Critical Minerals-U-Th, Recoverable from the Placer Valuable Heavy Minerals in Mineral Sand Deposits

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ABSTRACT

Critical Minerals (CMs) are important due to their high-tech industrial and strategic applications in many industries such as the green and renewable energy, electronics, alloys and super-alloys, metallurgy, space, nuclear, defence, fertilizer, etc. The heavy mineral sand (HMS) deposits constitute one type of ore deposit that is an important source of (a) Ti, Zr, Th, W and REE, (b) the industrial minerals such as diamond, sapphire, garnet and sillimanite, and (c) occasionally gemstones, with cost of their mining is much less as compared to that of mining of rocks. An overview of the global, including Indian, scenario on the HMS deposits is presented. Amongst the CMs, a few such as the REEs, Ti, Zr-Hf, V, Cr, Nb, Sc and phosphate, and nuclear fuels of U and Th occur in trace to major contents in the placer valuable heavy minerals (VHMs, such as ilmenite, rutile, monazite, zircon, sillimanite and garnet) of the shoreline and inland HMS deposits in India, as documented by the mineral chemistry of VHMs. These CMs, U and Th could be recoverable as value-added byproducts with (i) separation of individual VHMs by mineral beneficiation techniques on HMS deposits and (ii) processing of such VHMs by extractive techniques − of extraction, separation, purification, smelting and refining − together with appropriate additional R&D studies, with examples of LREEs, U and Th from monazite and HREEs from garnet. Furthermore, the silt-product (<63 microns grain-size) of mineral sand industry comprising above HMs, gangue like quartz and clays could also be a source for the above cited CMs-U-Th. The recovery and processing of the above cited CMs, U and Th from the VHMs and silt in HMS deposits have multiple benefits, including establishing their additional resources (e.g., from the present Indian monazite resource of 13Mte, it may be possible to recover ~6.5 Mte of ΣRE_2O_3 [with average of 50% ΣRE_2O_3 in monazite], ~3.25 Mte of phosphate [av. 25% P_2O_5], ~1.3Mte of ThO_2 [av. 10% ThO_2] and ~0.13Mte of U_3O_8 [~1% U_3O_8]), establishment of down-stream industries with employment generation and economic benefit to the mineral sand industry.

Keywords: Placer heavy minerals, mineral sands, critical minerals-U-Th, recovery-processing.

INTRODUCTION

Mineral sands (MS) are the secondary deposits of old beach, dune, river, stream or lake sands consisting of grains of the mineral quartz (SiO_2, specific gravity [sp.gr.] 2.65) with concentrations of the valuable heavy minerals (VHMs with sp.gr. >2.89) such as ilmenite, rutile, leucoxene, zircon, monazite, garnet, sillimanite and magnetite, with rarely sapphire, diamond, etc.). These VHMs are all hard, stable, inert and resistant to weathering. They originally grew as crystals in igneous and metamorphic rocks such as granite, basalt, charnockite and khondalite. Over millions of years, these, including quartz, were weathered, eroded, washed down and transported to the sea or a lake by heavy rainfall and fast flowing rivers and streams, and constitute *placers*, from the Spanish word “placer”, meaning “alluvial sand”. These placers are of economically important mechanical, secondary and detrital. The HMS deposits, by location and volume, can be divided into large volume ‘shoreline’ (beach, dune and offshore) and less volume ‘inland’ (fluviatile or riverine). Compared to the primary metallic and non-metallic deposits, the secondary placer deposits have unique attributes such as wide spectrum of mineralization, easy and less costly surface and open-pit mining, diverse controls, and wide-ranging cost of their metals such as Ti and Sn (low) and Au and Pt (high). *Critical Minerals* (CMs) are globally important due to their strategic applications in high-tech industries such as green and renewable energy, electronics, alloys and super-alloys, metallurgy, space, nuclear, defence, artificial intelligence (AI) etc. CMs comprise *metals and semi-metals* used in the manufacture of mobile phones, flat-screen monitors, wind turbines, electric vehicles and solar panels, and a few *non-metals* of phosphate and potash, mostly used as fertilizers. Their list (i) *varies* from country to country (e.g., during the years of 2023-24, the USA 50[1]; Australia 31[2]; and India 30[3] - Sb, Be, Bi, Cd, Co, Cu, Ga, Ge, Graphite, Hf, In, Li, Mo, Nb, Ni, PGE, P, Potash, REE, Re, Se, Si, Sr, Ta, Te, Sn, Ti, W, V, and Zr in 2023); (ii) is *dynamic*; and (iii) is to be *periodically updated*, taking into consideration the new mineral discoveries, geopolitics, mineral-trade trends and policies, supply-chain, advances in mining, mineral processing, extractive techniques from ore and waste, vulnerability and national security. The nature, occurrence, recovery, and uses of CMs are given by Dhana Raju (2020)[4]. Generally, they include rare earth elements (REEs), platinum group metals (PGMs), precious metals of Au and Ag, battery metals of Li-Ni-Co-Mn-graphite, rare metals such as Be and Nb-Ta plus Ga, Ge, In, W, Ti, Cu, Cr, V, Mo, Sb, Sn, Zr-Hf, Se, Te, Re, graphite, phosphate, and potash. They are recovered from primary and secondary geological sources[5] and extracted from waste such as electronic-waste, mine-waste and tailings. While CMs are found in large extent across the globe, their processing for *extraction and refining* is *costly*, *technically difficult*, *energy intensive and associated with some environmental problems*. In the current economic scenario, China dominates the entire value chain of some CMs with accounting for >50% world's production of battery metals and most of REEs. It produces 63% of the world's REEs, 45% Mo and controls 72% of world's solar modules, 69% Li-ion batteries and 45% of wind turbines. Currently, Australia is the world's largest producer of Li and many other CMs. Amongst the CMs, some such as the REEs, Ti, Zr-Hf, V, Cr, Nb and phosphate as well as nuclear fuels of U and Th are present in notable contents − from trace to major percentage − in the placer VHMs, possibly including in silt of <63 micron grain-size, from shoreline and inland HMS deposits, as demonstrated by the mineral chemistry of VHMs in the HMS deposits of India[6,7]. The *recovery* of (i) VHMs from HMS deposits and (ii) above cited CMs, U and Th from VHMs by *processing* (given in brief) comprising sequentially of extraction, separation, refining and purification is dealt with in this article.

GLOBAL SCENARIO OF HEAVY MINERAL SAND DEPOSITS

The heavy mineral sand (HMS) deposits constitute one type of ore deposit that is an important source of (a) Ti, Zr, Th, W and REE, (b) the industrial minerals such as diamond, sapphire, garnet and sillimanite, and (c) occasionally gemstones, with their mining and processing operations on every continent, except Antarctica. These deposits comprise sand-size HMs and dominant quartz, admixed with finer size (<63 microns) silt. Mineralogy of primary source rocks usually controls the composition of the economic VHMs in the HMS deposits. Usually, the primary source of placer (a) zircon, monazite, rutile, sometimes tungsten and some ilmenite is a granite, (b) ilmenite, garnet, sapphire and diamond is ultramafic and mafic rocks, such as kimberlite or basalt, and (c) garnet, sillimanite and kyanite is metamorphic rocks such as the high-grade granulites, gneisses and amphibolites – khondalites, charnockites, granite gneisses and hornblende schists. Precious metals are sourced from primary ore deposits hosted by either metamorphic or magmatic rocks. The concentration of HMs in a placer HMS deposit requires a source of sediment containing HMs depositing onto a beach system in a volume that exceeds the rate of removal from the trap site. Economic-grade HMS deposits include the Holocene sediments on modern coasts such as in India and Brazil, as well as the coastal deposits formed by transgressions and regressions of the seas during intervals in the Quaternary, Tertiary and Cretaceous, such as in Australia and SE USA, besides a few inland placer HMS deposits such as the Teri Sands in southern Tamil Nadu, India[8]. Major HMS deposits occur along the coasts of Australia, China, India, Brazil, South Africa, Vietnam, Mozambique, Madagascar, Ukraine, Kenya, the USA, Senegal, Sierra Leone (rutile sands), Indonesia and Myanmar (zircon sands) (**Figure 1**)[9], besides lakeshore HMS deposits such as in Malawi.

Figure 1.

Geographical locations of placer heavy mineral sand deposits (numbers in the map with corresponding names in the index, to the right side of the map) in the world. (Credit: Bisht, A. and Martinez-Alier, 2022)[9].

Australia leads the global HMS industry due to the availability of large deposits, both primary and secondary. It has large ore reserves of mineral sands amounting to 56.5 Mt, 6.7 Mt and 20.0 Mt of ilmenite, rutile, and zircon, respectively[10]. The grade of a typical heavy mineral sand ore deposit is usually low. Within the 21st century, the lowest cut-off grades of heavy minerals, as a total heavy mineral (THM) concentrate from the bulk sand, in most ore deposits of this type is around 1% heavy minerals, although several are higher grade. Of the THM, the components are typically Zircon, from 1% of THM to upwards of 50% of THM, Ilmenite, generally of 10-60% of THM, Rutile, from 5% to 25% of THM,

Leucoxene, from 1% to10% of THM, Gangue, typically quartz, magnetite, garnet, chromite and kyanite, which usually account for the remaining bulk of the THM content, and Slimes, typically minerals as above and heavy clay minerals, too fine to be economically extracted. Being ancient, stranded dune systems, the tonnage of most deposits is more than several tens of millions of tonnes to several hundred million tonnes. For example, the medium-sized Coburn mineral sands deposit, Western Australia, is 230 million tonnes at 1.1% heavy minerals and is 13 km long[11].

INDIAN SCENARIO OF HEAVY MINERAL SAND DEPOSITS

Shoreline Heavy Mineral Sand (HMS) Deposits

India, with a coastline of > 7,000line km, hosts some of the largest and richest shoreline placers, with beach and dune sands containing light heavy minerals (HMs) such as ilmenite, rutile, garnet, zircon, monazite and sillimanite. A combination of favourable factors such as hinterland geology, coastal geomorphology, sub-tropical to tropical climate and intricate network of drainage, aided by wind and coastal processes such as waves and currents, have influenced the formation of beach and adjoining dune sands. The heavy mineral assemblage varies widely from near mono-mineral as near Ratnagiri in Maharashtra to multi-mineral suite elsewhere. The ultimate source or provenance for the heavy minerals consists of khondalite, charnockite, granite gneisses (Precambrian) and the Deccan Traps (Cretaceous). The intermediate host-rocks are the heavy mineral-laden Tertiary and Quaternary sediments occurring in the coastal plains[12]. These contribute placer economic HMs of ilmenite-rutile-leucoxene-zircon-monazite-sillimanite- garnet-magnetite.

In India, the exploration, delineation and resource evaluation of HMS deposits have been carried during the last 75 years by the Atomic Minerals Directorate of Exploration and Research (AMD), Department of Atomic Energy, Government of India. The exploration efforts of AMD have established 136 beach HMS deposits/occurrences of varying dimensions and grades in diverse geological environments or provinces, which contain Total Economic Heavy Mineral resources of about 1,300 million tonnes (Mte), including 13 Mte monazite, 38 Mte zircon, 762 Mte titanium minerals, 218 Mte garnet, and 278 Mte sillimanite. The above resource base has been established over 2,500 sq. km of present-day shoreline (>7,000line km), over a width of a few hundred meters to a few km inland and up to a depth of 12m, except in a few cases of deeper levels (up to 50m) of the HM-bearing mineral sands[13]. Major shoreline HMS deposits are in the states of Odisha, Andhra Pradesh, Tamil Nadu, Kerala, besides a few coastal placer HMS occurrences (50) in the states of Maharashtra[12], Karnataka, Gujarat and West Bengal (**Figure 2**)[14]. In these, THM content is usually of 10-20 wt.%, and rarely >50 wt.% as in the Chavara coast, Kerala [see details of HMS deposits in the book chapters of ‘Indian Placer Deposits’][15]. In the offshore, different blocks of HMS are delineated by the Geological Survey of India (marine wing) as prospective locales. These include Goplapur, Baruva, Bavanapadu, Kalingapatnam, Bhimunipatnam and Pentakota with THM varying from 1%->15%, concentrated within 20m isobaths with sandy sediments (medium-fine)[16].

The coastal HMS deposits have been under exploitation (mining and processing) since a few decades at Chavara (Kerala), Manavalakuruchi (MK, Tamil Nadu) and Chatrapur (Odisha) (**Figure 2**)[14] by the Indian Rare Earths Ltd. (IREL), a public sector unit under the DAE, besides the Kerala Minerals and Metals Ltd. (KMML), a state government unit of the Government of Kerala at Chavara. Furthermore, a few private mining companies for garnet are working.

Inland HMS Deposits

There are many inland HMS deposits which are volumetrically less compared to that of the shoreline. Some details of the inland placer HMS deposits are presented below, state-wise:

(i) *Odisha*: To the west of Puri and east of Satpara towns, a potentially large HMS deposit, named after Brahmagiri (**Figure 2**) is of dune system and spans over 30km. The eastern margin of the deposit is 5km while the western margin is ~7km from Satpara on the eastern embankment of Chilika Lake. The average HM-grade for the deepest borehole is 10.82 wt.% and the average slime content of the borehole is 6.14%. The HM-estimation indicates a raw sand tonnage of 1,111Mte containing 114Mte of THM at 10.25% grade. Up to an average depth of 18m, an additional raw sand tonnage of 503Mte containing 30 Mte (grade 5.92%) of THM and up to 25m depth, 661Mte of raw sand containing 63 Mte (grade 9.47%) of HMs is estimated under the category of speculative I and II. Of the HMs, ilmenite accounts for 49.65%, (range 28.06-71.17%), leucoxene 0.77% (0-1.94%), rutile 2.92 (0.66-6.11%), zircon 1.09% (0.12-3.66%), monazite 0.51% (0.05-1.81%), garnet 13.97% (1.34-35.87%) and sillimanite 27.56% (18.23-44.07%). This is a unique deposit in India as no single deposit explored/identified so far has such a large, identified HM-tonnage[7].

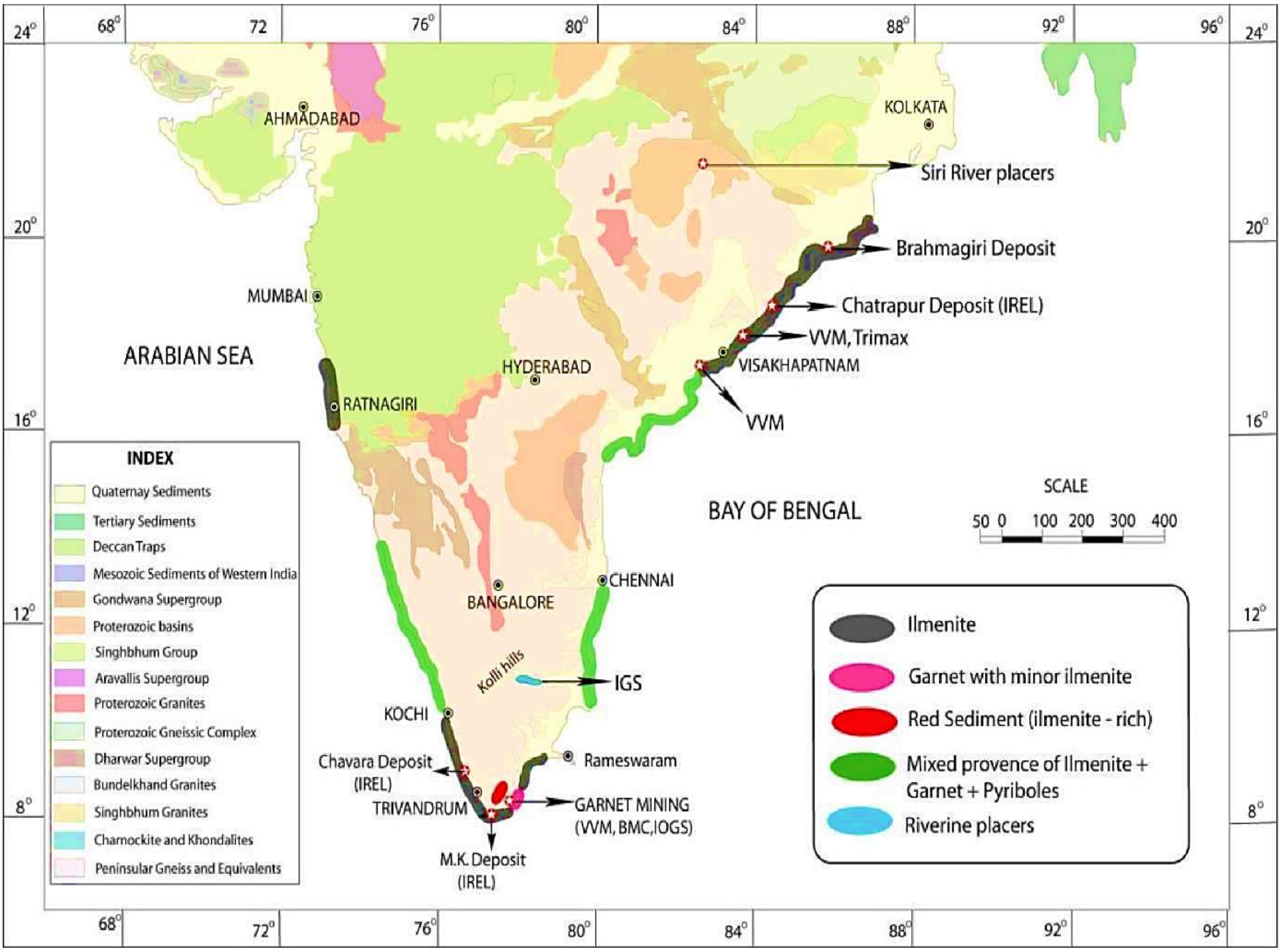


Figure 2. Geological map of the Peninsular India showing shoreline and riverine (inland) Heavy Mineral Sand (HMS) deposits/occurrences and their specific types along with the geology of the hinterland (Credit: Maithani, 2019, Fig. 37, IAEA-TECDOC-1877)[14].

(ii) *Andhra Pradesh (AP)*: Red sediments from Visakhapatnam to Bhimunipatnam on the east coast of India are of a highly ravaged belt of 25km and extend up to the foot of Khondalite hill and rise to +7.0m near the coast to +12.0m further inland. They are exposed variedly from vast expanses in the inland of Tamil Nadu to disconnected patches along the north AP and south Odisha coasts. Initially reported from the coastal areas of

Visakhapatnam district, they occur more widely and extend between the khondalite hill range and coastal sands. They are exposed as hills and gullies of over 15m in height near Bhimunipatnam, at surface and sub-surface level at Kalingapatnam, and as a basement for the beach sands near to the Bhavanapadu-Donkuru-Barua coasts. In the Donkuru-Barua coast, dune sands are perched on raised mounds of red sediments and apparently show an elevation of over 20m. The Red sediments occur as indurated, un-indurated and consolidated to semi-unconsolidated sediments, and as wave cut benches[6].

(iii)*Tamil Nadu*: Deposits of red sand/soil or Teri sands extend up to 20km inland. The deposits are discontinuous with the largest of them occupying 65 sq. km. They lie separated from corresponding shoreline placers by ~100-10,000m and stand out prominently in contrast to the surrounding buff coloured soil. These coastal red Teri sands are distinguished from the inland Teri sands, which are confined to the foothills of the Western Ghats where they occur in patches limited in number and extent. Inland Teri sands are mildly indurated, ferruginous and poorly sorted. The coastal Teri sands overlie the Quaternary calcareous sandstones/grit or limestone and have a thickness of up to 12m and are a valuable source for ilmenite, rutile, zircon, monazite and sillimanite. The reddening of sands is attributed to the release of iron of the garnet and opaque minerals[17].

(iv) *Chhattisgarh and Jharkhand*: Riverine placers, derived from intrusive granites and pegmatites in the Chhotanagpur Granite Gneiss Complex (CGGC) in parts of the Chhattisgarh and adjoining Jharkhand states in eastern India have been identified as a potential source for xenotime-bearing heavy mineral concentrates (HMCs). Various types of Proterozoic granites and the innumerable pegmatites associated with them constitute the primary source rocks for these xenotime-bearing riverine placers. Xenotime and monazite along with other heavy minerals, such as magnetite, ilmenite, zircon, garnet, apatite, etc., occur in varied concentrations in these placers. Potential xenotime placers are located in several rivers/streams in (i) the Ib River basin in the Kunkuri area of the Jashpur district, Chhattisgarh, (ii) the Mahan River basin in the Dhabi Dumhat area of the Surguja district in Chhattisgarh, (iii) the Deo River basin in the Kolebira area of the Simdega district, Jharkhand and (iv) the Kanhar River basin in the Balrampur-Bhandaria area in the Surguja district, Chhattisgarh and the Garhwa district in Jharkhand. There has been a pilot-scale recovery of xenotime concentrates from the Siri River and their up-gradation by magnetic separation to obtain two products: (i) xenotime-rich concentrate "A" of higher grade with 18-20% Y_2O_3, 8-9% HREEs and 15-20% LREEs, and (ii) monazite-rich concentrate "B" of lower grade with 3-4% Y_2O_3, 2-4% HREEs and 40-45% LREEs[18].

RECOVERY OF VALUABLE HEAVY MINERALS IN HEAVY MINERAL SAND DEPOSITS

Depending upon the constituent Valuable HMs (VHMs) in placer heavy mineral sand (HMS) deposits and their important physical properties, such as density, magnetic susceptibility and electrical conductivity, the appropriate equipment, methodology and sequence of operations for mineral processing of HMS deposits are selected by the various companies involved in their industrial-scale exploitation, as given in the following. The land-based wet concentrator plant (WCP) is based on a modular, transportable design concept making it easy to assemble and disassemble, and to move around a site or to other sites. Metallurgical testing in a laboratory-/ pilot-facility is required to determine an optimal processing route for the production environment. Wet concentration produces a high-grade HMs concentrate, maximising the content of VHM sand, whilst minimising the amount of non-valuable mineral(s). The initial processing in the WCP consists of: (i) screening to remove the coarse material such as oversized rock pieces, tree roots and other organic matter, and (ii) de-sliming (often via hydro-cyclones) to remove the fines, predominantly of clay and silt particles (waste). The de-slimed material is fed to a constant density (CD) tank. This is then pumped, at a constant density and feed rate (to optimise performance), to the distributors above gravity separation equipment in the form of a spiral or reflux classifier. The heavy minerals are separated from the quartz sand. In the case of spiral technology, the spiral troughs are angled, and the HM sand moves to the inside and the lighter gangue minerals to the outside of the trough, as the slurry travels down the spiral. Re-pulpers on the spirals aid in the recovery process. The waste tailings are typically pumped directly back to the mine void. To maximise the recovery and grade of VHMs, the WCP design may consist of multiple process stages to upgrade the material, including a primary (rougher) process unit, followed by middlings, cleaners, re-cleaner and scavenger (**Figure 3**).

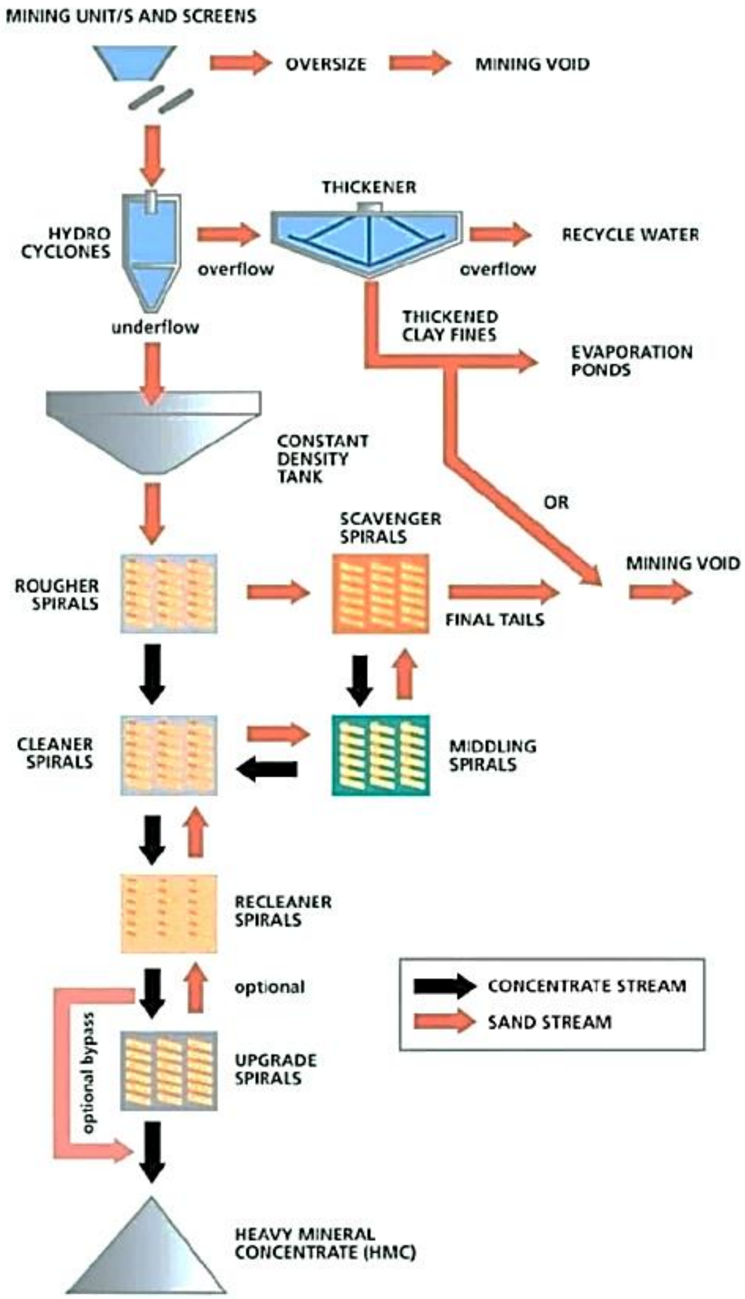
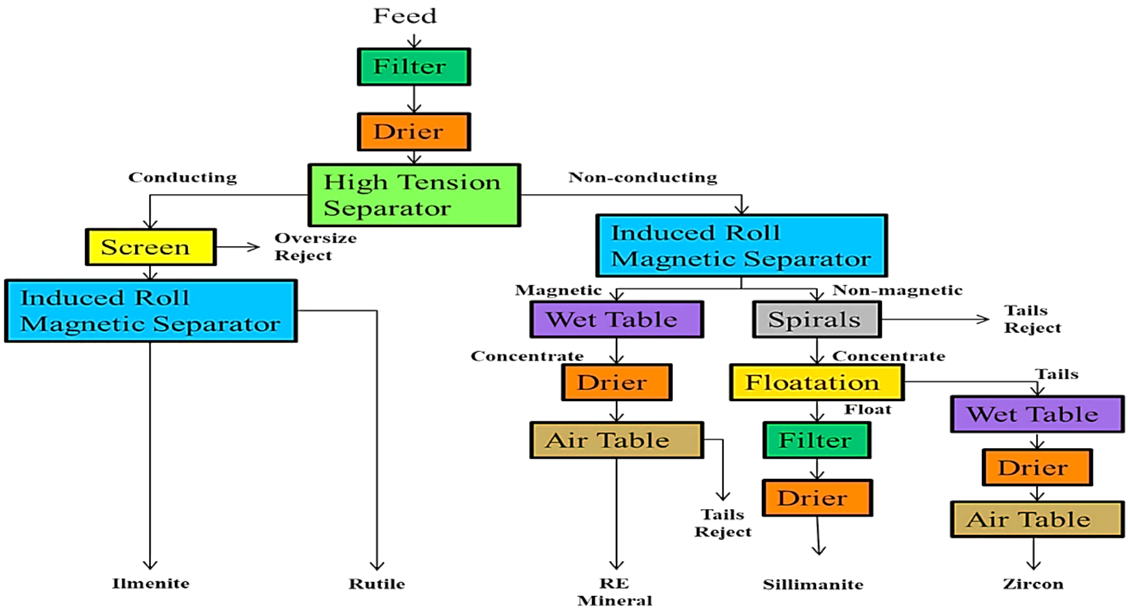


Figure 3. Mineral processing of raw sand for heavy mineral concentrate (HMC) of a placer HMS deposit. (Credit: Earth Science Australia – Mineral Sands)[19].

HM concentrate is stockpiled on site using dewatering cyclones and allowed to drain before being transported to the mineral separation plant (MSP). Following wet processing, the HM concentrate undergoes several dry processing stages to separate the VHMs and produce saleable products. Dry mill processing relies upon the unique physical properties of each HM to separate the non-valuable minerals from VHMs. Rare earth drum and/or roll magnets remove ilmenite as it is the most magnetic of the minerals in the concentrate. An electrostatic separation process is typically performed on the non-conductive minerals such as zircon, kyanite, staurolite, quartz, sillimanite and monazite, separating them from conductive minerals such as rutile, leucoxene and residual ilmenite. Furthermore, magnetic, electrostatic and/or wet gravity separation may be performed to clean up (reduce contaminants) and increase the saleability of the end-products. The products are stored in a dry area and then transported to market in a bag, container or bulk[19].

In India, the large-scale exploitation of HMS deposits has been carried out since 1965 by IREL. The IREL has been operating three mineral processing plants of HMS deposits, located at Chavara (besides one plant of Kerala Minerals and Metals Ltd., KMML, a state government undertaking of the Govt. of Kerala) in Kerala, Manavalakurichi (MK) in Tamil Nadu and Chhatrapur (Orissa Sand Complex, OSCOM, started in 1986) in Odisha (**Figure 2**). The general method of mineral processing of IREL is presented in the following:

The IREL plants collect raw sand either by the dry mining of beach washings or wet mining of inland HMS deposits. This operation is followed by wet concentration to get ~90% HM concentrate. This material is then fed into the "Concentrate Up gradation Plant" to make 97% grade concentrate that enters the dry mill for the separation of the six HMs namely, ilmenite, rutile, zircon, monazite, garnet and sillimanite. In the following, the flowsheet for the recovery of individual VHMs, adopted by IREL, is presented (**Figure 4**)[20].



(**a**) Flow sheet for recovery of individual heavy minerals

Figure 4. Flow-sheet for recovery of individual VHMs (ilmenite, rutile, garnet, monazite (RE mineral), zircon, and sillimanite, adopted by the IREL, India. (Credit: Singh et al., 2024)[20]

MINERAL CHEMISTRY OF VALUABLE HEAVY MINERALS IN INDIAN HMS DEPOSITS

Coastal HMS deposits (range, wt.%):

Monazite: ΣRE_2O_3: 45-64, with LREE (La-Sm) >> HREE (Eu-Lu); P_2O_5: 25-31; ThO_2: 6-23; UO_2: 0-2; Y_2O_3: 0.01-0.81 and Sc: 0.45-1.10 (Source: Chandrasekaran et al., 2021[17]; Panda et al., 2003[21] and Mohanty et al., 2003[22])

Ilmenite: TiO_2: 48-60, V: 0.13-0.41, Cr: 0.065-0.118, Co: 0.016-0.032, Cu: 0.006-0.011 and Zr: 0.035-0.113 (Source: Ravi, 2021[6]; Rao and Sengupta, 2014[23])

Rutile: TiO_2: 98-99.6, Cr_2O_3: 0.1-0.77, Nb_2O_5: 0.01-0.41 and Ta_2O_5: 0.01-0.05 (Source: Bangaku Naidu et al., 2020[24])

Zircon-concentrate from OSCOM: Zr (Hf)O_2: 64.5 and TiO_2: 0.25-0.7 (Source: Ravi, 2021[7])

Sillimanite-concentrate from OSCOM: Al_2O_3: 56.6, TiO_2: 0.25-0.4 and ZrO_2: 0.2-2 (Source: Ravi 2021[7])

Garnet (almandine-rich): ΣRE_2O_3: 0.15-0.53, HREE: 0.12-0.47 and LREE (La-Sm): 0.01- 0.013 (Panda et al., 2017[25])

Inland (Riverine) HMS in Eastern India (average, wt.%):

Xenotime: Y_2O_3: 41.1, P_2O_5: 31.2, La_2O_3: 0.5, Ce_2O_3: 0.13, Nd_2O_3: 0.5, Sm_2O_3: 0.5, Gd_2O_3: 1.6, Tb_4O_7: 0.5, Dy_2O_3: 4.6, Ho_2O_3: 1.1, Er_2O_3: 4.1, Tm_2O_3: 0.7, Yb_2O_3: 4.4, Lu_2O_3: 0.7, ThO_2: 1.0 and U_3O_8: 1.0; (Source: Rajasekaran et al., 1994[26])

Monazite: La_2O_3: 12.2, Ce_2O_3: 26.6, Pr_2O_3: 2.7, Nd_2O_3: 8.8, Sm_2O_3: 1.6, P_2O_5: 28.1, ThO_2: 11.3 and UO_2: 0.5 (Sarbajna et al., 2007[27]).

Other VHMs in the HM concentrate include ilmenite (9-43 wt.%), garnet (5-25 wt.%), zircon (2.4-6 wt.%) and magnetite (0.4-3%) (Source: Ramesh Babu, 2021[18]).

The above data indicate that the following CMs, besides U and Th, due to their notable contents in the VHMs may be recoverable:

Monazite:	REEs with LREE> HREE, Phosphate, Sc, Th and U
Xenotime:	REEs with HREE>LREE; Phosphate, Th and U
Ilmenite:	Ti, V and Cr
Rutile:	Ti, Cr and Nb
Zircon:	Zr-Hf and Ti
Sillimanite:	Ti and Zr
Garnet:	HREE

It may be added that the silt (<63-micron grain-size) comprising heavy minerals, gangue of quartz and clays of HMS deposits could possibly contain notable contents of CMs-U-Th (to be tested by chemical analysis) and, if so, it will constitute additional source for resources of the above. This possibility is suggested based on the analogy of the following:

(a) The clay-hosted, ion adsorption LREE and HREE-rich deposits of the Xunwu Lognan Dt., Jaingxi Province, South China are unique and genetically linked generally to the weathering of Ce-depleted, granites and less commonly to volcanic rocks and lamprophyres (Xu et al., 2017[28]; Wang et al., 2018[29]);

(b) Indications for such deposits in India in parts of Nongpoh granite, Ri-Bhoi district, Meghalaya has been reported (Sadiq et al., 2014[30]); and

(c) Possibilities of clay-hosted REE deposits in India such as the Chhotanagpur granitic gneissic terrain has been shown to contain both monazite- and xenotime-bearing granites with riverine placers (Sinha, 2001[31]; Krishnamurthy, 2024[32]).

By recovering the CMs, U and Th from VHMs in HMS deposits by appropriate mineral processing, employing extractive techniques given below, large potential additional resources of some CMs and U-Th can be obtained, as per the following examples:

(a) *CMs from monazite*: From the present resources of 13million tonnes (Mte) of Indian monazite[13], it may be possible to get 6.5Mte of ΣRE_2O_3 (taking average of 50% ΣRE_2O_3 in monazite), 3.25 Mte of phosphate (25% P_2O_5), 1.3Mte of ThO_2 (10% ThO_2) and ~0.13Mte of U_3O_8 (~1% U_3O_8);

(b) *CMs from garnet*: From the present resource of 218 Mte of Indian garnet[13], it may be possible to get ~54.5 Mte of HREE (~0.25% HREE) and ~76.3 Mte of ΣRE_2O_3 (~0.35% of ΣRE_2O_3); and

(c) *Chromium from Ti-minerals*: From the present resource of 762 Mte of Indian Ti-minerals[13], 7.62 Mte of Cr (~0.1% Cr in Ti-minerals).

It may be noted that the above range and average contents of the CMs and U-Th in VHMs of Indian HMS deposits may be taken as their general pattern, and exceptions in data of each VHMs and U-Th may exist from other deposits. Hence, before processing any VHMs in HMS deposits for CMs and U-Th, the heavy mineral(s) in a mineral sand deposit should be comprehensively analysed chemically for their contents of CMs and U-Th, based on which their processing can be taken up.

PROCESSING (IN BRIEF) FOR CRITICAL MINERALS FROM RECOVERED VALUABLE HEAVY MINERALS

Processing of individual VHMs by extractive techniques is carried out by *extraction* [(hydrometallurgy, leaching, solvent extraction and ion exchange), *separation-refining* (solvent extraction, scrubbing, stripping and calcination), *smelting* and *purification* (vacuum refining/distillation, sublimation, zone-refining and electro-transport) of individual CMs such as REEs from VHMs in HMS deposits; this is briefly given below by a few examples taken from literature:

Method for extraction and separation of rare earth elements:

Joseph Brewer[33] invented (and patented) the following method for extracting and separating REEs. It comprises providing a rare earth-containing ore (such as monazite and xenotime) or tailings, grinding the rare earth-containing ore to form powdered ore; leaching powered ore with at least one mineral acid, forming a leach solution comprising at least one metal ion, rare earth elements and a solid material, separating solid material from the leach solution to form aqueous-metal concentrate, precipitating the aqueous-metal concentrate to selectively remove the metal ion from the leach solution and obtain a precipitate of rare earth elements; heating the precipitate of rare earth elements in air to form oxide of rare earth elements, mixing the oxide of rare earth elements with an ammonium salt and heating in a dry air/nitrogen, forming a mixture of anhydrous rare earth salts in an aqueous solution, and separating rare earth elements from the aqueous solution by means of an electrowinning process[33].

Lynas REE-separation plant, near Kuantan, Malaysia[34]:

The three processes undertaken at Lynas plant in Malaysia (operated since 2012) are:

1. *Cracking and leaching*: Mt Weld concentrate is mixed with concentrated sulphuric acid and cracked at a high temperature to convert the rare earth phosphate minerals to rare earth sulphate. Water is added to the rare earth sulphate in the leaching stage and impurities in the form of iron phosphate are removed. The solution is neutralised to provide rare earth solution as feed to solvent extraction.

2. *Solvent Extraction*: Solvent Extraction (SX) employs two liquid phases (organic and aqueous) and is carried out in liquid-liquid counter current SX trains to progressively separate the rare earths into groups and individual elements and produce a solution.

3. *Product finishing*: In this final stage, the rare earth elements in the solution are precipitated as solid carbonates or oxalates. Some are then calcined (roasted) to make the respective oxides. Lynas Malaysia produces NdPr oxide, Ce carbonate, Ce oxide, LaCe carbonate and LaCe oxide, and SEG oxide and a mixed Heavy Rare Earths compound known as SEG.

Lynas second plant at Kalgoorlie, Western Australia has recently been operational.

Processing of REEs by Flash Joule Heating (FJH)[35]:

FJH has emerged as an ultrafast, scalable and versatile synthesis method for nanomaterials, such as graphene. FJH is a rapid, high-energy heating technique that uses a short-duration electrical pulse to generate intense heat within a material, enabling the synthesis and processing of various materials. MTM Critical Metals has announced its FJH technology has successfully removed nearly 50 per cent of the main impurities (iron, aluminium, calcium and phosphorus) from REE flotation concentrate in a single step. Now able to deliver a 50 per cent increase in REE concentration in the final product, the two-step solution, which includes rapid FJH and a water wash, is currently undergoing even more testing works to optimise it further. MTM chief executive officer Michael Walshe said the FJH breakthrough has significant implications for the rare earth industry, addressing critical challenges in sustainable production, onshoring refining and increased supply chain security. Producing REE chlorides directly from flotation concentrate simplifies the refining process, making REEs more accessible for key sectors such as renewable energy, advanced manufacturing and defence. “This transformative result validates the enormous potential of flash joule heating in simplifying and improving rare earth processing,” Walshe said. “Achieving such high impurity removal and REE concentration in a single step is a game changer and we are only at the beginning of this testing regime. We are continuing discussions with leading industry players to advance this technology towards commercial-scale deployment.” The FJH process offers an alternative to traditional “cracking and leaching” processing methods, which typically involve sulphuric acid baking at high temperatures to convert rare earth minerals into partially soluble REE sulphates. This conventional approach is resource-intensive, demanding substantial energy input for high temperature operations and vast volumes of water to dissolve the sparingly soluble REE sulphates. The FJH technology aims to bypass these inefficiencies by creating purified REE chlorides in a single operation. The benefits include using significantly less water through dry reactions, using less energy by heating the material directly, streamlining the downstream process and creating less waste. (Tibben, 2024)[35].

Zirconium and Hafnium from Zircon:

Zirconium and hafnium occur most commonly in nature as the mineral zircon ($ZrSiO_4$) and less commonly as baddeleyite (ZrO_2). In general, the commercial nuclear grade zirconium production route involves ore cracking, Hf-separation, calcination, pure chlorination and reduction to the pure metal. Zircon decomposition always requires the use of high temperature and aggressive chemicals. The most used method is the carbochlorination. It is processed by heating zircon sand and carbon in a fluidized bed to around 1200 °C under the fluidizing gas of chlorine. The $ZrCl_4$ powder product containing $HfCl_4$ at the same level of the starting ore is obtained at a lower temperature, and the liquid silicon tetrachloride is collected at an even lower temperature as a by-product, which is subsequently used to produce fibre optic cable, fumed silica and silicon metal for solar cells. The separation of hafnium from zirconium is the key of the nuclear grade zirconium production. Most of the commercially used separation methods are hydrometallurgical routes, including fractional crystallization, methyl isobutyl ketone (MIBK) extraction and tributyl phosphate (TBP) extraction. The fractional crystallization process was operated for many years on industrial scale, despite its multi-step characteristics and low process efficiency. The MIBK and TBP extraction are two conventional methods for the Zr–Hf separation and are still dominantly being applied in nuclear industry. In this case, the zirconium metal production process consists of pyrometallurgical ore cracking, hydrometallurgical Zr–Hf separation and final pyrometallurgical zirconium compounds reduction. The connections of pyro-, hydro- and pyrometallurgical-operations result in high production cost, intensive labour and heavy environmental burden. In order to enhance the whole production process, a lot of investigations have been focusing on pyrometallurgical routes for the separation of zirconium and hafnium during the past decades. The invention of the extractive distillation process is a great progress in Zr–Hf separation technology and it is the only pyrometallurgical method operating on industrial scale. On development level, the novel and compact process based on molten salt extraction for Zr–Hf separation, which starts from crude ore to hafnium-free zirconium metal product, shows a great potential for industrial application. However, it is still under investigation on laboratory scale. After the separation, the purified zirconium compound is subjected to a reduction apparatus for the pure metal production (Xu et al., 2015)[36].

BENEFITS OF RECOVERING-PROCESSING FOR CMs, U AND TH FROM VHMS IN HMS DEPOSITS

These include: (i) proving additional resources of some CMs, U and Th as byproducts of VHMs in HMS deposits; (ii) large indigenous supply of the above with no problems in supply-chain unlike in imports that involve foreign exchange; (iii) development of a few down-stream industries with employment generation; (iv) low-cost of surficial/safe open-pit mining of placer HMS deposits as compared to hard-rock mining involving high-cost underground mining; (v) addressing the environmental and ecological concerns of sustainable placer mining/processing due to refilling-recycling-rehabilitation-reuse (R-4) of the mined sites of HMS deposits; (vi) less displacement of personnel due to R-4 and (vii) economic benefit to the mineral sand industry.

CONCLUSIONS

- Critical Minerals (CMs) are important worldwide due to their strategic applications in many high-tech industries and their list (i) is dynamic, (ii) varies from country to country and (iii) is periodically updated taking into consideration different aspects of each country.

- Placer heavy mineral sand (HMS) deposits of shoreline, inland and offshore constitute one type of a secondary deposit with unique attributes, such as wide spectrum of mineralization of industrial and high-tech metals present in their valuable heavy minerals (VHMs), easy and less costly surface and open-pit mining and diverse controls; an overview of their global, including Indian, scenario is presented.

- Amongst the CMs, a few such as the REEs, Ti, Zr-Hf, V, Cr, Nb, Sc and phosphate, and nuclear fuels of U and Th occur in trace to major recoverable contents in VHMs, such as the ilmenite, rutile, monazite, zircon, sillimanite and garnet of coastal and inland HMS deposits, as revealed by the mineral chemistry of VHMs in HMS deposits of India. Apart from the VHMs, it is probable that the silt (<63 micron grain-size and comprising heavy minerals, gangue such as quartz and clay minerals) of HMS deposits to contain the above CMs-U-Th (to be tested by chemical analysis) and, if so, the silt could be an additional source for processing to recover some of CMs-Th.

- Recovery of (a) individual VHMs from the HMS deposits is given together with a flowsheet and (b) above given CMs, U and Th by processing of VHMs employing extractive techniques is briefly presented with a few examples taken from literature. Major benefits of such a recovery, such as (i) low-cost proving of additional resources of these CMs, U and Th as byproducts of VHMs in HMS deposits; (ii) large indigenous supply of these with no problems of supply-chain; (iii) saving valuable foreign exchange that is required for imports of CMs and (iv) development of a few down-stream industries with employment generation, etc., are listed.

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