in a substantial quantity in natural ores or in diffused state, secondary resources are exploited. Secondary resources are particularly critical for Ga, V, Mo, W, Se, Te etc. Possibilities for further research are indicated to ensure secured supply of these metals in future.

Keywords: rare metals, rare earth metals, resources, applications, processing, technology, R&D prospects.

1. Introduction

Of the 60 metals amongst the 83 naturally occurring elements, more than half is grouped under rare metals (Hampel, 1961, Zelikman et al, 1966). The term 'rare metals' which had a literal meaning was coined in the 19th century to describe those metals which were not readily available due to their dispersion in the earths' crust, difficulties in extraction and practically no major technological applications at that point of time. With time it is seen that many of these metals are not really rare and are quite often more abundant than the commonly known/ used metals. As is evident from Table 1 which gives a list of abundance of common elements on the earth's crust, titanium is one of the most abundant rare metals. Similarly metals such as zirconium, chromium, vanadium and some other 'rare' metals are more abundant than lead, tin, mercury, gold and silver. Though not very accurate, the generic term 'rare metals' and sometimes 'less common metals' still continue to be in current use for these metals of significant importance at present.

Rare metals can be broadly divided in to 5 groups based on the similarities, extraction and production, applications of metals and compounds as listed in Table 2 (Gupta and Bose, 1989). Usage of these metals has emerged immediately after the World War II with the ushering in of the high technology. For an instance, the light rare metals such as beryllium and lithium have become indispensable for modern electronic, nuclear and space applications (Table 2). Beryllium possesses light weight, high strength, excellent neutron –transparency and neutron scattering properties and thus finds applications inside the nuclear reactor core as well as in light weight space probes and satellites. Similarly lithium has not only its unique tritium-breeding characteristics, heat transport properties and coolant for fusion reactors, but is an important material for batteries. The name refractory rare metals stand for their high melting points above 1600^0C and useful strengths at temperatures higher than the service limits of Ni-& Co-based super-alloys. The use of metals such as tantalum, hafnium, zirconium, titanium for extreme chemical applications is due to their excellent corrosion resistance. High melting metals, molybdenum and tungsten are the materials for high temperature applications. The dispersed metals have their large usage in electronic applications.

The general uses of rare metals are given in Table 2. Applications in specific products are detailed in Table 3 which clearly shows that several of these metals possess unique physicochemical, chemical, electronic and nuclear properties which qualify them for special and strategic core applications. Generally, they find applications in alloy making and also in electronics, nuclear, space and missile technology, chemical, ceramics and catalysts, textiles, pigments, magnets, and medical appliances.

Table 1: Abundance of metals in the earth's crust

Element	Abundance (%)	Element	Abundance (%)
Oxygen	46.6	Vanadium	0.014
Silicon	27.7	Chromium	0.010
Aluminium	8.1	Nickel	0.0075
Iron	5.0	Copper	0.0055
Calcium	3.6	Zinc	0.0070
Sodium	2.8	Cobalt	0.0025
Magnesium	2.1	Lead	0.0013
Potassium	2.6	Uranium	0.00027
Titanium	0.44	Tin	0.0002
Manganese	0.095	Tungsten	0.00015
Barium	0.043	Mercury	$8x10^{-6}$
Strontium	0.038	Silver	$7x10^{-6}$
Rare earths	0.023	Gold	$<5x10^{-6}$
Zirconium	0.017	Platinum Metals	$<5x10^{-6}$

Table 2: Classification and application of general rare metals

Classification /name	Metals	Properties	General applications
Light rare metals	Li, Rb, Cs, Be	Low density High reactivity Unique nuclear properties	Electronics Nuclear energy Space technology
Refractory rare metals	Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re	High MP & temperature Strength, Corrosion resistance, Unique nuclear properties	Electronics Nuclear energy Space technology Chemical technology Metallurgical use
Dispersed rare metals	Ga, In, Tl, Ge, Se, Te, Re	Unique electronic properties	Electronics
Rare earth metals	Sc, Y, Lanthanides – La, Ce, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (15 elements)	Unique optical, magnetic and nuclear properties High reactivity	Catalysis Metallurgy Optics Refractories
Radioactive rare metals	Ra, Th, Pa, U, Pu, Po	Nuclear properties	Nuclear energy

Table 3: Rare metals (other than REs) - products and applications:

Sl. No.	Metal	Application	Products(s)
1.	Li	Alloys, Energy pack	Al-Li alloys & alloy composites , Li ion & LiMH batteries
2.	Be	Space structure, optics, medical , nuclear & ceramics applicatior	Alloying agent- springs, contacts and non-sparking tools, radiation window for X-rays, reflector & moderator in nuclear reactor, BeO - heat conductor & insulators
3	Ti	Alloys, medical, pigments, textiles, ceram catalysts, jewelry	Ti-steel alloys –spacecraft & airframes, engines, vehicles, vests, sport equipment, dental alloys and body implants, Oxides-pigments, floor coverings, textiles, ceramics, industrial usage,
4.	Zr	Alloys, nuclear, medical, jewelry, lining material, magnet, refractory, industrial applications	Magnet, lining materials, jet engines & gas turbines; cast iron, steel, surgical appliances, arc lamp, welding flux, jewelry; boride & carbides- refractory, cutting tools & thermcouple jacket etc.
5.	Hf	Alloys, space, nuclear reactor, electror applications	Fe, Nb, Ta-alloys for rocket engine parts, control for nuclear reactor, electrode for plasma cutting, bulb filaments, high-k dielectrics etc.
6.	Nb	Electronics, missile technology , ste chemical and medical applications	Superalloys, capacitors, Steel industry- as strengthener, dielectric resonators in microwave, tools
7.	Ta	As above	Superalloys, medical tools etc.
8.	V	Steel, Catalysts, chemicals	Structural steels, tools, industrial chemicals
9.	Ga	Electronics, alloys, solar cells, mirrors	Low melting alloys, optoelectronics device, LEDs, photovoltaic, touch panel, rectifiers & transistors, detectors
10.	Ge	Electronics, alloys, glasses	Xerography, optical & photonics, glasses for semiconducting & space usage, pulsed laser application etc.
11.	In	Electronics, solar cells, alloys	LEDs, photovoltaic, touch panel, solar cells, plasma device etc.
12.	Se	Chalcogenide glass, electronics	Optical and photonics, optoelectronics
13.	Te	Electronics, solar cells, alloys	IR-transmitting glasses, laser applications
14.	U	Nuclear & chemical applications	Energy generation, ceramics, X-ray production etc
15.	Th	Nuclear applications, alloys, catalysts	Energy generation, mentles for gas lamps, high refractive index glass, chemicals
16.	PGM	Alloys, fuel cells, catalysts, medicals Engineering applications etc.	Medicals, automotives, catalysts for petroleum, autocatalyst, coatings on turbine blades etc.

Thus, rare metals which include rare earth metals also occur in nature in very complex forms and often in very low concentrations and are critical core component applications.

Generally, rare metals and rare earths including some of the actinides (Th, Pa, U, Pu) may also be conveniently divided in two groups as listed below for the sake of further discussion.

***Rare metals**: Be, Li, Rb, Cs, Ga, In, Tl, Ge, Se, Te, Sn, Ti, Zr, Hf, V, W, Nb, Ta, Th, Pa, U, Pu.*

Rare earths (REs) group metals: Sc, Y and Lanthanides (15 elements)

The rare earth group contains seventeen elements namely, scandium, yttirium and lanthanides (15 elements from atomic numbers 57 to 71). Though they tend to occur together, the fifteen lanthanide elements are divided into two groups. The light elements are those with atomic numbers from 57 to 63 (La, Ce, Pr, Nd, Pm, Sm and Eu) and the heavy elements from atomic numbers 64 to 71 (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Rare earth metals are extensively used for various technological applications ranging from mobile phones to satellite systems. Demand for rare earths, which have a wide variety of uses in high-tech products, is increasing rapidly. The current global demand is reported to be 134,000 t which is expected to exceed 200,000 t by 2014. China is the world's largest producer of rare earths, accounting for 97 percent of production in 2009. In view of China's decision to reduce drastically the export of rare earth metals, it is imperative to develop technologies and exploit indigenous resources.

Currently, the dominant end use of rare earth elements globally is for auto catalysts and petroleum refining catalysts (Naumov, 2008). There are important defense applications such as jet fighter engines, missile guidance systems, antimissile defense, and space-based satellites and communication systems. Permanent magnets containing neodymium, gadolinium, dysprosium, and terbium are used in numerous electrical and electronic components and generators for wind turbines (Table 4). Table 5 shows that catalysts make the single largest usage in terms of volume, followed by glass, metal alloys, glass polishing. Magnets, phosphors, optical glass (lenses), dopants for optical fibres, lasers, advanced ceramics and capacitors. In terms of value, phosphors makes up most important group at ~ 30% of total market, followed by magnets, catalysts and alloys at 12-15% each.

2. Resources of Rare Metals

A. Natural resources of rare metals in India

Table 6 shows the mineral resources of rare metals in India (Sundaram and Gupta, 1984, IBM Year book, 2005). Besides, the concentrations of the rare metals in several wastes, byproducts and secondary materials are much more than that found in natural resources and therefore, processing of such materials are critical to ensure secured supply of these metals while minimizing the pollution.

Table 4: Rare Earth elements (Lanthanides): selected end uses

Light Rare Earth more abundant)	Major end use	Heavy Rare Earth (less abundant)	Major end use
Lanthanum	Hybrid engines, metal alloys	Terbium	Phosphors, permanent magnets
Cerium	Auto catalyst, petroleum refining, metal alloys	Dysprosium	Permanent magnets, hybrid engines
Praseodymium	Magnets	Erbium	Phosphors
Neodymium	Auto catalyst, petroleum refining, hard drives in laptops, head phones, hybrid engines	Yttrium	Red color, fluorescent lamps, ceramics, metal alloy agent
Samarium	Magnets	Holmium	Glass coloring, lasers
Europium	Red color for television and computer screens	Thulium	Medical x-ray units
Gadolinium	Magnets	Lutetium	Catalysts in petroleum refining
		Ytterbium	Lasers, steel alloys

Table 5: Rare Earth products and applications

Sl. N	Application	Products(s)	Rare Earths
1.	Glass polishing	Lenses, display screens (CRT, T, LC PDP)	Ce
2.	Glass additives	Optical lenses,.display screens	Ce, La, Nd
3.	Lighter flints	-	Mischmetal alloy
4.	Catalysts, fluid cracking	Petroleum refining	Mixed are earth products
5.	Catalysts , auto	Automobiles	Ce, La, Nd
6.	High intensity magnets	Electronic and electric motors, audio equipments	Nd, Sm, Dy, Pd, Tb
7.	Batteries & hydrogen storage systems	Electronic tools, hybrid cars	Mischmetal, La alloys
8.	Phosphors, display	Computer, TV & other display screens	Y, Eu, Tb
9.	Phosphors, lamp	Fluorescent and halogen lamps	Y, La, Ce, Eu, Gd, Tb
10	Phosphors, X-rays	X-ray films	La
11.	Fibre optics/ lasers	Rare earth dopants	La, Er, Y,
12.	Advanced ceramics	Nitrides, Y- stabilized ceramics	Y
13.	Capacitors	Multilayer ceramics	La, Nd, Ce
14.	Fuel additives	Gasoline, diesel fuels	Ce
15	Fuel cells	Solid oxide fuel cells	La, Y
16.	Pigments	Replacement for Cd in ed pigments	La, Ce
17.	Magnetic refrigeration	Magnet alloy	Gd
18.	Steel & foundry	Desulphurization	Mischnetal
19.	Alloys	Mg, Al and hydrogen storage alloys	Ce, Nd, La, Y

Table 6: **Proven/Prospective primary rare metal resources in India**

Sl. No.	Metal	**Minerals/ resources**	**Lacations/ remarks**
1.	Li	Spodumene- $LiAlSi_4O_{10}$, , lepidolite- lithium mica, petalite- $LiAlSi_4O_{10}$	TN, Rajasthan, Jharkhand, Orissa
2.	Be	Beryl–$Al_2Be_3(Si_6O_{16})$ (aquamari emrald, heliodro, morganite)	Bihar, Rajasthan, AP, MP
3.	Ti	Ilmenite -$FeTiO_3$, rutile -TiO_2	Beach sands of Kerala, Orissa, AP. TN
4.	Zr	Zircon- $ZrSiO_4$	Beach sands
5.	Hf	As silicate in zircon	Beach sands
6.	Nb	Columbite-(Fe,Mn) Nb_2O_6 ; Pyrochlore-$(Na, Ca)_2Nb_2O_6(OH,F)$ Cassiterite (SnO2) ores with Nb-Ta	Hazaribagh (Jharkhand), Mongh (Bihar) Dharmapuri(TN), Khammam (A Gujarat, Bhilwada (Rajasthan) Buster (Chhatisgarh)
7.	Ta	Tantalite-(Fe, Mn) $(Ta, Nb)_2O_6$ Microlite-$(Ca, Na)_2 Ta_2O_6$ (O, Oh, F)	Hazaribagh, Monghyr Hazaribagh, Monghyr(Bihar)
8.	V	Vanadinite, in magnetite, bauxi uranium ores, coal, shale,	Jharkhand, Nagaland, TN, A Maharashtra
9.	Ga	Gallite (CuGaS2), trace in bauxite, sphalerite, pyrite, magnetite & coal.	Orissa, MP, AP, Rajasthan, Jharkhar TN, Bihar, UP
10.	Ge	Argyrodite- $Ag_8Ge\ S_6$, seconda mineral in sphalarite (ZnS), coal	Rajasthan, AP., Jharkhand, Bihar, W Maharashtra
11.	In	Suiphides/ oxides with sphalerite	-
12.	Se	Sulphide - chalcopyrite, sphaleri pyrite etc.	Jharkhand, Rajasthan, Karnataka, A TN, Maharashtra
13.	Te	Sulphide - chalcopyrite, sphaleri pyrite etc.	Jharkhand, Rajasthan, Karnataka, A TN, Maharashtra
14.	U	Uraninite-$(U_{1-x}{}^{4+} U_x{}^{6+})O_{2+x}$ Pitchblende- a variety of uraninite	Jaduguda(Jharkh.), Nagaland, AP South Kanara (Karnataka)
15.	Th	Monazite –$(Ce,Y,Ca,Th)PO_4$	Beach sands

B. Rare earth resources in India

Rare earths elements are relatively abundant in the Earth's crust. The principal sources of rare earth elements are bastnaesite (a fluorocarbonate occurs as carbonatites), xenotime (yittium phosphate in mineral sand deposits) and loparite (in alkaline rocks) and monazite (a phosphate). Bastnaesite deposits in the United States and China account for the largest concentrations of REEs, while monazite deposits in Australia, South Africa, China, Brazil, Malaysia, and India account for the second largest concentrations of REEs. The world reserve base in terms of rare earth oxides (REO) content is estimated at 120 mt of which China alone accounts for about 55 mt followed by CIS, USA and India.

In India, monazite is the principal source of rare earths and thorium containing 0.4 – 4.0% rare earths. The resource estimates of monazite in the beach and inland placer deposits stands at 10.21 mt in 2005. India holds only 3% of the world reserves (3.1mt out of 99 mt) as compared to 36% by china and 13% by USA.

Indian monazite contains about 60% of the rare earths of the cerium group expressed as oxide plus an average 7.2% thorium and minor yttrium. it occurs (0.4-4.3%) in association with other heavy minerals (Table 7) such as ilmenite, rutile, zircon, garnet etc (Sundaram and Gupta, 1984). Presently Indian Rare Earths Ltd. (IREL) and Kerala Minerals and Metals Ltd. (KMML) are actively involved in mining and processing of beach sand minerals. IREL at Chavara (Kerala), Manavalakurichi (Tamil Nadu) and Chhatarpur (Orissa sand complex-OSCOM) is producing industrial minerals. IRLE also produces rare earth (Chlorides, Oxides) and thorium hydroxide at Alwaye, besides Nd oxides for magnet applications. As per IREL reports, the current production level of 2700 t year, stagnated for years, is being raised to 7700 t possibly by the end of 2011.

Table 7: Typical mineral composition of beach sands in India

Constituent	Amount(%)
Monazite	0.4-4
Ilmenite	65-80
Rutile	3-6
Zircon	4-6
Sillimanite	2-5
Garnet	1-5

3. Technology for Extraction of Rare Metals in India

The technology for extraction of rare metals is generally different from the conventional reduction, smelting and refining processes usually adapted for common metals. A basic schematic of extraction and refining of rare metals are given in Figure 1 (Gupta and Bose, 1989). It may be seen that the elaborate processing steps starts for the separation methodologies to recover metals from the low and complex minerals/ substances and the purification process follows the separation and recovery steps because of stringent requirements of purity of the metals for designated applications. desired purity state which includes solid state purovacuum treatment, vacuum melting and electron beam melt refining, iodide refining and ultra purification methods of zone melting - refining and electro-transport. Among the separation processes, Zr - Hf, Nb - Ta by solvent extraction and rare earths from each other by either solvent extraction or ion exchange are predominant to produce oxides or halides of individual metals of desired purity.

3.1 Extraction of lithium and beryllium:

The current demand of lithium is 14.0 m t as metal and about 74.0 m t of carbonate and the global demand for lithium chemicals is ~84,000 tonnes as lithium carbonate equivalents (16,000 t of Li). As such there is no production of lithium in India from the primary resources, although some efforts were made earlier on the recovery of lithium from the brine by adsorption process tried out at a CSIR laboratory. The development is not complete at the moment to go for indigenous production. Similarly efforts are on to recover lithium from the lithium ion batteries by following hydrometallurgical processes that includes leaching in acid and precipitation of lithium as a salt.

Table 8: Prospects of rare metal extraction from wastes/ Secondary resources

Sl. No.	Secondary material/ source	Metal values	Processing approach
1.	Super alloys of Ni and others	Nb, Ta, Re, Ni etc	Leaching- metal separation & recovery by SX
2.	Spent Li batteries	Rare earths, Li, Co & other metals	Leaching –metal separation & recovery by SX/IX
3.	Electronic wastes/ scraps- PCBs	Rare metals, Rare earths, PGMs	Hydrometallurgical processing
4.	Bayers' liquor of alumina plants	Ga & other rare metals	Hydrometallurgy-SX/ IX
5	Anode slime of copper electrolytic plants	Se, Te, PGMs, Ni etc	Leaching-Precipitation / SX/ IX
6.	Fly ash of gasification plants	Ga, Ge	Hydrometallurgy
7.	End-of life magnets from electronic equipments	Rare earths- Gd, Sm, Pd, Nd	Hydrometallurgy
8.	Monitors & Screens / LCDs	In	Hydrometallurgy-precipitation/ IX
9.	Sludge of alumina plant	V, Ga	Hudrometallurgy
10	Spent petroleum catalysts	Mo, Co, V, PGMs	Hydrometallurgy-leaching- metal separation & recovery

A pilot plant involving fluoride route is currently operational in Mumbai (Gupta and Saha, 2002) to produce beryllium fluoride in pure form. Beryl is the only source of beryllium in India which occurs primarily in the pegmatites of Bihar in Hazaribagh district and Rajasthan in Bhilwara district. In India, in terms of contained beryllium are 64,400 t and the resource base 118,000 t. Mining of beryl in India is related to mica mining.

The beryl ore from the pegmatites (typically containing 10-12% BeO) is physically beneficiated and then mixed with mostly Na_2SiF_6 and a part of iron cryolite, and sodium carbonate to make briquettes for sintering at 775^0 C. The sinter is crushed, wet ground and water leached to dissolve beryllium. The filtered solution is aged for some time and then the aged leach solution is neutralized to11.8 pH by adding sodium carbonate and heated at $90\text{-}95^0$ C to precipitate beryllium hydroxide (Gupta and Saha, 2002). Beryllium hydroxide is leached in ammonium hydrogen fluoride (NH_4HF_2) from which beryllium fluoride in anhydrous form is obtained. Thermal decomposition of ammonium beryllium fluoride is required at 900°C.

$$(NH_4)_2BeF_4 = BeF_2 + 2NH_4F \quad (1)$$

Beryllium metal in the form of pebbles is subsequently produced by magnesium reduction of beryllium fluoride (Sharma and Sinha, 1984). The metal pebbles are refined by vacuum induction melting.

3.2 *Extraction of gallium and associated metals (In, Tl)*

The gallium metal's production in India is restricted to only 45 kg, the country's requirement being more than 700 kg per annum at present. The spent liquor generated in the Bayer's digestion process of bauxite ore in alumina plant is the rich source of gallium with ~ 200ppm Ga. The technology developed at NFC, Hyderabad (Mirji et al., 1999) has small production. Electrolysis is carried out in an amalgamation cell in which agitated pool of mercury acts as a cathode while Ni-plated steel acts as anode. During electrolysis Na-Hg amalgam converts to Na-Hg-Ga amalgam. The Na-Hg-Ga amalgam is decomposed by electrolysis. The week gallate liquor is concentrated from 10g/L Ga to 60g/L Ga for efficient processing in a batch type evaporator. Activated carbon is added for recovering the impurities and the mixture after cooling is filtered to get the strong gallate liquor which is electrolysed at 1000-1500A/m^2 and 500^0 C to deposit gallium metal on the vertical nickel plate which drips down to the bottom of the cell. The process produces 5N pure gallium metal in a "clean house set" subsequently.

Recently, efforts were made at NML to recover gallium from the Bayer's liquor by solvent extraction. The process developed (Puvvada et al., 1996) at NML involved gallium extraction by KELEX-100 in kerosene to recover 300-400 ppm Ga available in a typical plant solution. Gallium was extracted with an anionic solvent to purify the metal in the next stage and electrolysed to produce 99.9% Ga metal or gallium salt. As regards extraction and separation of gallium, Indium and thallium, a few publications are available dealing with the basic studies on separation from the synthetic solutions by a high molecular weight amine (Chandrasekhar et al, 1986), n- octyl aniline (Kuchekar et al, 1988) and Cyanex -925 (Iyer and Dhadke, 2001).

3.3 *Extraction of selenium and tellurium*

Principal resources of selenium are sulphide deposits and anode mud or slime obtained in the electrolytic refining of copper. Tellurium is found mostly as tellurides associated with metals such as bismuth, lead, gold and silver and is also found with the anode slime of electro-refining of copper. During the copper electro-refining the insoluble impurities (~ 3-5 kg/t) as anode slime collects at the bottom of the tank which contains metals such as Cu, Ni, Se, Te, Au and Ag and platinum group metals (PGMs). Total amount of anode slime generated world over is estimated to be ~55, 000 t/year (Hait et al, 2009). Selenium and tellurium are also recovered during lead-zinc, gold and platinum ore processing. In UK and Canada, selenium is also recovered from the used electronic and photocopier components and recycled. The world production of selenium and tellurium stands at 1570 t and 500-600 t, respectively in the year 2007.

In India, selenium and tellurium are recovered as allied products at ICC, Ghatsila. The installed capacity of this plant is to treat 70 t of anode slime of Ghatsila plant and also to produce 14.6 t of Se of 99.95% purity whereas for tellurium it is ~ 0.5 t. ICC used to produce 2.35 t of Se and 0.03 t of Te in 2003-04 and 7.72 t of Se in 2005-06 after which they discontinued the production. At present these slimes from ICC, KCC and other copper industries in India are exported / sold for toll smelting overseas. As regards the technology for the processing of anode slime, it was based on M/s Outokumpu Oy, Finland and with several major modifications carried out by in-house R&D division of ICC, Ghatsila.

Some efforts were also made (Bajaj, 1989) for the recovery of mercury and selenium from the scrubber sludge of the Fluid - bed Roasting furnace of Vizag zinc smelter of HZL by hydrometallurgical process. The sulphide cake and the sludge from the scrubber and other units was leached in NaOH to convert mercury to Hg_2O if in halide form, and then mixed with lime to recover mercury by distillation followed by selenium recovery from the residue by sulphuric acid leach-SO_2 reduction method.

3.4 *Extraction of titanium, zirconium and hafnium*

Starting with titanium, it is found in the form of oxide in particular, ilmenite ($FeO.TiO_2$) and rutile (TiO_2). World ilmenite and rutile reserves are estimated at 3053 and 1394 mt (of TiO_2) respectively and Indian ilmenite are the world's largest and account for as much as 45% of the total world reserves (Chintamani et al., 1999).

Ilmenite from the beach sand can be processed by a variety of methods including the hydrometallurgical route. Titania slag smelting process, popular in several countries like South Africa, Norway, Canada, and elsewhere prior to leaching and TiO_2 production, is another alternative (Chintamani et al, 1999; Mukharjee, 1999; Sridhar Rao, 1999). Ilmenite after reduction or the slag from the smelting undergoes processing either by sulphate route or the chloride route to produce synthetic rutile or pigment grade TiO_2. Pure $TiCl_4$ is produced from the synthetic rutile or pigment grade titanium dioxide by carbo-chlorination. The crude $TiCl_4$ is purified by fractional distillation and pure titanium is produced by ***Kroll process*** using magnesium (Sridhar Rao, 1999) and ***Hunter process*** using sodium metal. The Kroll process developed at BARC was finally up-scaled at DMRL, Hyderabad to produce titanium sponge at 2.0 t/ batch and subsequently at 4.0 t/ batch under technology demo plant. Currently the slag smelting process for ilmenite in DC arc furnace to form sulphatable slag is being planned (Mukharjee, 1999) in India including those at NML.

For zirconium two minerals are zircon, an orthosilicate of zirconium- $ZrSiO_4$ (61-67% ZrO_2) and baddeleyite, ZrO_2.The world reserve of Zr is estimated to be about 57 mt out of which 18.5 mt are estimated in India, almost 32% of the world reserves. The metal hafnium is mostly associated with zirconium and is found to be about 0.5-2.0% Hf in zircon mineral while baddeleyte contains about 1-1.8% Hf. Presence of Hf does not hinder its use for non-nuclear application, but is considered a poison in nuclear application. The process followed at NFC involves caustic fusion - dissolution of Zr/Hf in concentrated nitric acid -separation of Zr-Hf by TBP (35%) for producing the reactor grade ZrO_2. Hafnium from the raffinate is precipitated by ammonia and hafnium hydroxide is calcined to obtain oxide. The zirconia from the SX plant is further processed by carbo-chlorination to produce chloride, Kroll reduction with magnesium to obtain Zr sponge, and Electron beam (EB) melting to get ingot. The Kroll hafnium needs further purification by iodide process under inert atmosphere to produce tetra iodide which is decomposed at 1400-1500^0 C to get high pure hafnium as crystal bars (Gupta et al., 1989).

3.5 *Extraction of vanadium, niobium and tantalum*

The primary ore reserves of vanadium like the Peruvian patronite having been exhausted, most of the vanadium currently produced is from byproduct and secondary resources (Mukherjee et al 1983). NML has developed a process to extract vanadium from the alumina plant sludge and commercialized the technology. The process entails production of V_2O_5 and also Fe-V by thermit route

The process applied to these resources is invariably the salt roast leach sequence. The sized ore is mixed with a sodium salt (e.g. NaCI, Na_2CO_3, $NaHCO_3$ or Na_2SO_4) and roasted at 900-1100°C under an oxidising atmosphere. The roasted product is leached with water and the vanadium-laden solution is treated with sulphuric acid to adjust the pH to 2.4-2.8 and precipitate the vanadium in the form of a red cake or sodium hexavanadate. The fused red cake containing 85-90% V is widely used for commercial production of Fe-V. Aluminothermic reduction (Gupta et al., 1989) of vanadium pentoxide followed by inert atmosphere electrorefining of thermit metal in a fused salt bath, NaCI-KC1-$VC1_2$, produces ductile vanadium.

Unlike titanium, physical and chemical separation process for niobium and tantalum is needed for extraction of these metals by halide metallurgy. Tantalum and niobium occur as mixed oxide, columbite- tantalite mineral of general formula (Fe, Mn) $(Ta, Nb)_2 O_6$. This mineral has been the major resource in India and is obtained as a by-product in the mica mining. The process includes hydrofluoric acid dissolution to bring Ta and Nb values in solution, separation by SX system using TBP (Mirji et al., 1999). The process steps in the separation of Nb-Ta are: material preparation through crushing-grinding; direct dissolution in HF/sodium hydroxide fusion; solvent extraction by TBP; precipitation of niobium / tantalum hydroxide; and calcination of hydroxide to fluoride salt. After scrubbing and stripping and further extraction of Nb, the pure solutions of these metals are obtained. The pure $Ta(OH)_5$ is precipitated from the purified solution and so is niobium hydroxide. The calcined Ta_2O_5 and Nb_2O_5 are processed by reduction method. A process based on the slag (with Nb and Ta) produced from the smelting of the cassiterite ore containing tin of Bastar, Chhattisgarh has also been developed by following the similar approach.

3.6 Extraction of molybdenum and tungsten

The molybdenum and tungsten metals are mostly available in low concentrations in their most abundant ore viz. molybdenite, and wolframite and scheelite. As regards molybdenum, it is available only as by-product in the uranium milling operation at UCIL, Jaduguda. The recovery of molybdenum from Jaduguda molybdenite concentrate has been carried out (Gupta et al, 1989). The molybdenite was oxychlorinated in a fluidised bed resulting in the formation of molybdenum oxychloride, MoO_2C1_2 which was dissolved in water followed by the recovery of molybdenum as calcium molybdate, $CaMoO_4$. The Fe-Mo from the Jaduguda molybdenite concentrate was produced in small scale sector by alumino-thermic process. The R&D work on up-grading molybdenite concentrate generated at Jaduguda was carried out at NML and elsewhere. To remove the impurities such as alumina and silica, besides base metals, pressure leaching was carried out in HF-HCL and the enriched molybdenite was found suitable for lubricant applications. From the leach liquor, sodium silico-fluoride (Na_2SiF_6) and cyolite (sodium alumino-fluoride- $Na_3Al Fe_6$) can be recovered (Kumar et al., 2010). The processing of spent hydroprocessing catalysts containing molybdenum, vanadium and other metals at NML by acid leaching –solvent extraction – precipitation has shown technical viability.

Tungsten is available as wolframite at Degana, Rajasthan, and scheelite at Bundalamottu, Andhra Pradesh as low grade materials with tungsten in the range 0.1-0.3% WO_3. Earlier the only pilot plant for physical beneficiation of wolframite ore at Degana was producing off-grade concentrate for Fe-W production; the low grade was due to the presence of silica and alumina as impurities. A very detailed process flow-sheet to beneficiate wolframite ore of Dagana was developed at NML in early 1990s. The wolframite concentrate may be converted to Fe-W by thermit process for alloying in steel, but the same may not be suitable for applications such as catalysts, chemicals, etc. The off-grade concentrate was purified by HF treatment at NML to upgrade tungsten values from 56% to above 62% WO_3 for producing high pure tungsten products. The Degana jig concentrate containing 4.5-5% WO_3 was processed for metal recovery as ammonium paratunstate (APT) by soda pressure leaching-solvent extraction – crystallization (Premchand et al., 1995).

The tungsten recovery from the waste / worn out tools etc was researched at NML by alkali fusion followed by leaching - precipitation method. The Sandvick Asia at Pune has been recycling the waste tools in their production plant by alkali fusion- leaching route based on the technology from their principal company. Of late NML (Kumar, 2008) has worked on the extraction and recovery of tungsten values from the tungsten-copper alloy scrap by selective dissolution / recovery of copper in ammoniacal solution followed by recovery of tungsten.

3.7 Extraction of rare earth metals

India has proven resource of monazite in the beach sands in Kerala, Tamil Nadu, Andhra and Orissa containing light rare earths and some recently located reserves of xenotime which is the main source of the heavy rare earths and yttrium. Earlier studies (Gupta et al., 1989) on rare earth processing in BARC have been mainly on ion-exchange separation of the individual rare earths and at present most of our rare earth production (about 7000 tpa), is exported in the form of various compounds. **Most of the initial development and the associated technologies even afterwards are guarded, fall under the classified category and hence can't be described in any detail.** In the programme presently carried out at the BARC and other national laboratories, in collaboration with Indian Rare Earths Ltd., the objective is to divert a part of the raw materials for the preparation of metallurgical products that have local commercial value besides export potential. Extensive work has been carried out in the following areas:

1) Development of extraction technology for uranium recovery from uraninite ore of Jharkhand region by following sulphuric acid leaching and ion exchange process.The technology is under commercial production for almost 40 years at UCIL, Jaduguda.
2) Purification and preparation of uaranium from the yellow cake produced at UCIL, Jaduguda at NFC, Hyederbad for various applications.
3) Electro-winning of pure rare earth metals and misch metal,
4) Preparation of rare earth based permanent magnet materials, and
5) Preparation of rare earth-silicon alloy additive for the iron and steel industry.

Recently, R&D work on bioleaching of uranium from the uraninite ores of Jharkhand area was carried out at NML (Pandey et al, 2007) and the bioleaching process with about 70% recovery was established at 2.0 t column scale. The technology is being considered for further scale-up to prove the commercial viability of the process in heap leaching conditions.

For the preparation of rare earth metals from the salts the metallothermic reduction processes have certain advantages with regard to purity of the reduced metal, electrolysis remains the least expensive and incidentally the most widely used process, particularly for the light rare earth metals (with, low melting points) and also misch metal. The fused salt electrowinning has been applied for the production of lanthanum, cerium and misch metal. The purity of the metals obtained exceeds 99.9%.

4. Scope of Recycling and Reuse of Rare Earths and Rare Metals

As a result of the expanding use of rare earth-bearing materials, for example, in the form of rare earth-iron alloy magneto-restrictive transducers, variable frequency resonators and filters and rare earth-iron-boron alloy permanent magnets, the cost and environmental problems associated with their waste and scrap disposal have become a concern. Till now, there have been no large scale operations to recover rare earth metals from scrap and waste materials. Only about 1% of the total RE's in used and obsolete components are being recycled. Wider recycling and re-use could significantly lower world demand for rare earths and other strategic materials. Hitachi has recently developed technology for recycling rare earth magnets from hard disk drive motors and ACs and compressors. They also developed machinery to separate and collect rare earth magnets from end-of-life products, and successfully extracted rare earths using an a dry process and may commence full recycling operation by 2013.

As regards the recycling of rare metals (other than REs) very limited attempts have been made. Consequent to the advent of advanced technologies of day – to - day consumer and electronic goods and other applications, the exploitation of the rare metals and their resources are on rise. The extraction of metals from such secondary resources may utilize the similar processing approach as those in vogue for the ores/ minerals. Utilization of such processes to treat the secondary materials as outline in Table 8 would ensure high return because of fact that the recovered materials are of high value and the substances being processed are rich in metal contents.

5. Scope of Future R&D for Rare Metal Extraction

R&D institutions could be involved in partnership with the DAE (India)- Indian Rare Earths Ltd, private industries involved in the beach sand processing in India, and other Indian and international players to synergize the R&D activities related to the following as given by way of examples and not to restrict to:

a. Processing of different placer deposits of India and elsewhere to produce industrial minerals by physical beneficiation and subsequent treatment to recover value added products and materials.
b. Processing of individual beach sand minerals like monazite, sillimanite and garnet by using the NML's column flotation technology to produce values.
c. Extraction of values from the ilmenite and zircon minerals by suitable processing technologies relevant to the country and the partners.
d. Extraction and separation of select rare metals of high values from indigenous raw materials/ resources (Li, Mg, Ti, V, U, Zr/Hf, PGMs, etc) including Li from land resources and sea water.
e. Processing of wastes and byproducts as secondary resources for rare earths and rare metals (as given in Table 8)

f. Preparation of high purity metals and materials by following extractive metallurgy routes
g. Process optimization, techno-economic evaluation and design of select rare metal extraction processes.

6. Conclusion

7.

The paper gives a glimpse of Indian efforts and achievements in process technology development and the adaptation of the appropriate technologies of rare metals including rare earths. Operating production facilities for the metals such as beryllium, zirconium, titanium, tantalum, gallium, vanadium, selenium, tellurium, molybdenum, tungsten, and several other rare metals have been set up. Further work on established processes is in progress with particular emphasis on the reduction of the inherently high cost of rare-metal production. In this context, the study of the separation of zirconium and hafnium, extraction of selenium and tellurium from the anode slime and gallium extraction from the Bayer's liquor by establishing the innovative processes assumes great significance. Extraction of titanium from ilmenite by slag route assumes great importance in the light of pollution problems associated with the conventional hydrometallurgical processes. The extraction of metals from the secondary resources such as spent catalysts, e-wastes, slags, sludges, effluents and several other used / worn out materials have promise to recover the high value low volume metals for modern electronic and space applications

Though the effort so far has been sustained, there are several areas, particularly in rare earth technology, which need urgent R & D attention and activity. Another aspect that has been somewhat overlooked is the application of rare metals in non-nuclear and conventional chemical process industries in the country. Such applications may not only herald the era of high performance materials in conventional industries but also provide great impetus to accelerated R & D in rare metal process technology.

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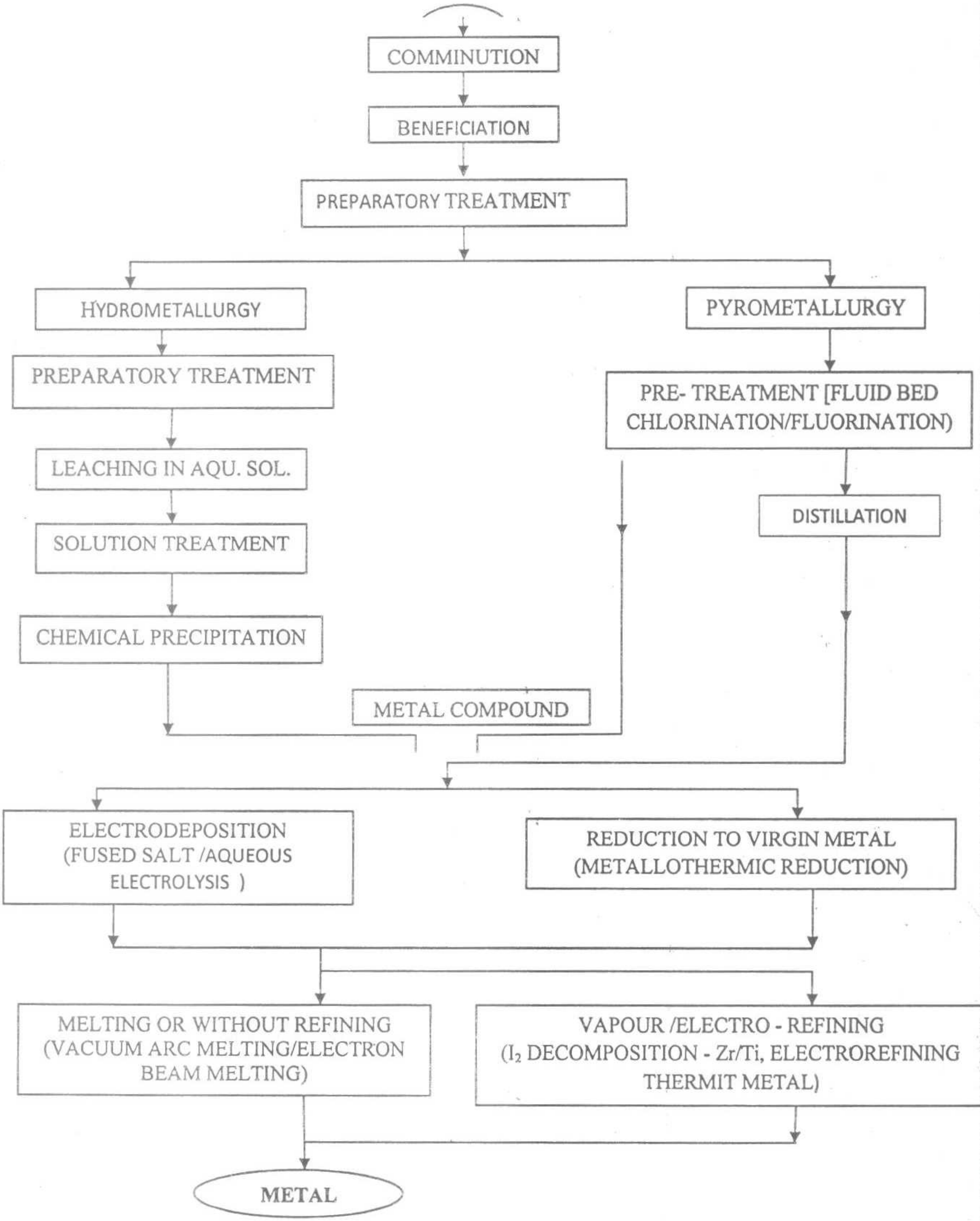

Fig 1. General scheme showing principal steps in the extraction and refining of rare metals