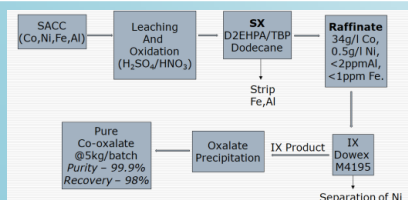
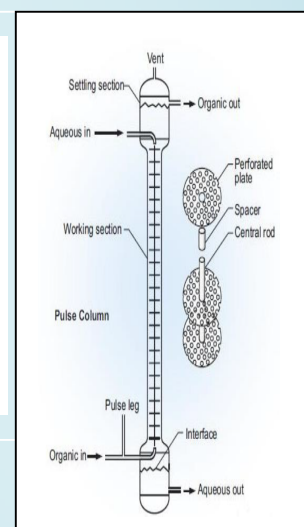
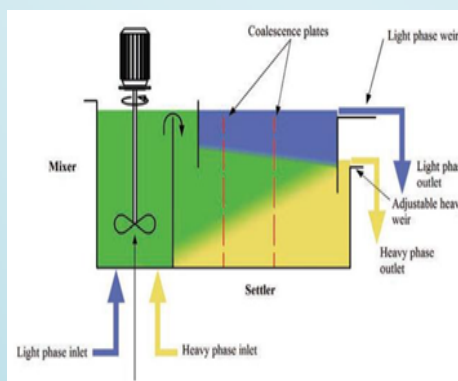
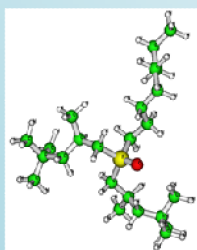
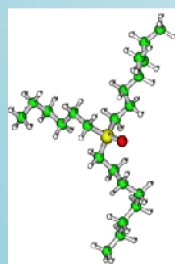
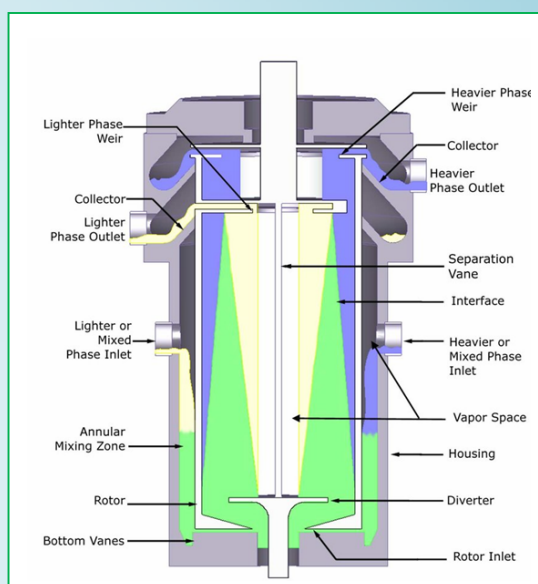
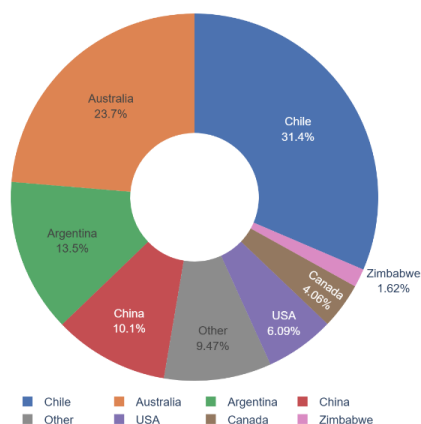




ASSET Bulletin

Separations in Preparation of High Purity Critical Elements

Share of World Li Reserves by Country (2024)
Source: USGS MCS 2025 | Total ~ 30 Mt Li



Message

**Guest Editor, ASSET Bulletin on "Separations in Preparation of High Purity Critical Elements
Separations in Preparation of High Purity Critical Elements"**



Greetings to all the members of ASSET.

As you are aware the primacy of critical elements has been well recognised in the recent past by the policy makers and research fraternity given its role in energy security and the overall development of the country as part of transforming India a *Viksit Bharat by 2047*. There has been deliberate policy thrust in this regard in terms of setting up of National Critical Minerals Mission by the Government of India to reduce the dependence on imports. I would like to mention that some of the critical minerals having bearing on energy security as well as resource security and strategic, importance have been brought out in this special Asset Bulletin viz., cobalt for electric vehicles and batteries gadolinium, dysprosium, hafnium which are required for control purposes in nuclear reactor, zirconium, niobium for structural applications in nuclear reactors, tellurium and gallium for solar power applications, Nd, Pr, Dy, Tb, Sm) for wind energy and for strategic purpose, Nd-Fe-B magnets for hybrid and electric vehicles, rare earth based phosphors comprising of europium, terbium and yttrium for consumer goods, and application of Lithium based batteries in electric vehicles etc to name a few.

I sincerely thank the President for providing me the opportunity to serve as Guest Editor, and I express my gratitude to all the authors who contributed to this special bulletin on this important and timely subject.

Dr. Smt. M Anitha

Message

President, ASSET



Dear Members,

Greetings from ASSET!

I am delighted to learn that the third ASSET bulletin of this year is on the topic "Separations in preparation of high purity critical elements". Critical elements, also known as critical minerals, are specific metals and minerals that are essential for modern technology, economic development, and national security. They are crucial for the manufacturing of everyday devices, enabling the green energy transition, and constructing advanced defense systems, yet they face significant supply risks. The importance of critical elements spans various high-impact sectors. They are the foundational building blocks of renewable energy. Minerals such as lithium, cobalt, and nickel are fundamental for the batteries that power electric vehicles (EVs) and store energy. Similarly, rare earth elements are utilized to create the permanent magnets required for wind turbines. Digital devices and smart grids heavily depend on these elements. Semiconductors, LEDs, and high-speed microchips require materials like silicon, gallium, indium, and germanium. Critical elements—such as tantalum and gadolinium—are necessary for producing life-saving hospital equipment, advanced medical imaging systems, and MRI machines. Due to the geographical concentration of these elements, heavy reliance on them exposes global supply chains to geopolitical vulnerabilities, monopolization, and trade disruptions. Many countries, including India, have established strategic policies—such as the National Critical Mineral Mission—to secure domestic production, promote recycling, and reduce import dependency on these strategic resources.

I thank Dr. Smt. Anitha M., MPD, BARC, for being the guest editor of this bulletin and also for shouldering the editorial responsibility in bringing the bulletin into shape. I record my heartfelt thanks to all the authors. I am highly indebted to Prof. P.K. Mohapatra and Prof. V.K. Manchanda for their wholehearted support. My special thanks to the vice presidents, the secretary, and all the executive committee members of ASSET.

Dr. Jeyakumar Subbiah

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Critical metal Cobalt -Scenario, Usage and Hydrometallurgy

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Introduction

Natural resources form an important asset for any nation and mineral wealth occupies critical position amongst them. The uneven distribution of mineral wealth and dynamic nature of geo-political conditions have put stress on supply-chain of minerals/metals. The world-wide desire for "Clean Energy" and "Climate Control" has further increased the demand for minerals / metals, especially the energy critical metals/minerals. A Report of International Energy Agency released in 2021[1] on climate control, already flagged large mismatch between the world's strengthened climate improvements and the availability of minerals essential for realizing those targets. Some of metals needed for clean energy and climate control include Li, Co, Ni, Cu, Rare Earths, U etc.[2,3]

Any effort for securing the resources necessarily involves augmentation of exploitable resources of minerals/metals. Resources can be either primary or secondary type. Utilization of "Secondary Resources" for metal / mineral values assumed significance as this path serves the objectives of "Wealth from Waste" and/or "Sustainability" goals[4]. Assessment of exploitability of a resource involves exhaustive geo-metallurgical studies such that at the end industrially acceptable or scalable process/processes emerge. Amongst the various options possible for utilization of secondary resources for recovery of mineral / metal values, the path of "Hydrometallurgy" stands ahead because this approach is highly suitable for lean resources of complex and challenging compositions.

Also, steady depletion of high-grade primary resources of minerals world-over shifted the focus on the utilisation of secondary resources. The emphasis on implementation of 'Sustainable Development' technologies and 'Waste to Wealth' approaches has further amplified the importance for utilization of secondary resources in the present era. Another

driving force for mining of metals from secondary resources is the ever-increasing competition in metal markets for cheaper production of commodities. Though the economics of recovery of mineral/metal from a secondary resource depends on the characteristics of the feed or input raw material, it is generally perceived that production of a metal from a secondary resource is relatively economical in comparison to production from a primary resource.

In this context, the mapping of the opportunity in terms of available sources in our country, in house strength lying in technologically experienced groups is very much apt to discuss against the challenge of lean nature of those sources and economic viability of those technologies. This article is aimed to discuss importance of cobalt through understanding the nature of the resources in terms of mineralogy and composition, demand and supply scenario, literature review emphasizing upon the attempts already made to recover cobalt from different sources specifically from laterites. Also the efforts of the Materials Group of BARC towards cobalt recovery from various secondary sources will be touched upon.

Uses

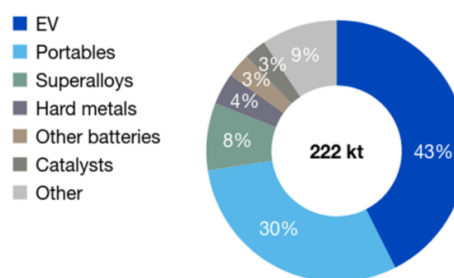


Fig. 1: Cobalt demand for major end uses worldwide [16]

Co is recognised as an important technology enabling energy critical metal [5]. It has diverse range of uses from electric vehicles to super alloys in gas

turbines and hard metals to rechargeable batteries and industrial catalysts, which are vital in the development of sustainable energy technologies [Fig. 1]. Besides serving as a cathode material of many types of batteries, Co is also used to make powerful magnets, high-speed cutting tools, and high-strength alloys for jet engines and gas turbines [6]. Unique catalytic properties of Co are utilised in desulphurisation of hydrocarbons, which is crucial to clean fuel technology and also in the removal of NO_x to minimize emissions of greenhouse gases. Its catalytic qualities are also used in the emerging technology of converting natural gas to liquid hydrocarbons, thus using carbon based resources more efficiently. Recently scientists have developed catalysts capable of efficiently converting carbon dioxide into methanoic acid - a liquid fuel [7]. So versatile is Co that apart from having imparted great physical attributes to many industrial applications it also has uses in enabling digital storage and processing. In particular, Co will be at the heart of the drive for alternative and renewable energy systems, whether as a hard wearing/magnetic alloy in wind and wave generators, as a catalyst used for 'splitting' water in the newly developing solar energy technologies, or helping power electric vehicles of the future[8]. In the case of India, a National Mission on Electric Mobility (NMEM) was announced with a countrywide goal of deploying 6 to 7 million hybrid and electric vehicles(EVs) [9] which needs a minimum of 10 GWh of cells and can be expanded to about 50 GWh in near future. As seen in Fig. 2, the market is quite stable in terms of cobalt demand for portable items, but the total demand by 2030 is showing a trend of substantial expansion [Fig. 3].

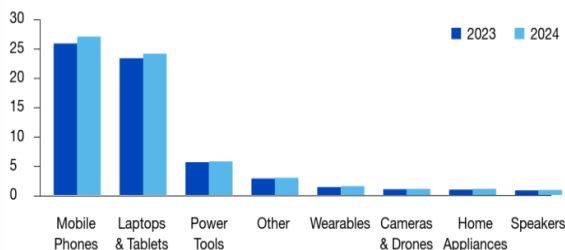


Fig. 2: World scenario of Cobalt demand in portable items

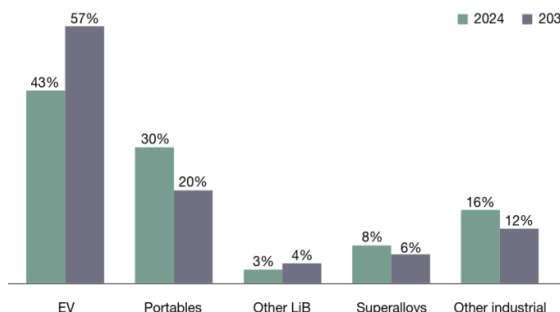


Fig. 3: Projection of world cobalt demand

Resources

About two thirds of global Co production is derived from stratiform sediment hosted Cu-Co deposits, with about 27% from leaching of Ni-Co laterites or smelting of nickel sulfides from magmatic sulfide deposits [10,11]. India does not have any primary resource of Co. At present all the indigenous requirements, estimated to be about 100 tons per annum, are met through imports only [12]. However there exists two important secondary resources of Co in India namely the nickel-bearing laterite deposits in Sukinda, Odisha assaying about 0.02-0.05% Co and the copper converter slag produced by Hindustan Copper Limited at Ghatsila (Jharkhand) [13] besides recycling of used batteries [14]. The resource in Odisha corners 69% of the total available Co values and the rest are in Jharkhand and Nagaland [2]. The lateritic nickel ore also known as overburden of chromite mines (COB) is a secondary source of Co in the Sukinda Valley of Odisha, India. On an average about 10 tons of lateritic ore has to be taken out for every ton of chromite mined. It was reported that 150 million tons of laterite is stockpiled at site and the quantity of overburden would increase with depth of mining and dip of ore body [14]. Any effort for resource security necessarily involves augmentation of exploitable resources of minerals/metals. Considering the projected demand of Co and its status as a critical metal, utilization of vast resource of COB of Odisha, a secondary resource, is a national need.

Occurrence, Geology and Mining

The crustal abundance of Co in Earth's crust is about 25 ppm [15]. Total cobalt reserve in the world is about 76 lakh tones mainly occurring in Australia, Congo,

Indonesia, Canada, Phillipines, Russia etc. [16] Typical physical and chemical properties of Co are responsible for its applications in diverse fields like batteries, alloys, chemicals etc. as illustrated in Fig.1. The demand for Co is expected to increase by a factor of 10 to more than 20 towards 2050 [17] driven by its application in both non-EV and EV batteries.

Co has hardly been found as an independent mineral among ~100 different cobalt-bearing minerals identified till date [15]. It is mostly an accompanying metal generally bound to Fe, Ni, Cu and S forming various sulfides and sulfarsenide phases. Huang et al. [15] gave exhaustive account on relative distribution of these resources. The only operating mine with Co as the main product is the Bou Azzer mine in Morocco [15] and all other supplies are as byproduct in Cu and Ni mining. About two thirds of global Co production of [18] is derived from stratiform sediment hosted Cu-Co deposits, with about 27% from leaching of Ni-Co laterites or smelting of nickel sulfides from magmatic sulfide deposits. Much of the remainder is from volcanogenic massive sulphide deposits.

Co bearing ores are mined by underground and open pit mining depending on the nature of the ore body. Subsequent to mining of the ore, Co values are extracted by both hydrometallurgy and pyrometallurgy routes. However about 70% of the mines follow hydrometallurgical route only [15] because of obvious environmental issues accompanying the pyro processes.

Significant resources (120 million tonnes) of Co also occur on the sea floor in iron-manganese-rich nodules and Co-rich crusts; although to date no Co has been commercially extracted from these resources [19]. Other resources of Co include metallurgical mattes and other intermediate products of Co metallurgy, including waste and scrap.

Extraction of Co from Sulfide Deposits

A generic flowsheet for recovery of Co as a byproduct of Cu/Ni ores is given in Fig. 4. Ores amenable to physical beneficiation like the Co bearing Cu or Ni sulfidic ores adopt froth flotation as a means of pre-concentration of mineral values prior to pyro or hydrometallurgical processing. In

the pyro-metallurgy based processes followed for Ni-Co sulphide mineral concentrates, there exists two routes for smelting and conversion of Ni-Co concentrates to produce matte. Matte smelting operations have a telling effect on environment as they emit harmful gases and that has led to the development of purely hydrometallurgical processes [20]. Heap and bioleaching technologies were also used for Co resource processing [20,21-23].

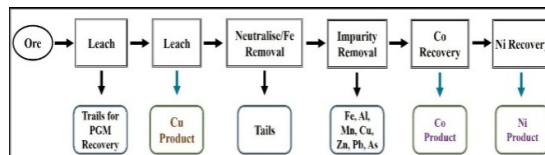


Fig.4: Generic flowsheet for Recovery of Co from sulphide deposits [48]

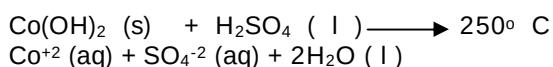
Significant improvements to heap design, feed preparation, irrigation etc. have enabled some Ni-Co projects in Turkey, Phillipines, some mines in DRC to adopt this technology especially for lean tenor ores. Co metal is produced by electro-winning or by H₂ reduction from purified leach solution [24].

Extraction of Co from Laterites

Of the recoverable global Co resources, almost 42% occur in Ni-Co laterites [25]. Laterites are part of the earth that develop in humid tropical climates during the weathering of various types of soil, where they are developed over rocks they may also contain appreciable concentrations of Co at grades between 0.025% and 0.18%, which occur together with Ni values [26-27]. The ore zones are generally in the range of 10–40 metres thick and close to surface, therefore economical for mining. Three sub types of Ni-Co laterite deposit sub-types are recognised include: (a) clay silicate; (b) hydrous magnesium silicate and (c) iron oxide – limonite deposits [28-29]. The most important ore minerals include serpentine, talc, chlorite, clays, erythrite, heterogenite, asbolane, heazlewoodite, millerite, goethite, limonite and lithiophorite. The list of some of the prominent Co bearing laterites across the world is documented in USGS report 2020 [30]. The Kalgoorlie and the Murrin Murrin deposits in Western Australia and the Goro deposit in New Caledonia are

examples of some of the world's many large Ni-Co laterite deposits.

High Pressure Acid Leaching (HPAL) is an established technology for extracting Co from various lateritic ore bodies [31]. In HPAL the ore is leached with sulphuric acid at high pressures (up to 5.4 MPa) and high temperatures (245 to 270°C) in a titanium-clad autoclave following the chemical equation below [20].



In laterite 98% sulfuric acid
Leach solution

In addition to the favourable selectivity, resulting in improved metal recovery and higher product purity, implementation of SX is followed in some plants as an alternative to sulphides or hydroxide precipitation as they circumvent handling of solids and use of toxic gases like hydrogen sulfide [32]. Some of the common solvent extractants in use include di-2-ethylhexyl phosphoric acid (D2EHPA), tributyl phosphate (TBP), PC-88A, Cyanex 272, organodithiophosphinic acid like Cyanex 301 and ketoximes (LIX 84I).

Atmospheric acid leaching (AAL) of Co (also Ni) values in laterites is gaining importance in the industry especially for lean ores [33-34]. Sulfuric acid leaching under atmospheric pressure has been reported for various laterites like limonitic and saprolitic laterite varieties [35-36]. However, the requirement of significant excess acid and poor Ni and Co extractions (40-90%) do not make this approach particularly attractive. The other alternatives investigated include sulfuric acid pug-roasting followed by water leaching [37], sulfuric acid leaching of high temperature calcined ore and dilute acid leaching of the ore roasted in a sulfur dioxide-air mixture [38], all under atmospheric conditions. The atmospheric acid leaching using HCl was also reported [39-40] and so with nitric acid [41]. Since both the acids are very expensive regeneration and recycle were essential components in flowsheets / technologies using HCl and HNO₃. Lakshmanan et al. has developed chloride metallurgy for the extraction of Ni and Co from the laterites [42]. Atmospheric leaching of the ore in mixed HCl-MgCl₂ lixiviant was very efficient for metal recovery. Pyrohydrolysis

process was used to regenerate HCl which can be recycled.

Studies by many researchers indicated that reductive leaching of laterites including those of limonitic and saprolitic varieties can be accomplished using SO₂ under atmospheric pressure leaching conditions in acidic media resulting in enhanced dissolution of Co values contained in different phases of the ores [33,43-46,33,47,48-51]. SO₂ performs multiple functions in hydrometallurgy viz. it acts as a reducing and complexing agent as well as an acid.

Co from Indian Laterites

The major reserve of India's lateritic deposits is found to be in the chromite deposits of Sukinda valley of Odisha [52]. These chromite mines generate huge amounts of overburden called chromite ore overburden (COB) along with the chromite ore, which contains Ni in lateritic form as well as Co [53-54]. It has been estimated that the Sukinda deposit contains about 150 - 180 million tons of chromite ore and mining of every ton of chromite ore generates 10 times weight of laterite [55-56]. The laterite sample consists mostly of goethite and quartz followed by minor amounts of chromite, hematite, serpentine, kaolinite, montmorillonite, chlorite, magnetite and Mn-minerals [56]. The laterite contains several other useful metals like Cr, Fe, Ni (0.4 - 0.9%) and Co (0.02 - 0.05%) [52,55]. Ni and Co both values are entrapped in the goethite matrix where Co also occurs in manganese mineral phases [54,57].

Studies on leachability of pre-reduced limonitic laterite in ammonia - ammonium carbonate solution by Panda et al. [58] yielded 90% recovery of Ni but the leachability of Co was sub-optimal upto about 50% due to co-precipitation with Fe. Leaching studies [58] on a beneficiated sample of nickeliferous limonitic overburden of chromite ore of South Kaliapani chromite mine in Sukinda using hydrochloric acid and sulfuric acid at atmospheric pressure indicated that both the acids are effective in dissolution of Co values. Compared to H₂SO₄, the HCl gave enhanced leachability. With 4N acid strength, the leachability of Co was 81% with HCl while the corresponding value for

H₂SO₄ was 51% only. Near complete leaching of Co values was observed when the overburden sample was pre-roasted at 500° C before subjecting to leaching. The beneficial effect of roasting of the ore was also observed [59] when dilute H₂SO₄(20 g/l) was used as leachant.

Studies were carried out on reductive leaching of Co values in laterites using aqueous SO₂ in acid media and additives under atmospheric leaching conditions[43,60]. Soak leaching of the un-roasted ore by Kanungo et. al. (1988) [50] in dilute solution of SO₂ for 72 h at ambient temperature and pressure brought about 68% solubilization of Co values. This enhanced to 80% leaching with rise in temperature to 75° C and addition of 2 – 4% by weight of carbon in 1-2% by weight of SO₂ solution acidified either with sulfuric acid or hydrochloric acid, in just 3 h time.

Biobleaching of Sukinda chromite overburden was reported by many researchers [52,55,61-63] and was found to be non-effective. The extraction of metals was studied (Co& Ni) by Biswas et. al.[64]from COB of Sukinda mines of Odisha, India, with the culture filtrate of Aspergillus niger. Their studies indicated leachability of 65% of Co on roasted ore in 21- days with culture filtrate at 80 °C.

Behera et. al.[63] improved recovery of Co to 86% in a bioreactor. These heterotrophic microbes perform the leaching of metals through the secretion of metal chelating organic acids (citric and oxalic acids).

Cobalt from spent ammonia cracker catalyst (SACC)

To meet the requirement of Co-60 as γ irradiation source for industrial and medical applications, cobalt oxalate (99.9% pure) in kilogram scale is recovered from spent ammonia cracker catalyst (SACC) as per composition given in table 1.

Table 1 : Composition of SACC pellets

Constituent	wt. %
Al ₂ O ₃	36.5
Fe ₂ O ₃	31.5
CoO	29.5
NiO	0.27
K ₂ O	0.70
Binder	1.53

These catalyst pellets, obtained from heavy water plants, are an important secondary source. The indigenously developed process for the recovery of cobalt from spent ammonia cracker catalyst has gone through many phases before finalizing to the flow sheet (Fig. 5) which consists of leaching, oxidation, decantation and repulping, solvent extraction in mixer settlers for removal of Fe(III) and Al(III), passing through activated charcoal column for removal of entrained/ dissolved organic, pH adjustment, IX process for removal of Ni(II), precipitation of Co-oxalate, filtration and drying.

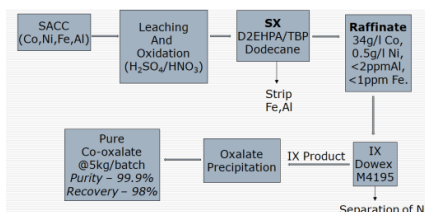


Fig. 5: Flow sheet of indigenously developed process for cobalt recovery from secondary source like spent ammonia cracker catalyst to meet internal demand of DAE

The cobalt recovered from SACC was supplied to Board of Radiation and Isotope Technology (BRIT, Vashi, DAE) for irradiation to its Co-60 isotope which was used as a source for indigenously developed Bhabhatron therapy machine meeting the demand of 50 kg/annum.

Cobalt from Manganese ocean nodules

Ocean nodules contain nearly 0.25% of cobalt. Earlier, a three cycle solvent extraction scheme has been developed and adopted for the separation of Ni, Co, Cu and Zn from leach liquor generated from the sulfur dioxide-ammonia leaching with the same team of cobalt recovery from SACC at Engineering hall no. 6, BARC. Both D2EHPA and PC 88A have been selected as organic extractants as these are quite suitable for the separation of specified metals from their acidic sulfate solution. In the 1st cycle, Cu & Zn are extracted from the leach liquor by saponified D2EHPA leaving Ni & Co in the raffinate. The 2nd cycle utilizes PC88A to selectively extract Co leaving behind Ni in the raffinate [Fig. 6]. Co is recovered from the product solution by precipitation as oxalate and converted to pure Co powder by controlled reduction at high temperature under hydrogen atmosphere.

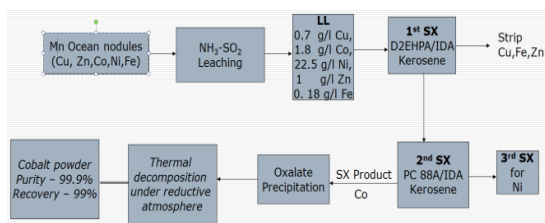


Fig. 6: Flow sheet of indigenously developed process for cobalt recovery from secondary source like manganese ocean nodules

Cobalt from AlNiCo scrap

AlNiCo, a magnet alloy scrap contains Fe, Al, Ni and Co. The leach liquor obtained from cupric chloride leaching formed the feed for the solvent extraction (SX) process. The leach liquor contains ~14g/L Co along with other elements. A two step SX scheme of separation and purification was developed. 50% saponified D2EHPA for Fe and Al separation for the 1st cycle and 50% saponified PC 88-A in kerosene was used for purification of Co by separating it from Ni finally obtaining 99.5% pure cobalt with 95% recovery from the 2nd cycle of the in house developed process [Fig. 7].

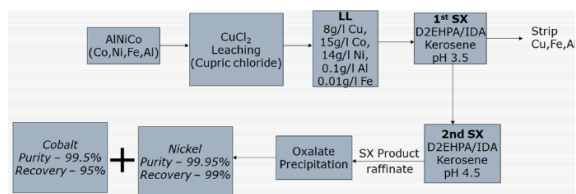


Fig. 7: Flow sheet of indigenously developed process for cobalt recovery from secondary source like spent ammonia cracker catalyst to meet internal demand of DAE

Conclusion

Cobalt market in India is comparatively smaller than developed countries like China. Till a few years back, the entire demand for cobalt was met by imports. Even now, such imports are continuing to meet the special requirements for metallurgical applications in public/defense sector and also part of the demands for glass and catalyst applications. Hence the cobalt refiners in India have by and large catered to the market for chemical application. Or where the cobalt metal or salt is dissolved once again and converted to cobalt oxide for cutting tool application. On the processing side, there have been many attempts to recover cobalt from Sukinda COB, but more value addition is required to make the process see the light of the day

mostly by attempting nickel extraction from the same source and recovering cobalt as a byproduct. On the other hand, as we have already observed in the article, some scattered attempts were made towards Co recovery from different strewn sources by the hydrometallurgy group of BARC. When these are not enough to meet the demand of our own country, Co supply is largely dependent on the import-based feed. This may be owed to lack of sizeable source or the lean nature of the available sources making it technologically long drawn and economically non-attractive. When our country is devoid of apparently exploitable resources of cobalt, we are rich with exploiting techniques of Co recovery from any sources. Thus, some yet to develop countries like Congo, Morocco etc. which are having good Co sources may be opted for import of ores to our country and get the metal values using our expertise. Though some companies like Rubamin and Nicomet tried to operate that way, demand is even higher. Government initiatives of late might solve that issue also.

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Dr Soumyadip Mondal has obtained bachelor of engineering degree in metallurgy discipline from Bengal Engineering College (Shibpur, Howrah, West Bengal) in the year of 2002. Subsequently he joined BARC from 46th batch of training school in the then hydrometallurgy section of Materials Processing Division (MPD) under Materials Group (MG). In 2023, he was conferred Philosophy of Doctorate degree for his research in the field of engineering sciences by Homi Bhabha National Institute (HBNI), Mumbai. Presently scientific officer 'G, Dr Mondal in his service spanning 23 years, has gathered experience in developing hydrometallurgy-based processes specifically for critical metals like uranium, cobalt, nickel and rare earths from various sources. In the field of rare earths, Dr Mondal have developed processes to map, estimate and recover rare earths from three major industrial wastes like coal fly ash, phospho gypsum and red mud. His expertise is versatile in the field of extractive metallurgy and is spread across skills based on process development at laboratory, implementing developed process to plant level through systematic scale up, plant design and operation in bench scale /pilot scale etc,. He has 15 peer reviewed journal papers and 30 conference papers to his credit so far. In view of his effective contribution as a team member, four DAE group achievement awards have been bestowed upon him till date.

Separations in Preparation of high purity Lithium

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Introduction

1. Discovery and early history

Lithium (Li, $Z = 3$) is the lightest solid element (0.534 g/cc under STP) and has the highest standard reduction potential ($E^\circ = -3.04$ V vs SHE).[1] The Swedish chemist Johan August Arfvedson, working under the distinguished Jöns Jakob Berzelius, identified an alkaline anomalous component while analysing samples of the mineral petalite ($\text{LiAlSi}_4\text{O}_{10}$) in 1817, and that Berzelius named as lithion from the Greek word lithos (stone) to distinguish it from the then known sodium and potassium which were derived from plant sources. [2]

Metallic lithium was first isolated independently by William Thomas Brande and Humphry Davy in 1818 through the electrolysis of lithium oxide, but it remained as a laboratory rarity for long time.[2] Early commercial applications of lithium and its compounds were modest, viz lithium bromide as a sedative, lithium minerals as flux in glass and ceramics, and lithium grease as lubricant. It also found a clinical role, after the usage of lithium carbonate in the treatment of bipolar disorder.[3], [4]

The mid-twentieth century elevated lithium to strategic significance. ^6Li , comprising ~7.5% of natural lithium, is a critical precursor in tritium (^3H) production. Large-scale ^6Li enrichment by the COLEX (column exchange) process by exploiting the small isotopic fractionation of between a lithium-mercury amalgam and aqueous LiOH has been demonstrated in the United States (Oak Ridge, Tennessee) and the Soviet Union during the 1950s–60s.[5]. LiOD is a candidate reagent for pH control in the primary coolant loops of Pressurised Heavy Water Reactors (PHWRs).[6]

The run-away success of lithium-ion batteries (LIBs), commercialized by Sony in 1990s led to an exponential growth in demand for lithium[3], and the current

usage of Li is dominated in electrochemical energy storage devices.

2. Global abundance: geological and geographical distribution

2.1 Crustal Abundance and Geochemical Context

Lithium is the thirty-third most abundant element in the Earth's continental crust at a mean concentration of approximately 20 ppm.[3] Although this exceeds the crustal abundances of lead (~17 ppm), and tin (~2 ppm), its wide geochemical dispersal renders rarity in high-grade economic concentrations rare and geologically specific. Lithium is a strongly lithophile element (as per Goldschmidt classification)[7], partitioned entirely into the silicate fraction during core formation. Its ionic radius (0.76 Å in octahedral coordination for Li^+) is similar to that of Mg^{2+} (0.72 Å), and that allows its substitution into ferromagnesian silicates. However, Li^+ is systematically rejected relative to Na^+ (1.02 Å) and K^+ (1.38 Å) during crystallization of common rock-forming silicates due to its high mobility arising from smaller size and lighter monovalent nature.[1] Most known lithium minerals are observed in the form of granitic rocks, referred to as lithium-cesium-tantalum (LCT) pegmatites.[8]

Broadly, two geological environments dominate economically viable lithium resources:

2.2 Continental Brine Deposits — “The Lithium Triangle”

The Andean “Lithium Triangle”—encompassing the salt flats of Salar de Atacama (Chile), Salar de Uyuni (Bolivia), and the northwest Argentine salares—hosts approximately 80% of global identified lithium brine resources.[9] Lithium concentrations in Atacama brines reach 0.14%, sustained by Cenozoic volcanism, hydrothermal leaching of surrounding volcanic rocks, and intense solar

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evaporation in closed endorheic basins at 3,500–4,500 m altitude. Bolivian Uyuni brines are lower in lithium grade 0.096% but carry extremely high Mg/Li mass ratios (up to ~ 19:1), a processing complication discussed in Section 7.[10]

2.3 Hard-Rock Pegmatite Deposits

Australia dominates hard-rock lithium production, accounting for approximately 37% of global mine output in 2024 [17], almost entirely from spodumene-bearing leucogranite pegmatites. Major hard-rock deposits are also found in China, Zimbabwe, Canada, Brazil and Europe.

2.4 Country-wise Production and Reserve Statistics

Global lithium mine production in 2024 reached approximately to 240,000 tons of contained lithium; a substantial increase from 204,000 t in 2023.[11] Zimbabwe's output surged from 14.9 kt in 2023 to 22 kt in 2024 with two of their mines (Bikita and Arcadia mines) ramped to full capacity, making it the world's fourth-largest producer. Argentina's lithium production rose to 18 kt after production from a new salar project was started. The global lithium production and identified reserve are compared in Table 1 and Fig 1.

Table 1: Global lithium mine production and identified resources by country, 2024.[11]

Country	Mine Production (kt Li; 2024)	Identified Reserves (Mt Li; 2024)
Australia	88	7.0
Chile	49	9.3
China	41	3.0
Zimbabwe	22	0.48
Argentina	18	4.0
Brazil	10	0.39
India	Nil	—
Other	~22	—
WORLD TOTAL	~240	~30

Share of World Li Reserves by Country (2024)
Source: USGS MCS 2025 | Total ~ 30 Mt Li

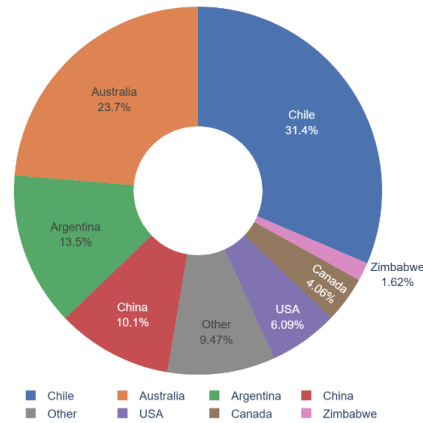


Fig.1. Identified lithium reserves by country. [11]

2.5 India's Lithium Geology — still under survey

In the Indian context, until 2023, minerals containing lithium were found in Jharkhand (lepidolite: ~2-6 % Li₂O) followed by pegmatite found in Chhattisgarh (2.5% Li₂O), pegmatite and zinnwaldite in Rajasthan (2.25% Li₂O). Some spodumene in Raichur, Karnataka, amblygonite and lepidolite in Kashmir and Assam, respectively, have also been reported.[12] This changed dramatically on 9 February 2023, when the Geological Survey of India (GSI) formally notified an inferred lithium resource of approximately 5.9 million tonnes of ore (at an inferred grade) in the Salal-Haimana area of the Reasi District, Jammu & Kashmir.[13] It is important to note that this figure refers to ore tonnage at an inferred grade—not contained Li metal. Currently, India is primarily importing processed lithium chemical for all its need.

Unlike conventional hard-rock lithium deposits hosted in granitic pegmatites, the Salal-Haimana lithium occurrence is a bauxite-hosted clay-type deposit dominated by lithium-bearing clay minerals, especially kaolinite and cookeite(LiAl₄(Si₃Al)O₁₀(OH)₈; a Li-rich chlorite).[14], [15]

The Mines and Minerals (Development and Regulation) Amendment Act of 2023 of Government of India liberated the exploration and mining regulation for lithium to accelerate exploration activity, and that extended the possible sources to wider geographical regions in the country.[16]

3. Technological Importance of Lithium

3.1 Electrochemical Energy Storage

The dominant and fastest-growing application of lithium is in rechargeable batteries.[3] The Li^+/Li couple's high standard reduction potential (-3.04 V vs. SHE), combined with the small atomic mass and ionic radius facilitates fast solid-state diffusion, this makes lithium uniquely suited as a charge carrier in high-energy-density secondary batteries. Battery applications consumed approximately 87% of global lithium supply in 2024,[11] a share that has risen from 23% in 2010.[17] The principal cathode chemistries in commercial LIBs— LiCoO_2 (LCO), LiFePO_4 (LFP), $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC), and LiNiCoAlO_2 (NCA), etc. require high-purity lithium carbonate ($\geq 99.5\text{ wt\%}$) or lithium hydroxide monohydrate ($\geq 56.5\text{ wt\% LiOH}$) as precursor materials.

3.2 Ceramics, Glass, and Lubricants

Glass and ceramics applications historically comprised the largest end-use for lithium (23% in 2010); they still account for approximately 14% of global consumption in 2024.[11] Lithium carbonate and spodumene concentrate are added to glass formulations to reduce thermal expansion, lower viscosity at melting temperature, and improve chemical durability. Lithium hydroxide monohydrate is the essential component in lithium-complex soap greases, produced by saponification of fatty acids, which exhibit superior high-temperature performance over calcium or sodium soap greases[18]

3.3 Demand Projections, LCE Price Dynamics, and Supply

Global lithium demand is projected at $\sim 5.3\text{ Mt LCE}$ (lithium carbonate equivalent; $1\text{ t Li} = 5.32\text{ t LCE}$) by 2040 under announced pledges scenario, against approximately $\sim 0.9\text{ Mt LCE}$ consumed in 2023.[19] India's share of this demand, currently modest ($\sim 3\%$ of global LCE consumption), is projected to rise to 8–12% by 2030 as the EV transition accelerates [22]. India's National Critical Minerals Mission (launched 2024) lists lithium as the highest-priority mineral.[20] Khanij Bidesh India Ltd (KABIL), and subsequently the exploration for mining from domestic sources and import of lithium blocks are being expedited.

3.4 Battery Cathode Chemistry Trends and Their Implications for Li Product Specifications

The demand between Li_2CO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ as the refinery output is dictated primarily by the dominant cathode chemistry in the end-use battery market. High-nickel NMC i.e., NMC811) and NCA cathodes require $\text{LiOH}\cdot\text{H}_2\text{O}$ as the lithium precursor, while LFP can accept Li_2CO_3 as a simpler and lower-cost precursor. This difference arises from the higher synthesis temperature of LFP ($\sim 800 - 900\text{ }^\circ\text{C}$) where the higher melting point ($720\text{ }^\circ\text{C}$) of Li_2CO_3 is not an issue. High nickel NMC and NCA cathodes need to be synthesized at lower temperatures to reduce cation mixing (Ni-Li) and avoid reduction of Ni^{3+} to Ni^{2+} , whereby the more reactive LiOH is preferred.[21]

4. Lithium Minerals, Ores, and Their Classification

Approximately 150 lithium-bearing mineral species have been identified, but very few are of commercial or near-commercial significance.[9], [22] These fall into three broad chemical families: chain and sheet silicates (dominant industrially), phosphates, and brine/evaporite deposits. Figure 2 provides a visual representation of where the different Li resources lie on their Li-content vis-à-vis ease of extraction parameters. It plots ore grade against ease of extraction, with bubble size proportional to theoretical Li_2O content.

4.1 Silicate Minerals

Spodumene [$\text{LiAlSi}_2\text{O}_6$; pyroxene group] is the world's premier lithium ore mineral, with a theoretical lithium content of 3.73 wt% Li. It occurs as large prismatic crystals and is the principal ore mineral at Greenbushes, Mt. Cattlin, and Wodgina mines in Australia. Ore-grade spodumene bodies typically assay 1.0–2.5 wt% Li_2O , upgraded by flotation to concentrates of 6–7.5 wt% Li_2O . [23]

Lepidolite [$\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$; phyllosilicate (sheet silicate)] is a lavender-coloured Li-rich mica with Li_2O contents ranging from 1.2 to 5.9 wt%. [23] It is commercially exploited in Zimbabwe (Bikita), Brazil, and Portugal. Its fine-grained, flaky nature makes flotation-based beneficiation more difficult than for

spodumene (higher reagent consumption, lower grade concentrates) and its layered phyllosilicate structure requires more aggressive acid conditions for complete leaching. Lepidolite is relevant to India both as a possible phase in the J&K deposit and as an accessory mineral in the Rajasthan and Jharkhand mica belts, where it occurs as a by-product of muscovite mining. Recovery of lithium from Indian mica tailings represents an underexplored secondary resource opportunity.[24]

Petalite [$\text{LiAlSi}_4\text{O}_{10}$; tectosilicate] contains approximately 2.27wt% Li (4.88wt% Li_2O) theoretically. While it was the source mineral for lithium's discovery, its dense framework silicate structure renders it the most resistant to chemical attack compared to the most lithium silicates. Eucryptite [LiAlSiO_4] carries the highest Li_2O of common lithium silicates (~11.8 wt% theoretical) but is rare as an economic ore mineral, occurring primarily as an alteration product of spodumene.

Zinnwaldite [$\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{F},\text{OH})_2$] is a lithium-iron mica with Li_2O contents of 1.0–2.0 wt%. It maybe considered an impure form of lepidolite, and the high iron content (up to 11.5% FeO) in it complicates downstream purification. Occurrence of zinnwaldite in Indian mica-belt has been anticipated.[12]

4.2 Phosphate Minerals

Amblygonite [LiAlPO_4F] and the hydroxyl analogue montebrazite [LiAlPO_4OH] are one of the highest Li_2O containing minerals (~10.1 wt% theoretical) but they are scarcely abundant and hence they are not considered as standalone ore deposits. Triphylite [LiFePO_4] and lithiophilite [LiMnPO_4] form an isomorphous series of phosphates mineralogically related to the LFP battery cathode material but are not considered as primary lithium extraction minerals due to their scarcity. No significant phosphate-class lithium minerals has been reported from India.

4.3 Brine and Evaporite Deposits

Continental salar brines are basically lithium-enriched aqueous solutions, not discrete minerals. Atacama-type brines (200–1,800 mg Li L^{-1}) are the lowest-cost lithium resource globally due to their amenability to low-energy solar evaporation. Bolivia's Uyuni remains largely undeveloped due to political factors and its

challenging Mg/Li ratio (>19). Atacama brine scores highest on extractability while clays and geothermal brines score lowest. Spodumene dominates the high-grade, moderate-extractability quadrant.

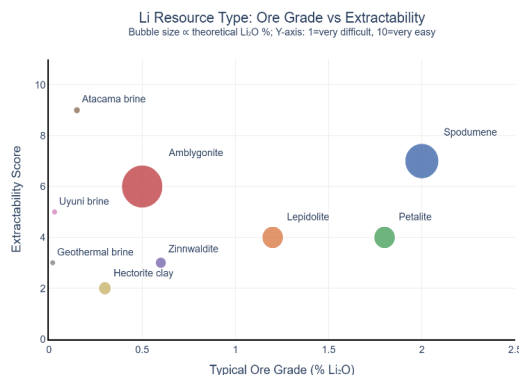


Fig.2. Li resource types plotted by typical ore grade vs. qualitative extractability score (1=very difficult, 10=very easy).[25], [26] Bubble size represents theoretical Li_2O content.

4.4 Crystal Chemistry of Lithium Ore Minerals: Structural Control on Extractability

The principal ore minerals differ profoundly in the dimensionality of their silicate or phosphate framework, the coordination geometry of the Li^+ ion, and the geometric accessibility of the Li site to reagents. These features collectively govern dissolution thermodynamics, reaction kinetics, the temperature required for reactive phase transformation. Table 2 summarises the structure–lithium site and content in different minerals.

Spodumene (α - form monoclinic C2/c ; inosilicate): Spodumene occurs naturally in the monoclinic (α) form, where the structure consists of continuous single-chain (SiO_3) units running parallel to the c-axis, cross-linked laterally by chains of LiO_6 and AlO_6 octahedra. Every oxygen atom bridges either two Si tetrahedra or one Si and one M-site cation, creating a dense, fully interlocked framework with no channels or cleavage planes through which H^+ or SO_4^{2-} can reach Li^+ without rupturing bonds. Processing therefore requires the reconstructive $\alpha \rightarrow \beta$ phase transition at 1000–1100°C, which reorganises the single-chain topology into an open tetragonal (keatite-type) framework in which Li^+ occupies an accessible 4-coordinate site. Figure 3 illustrates the key crystal structures schematically.

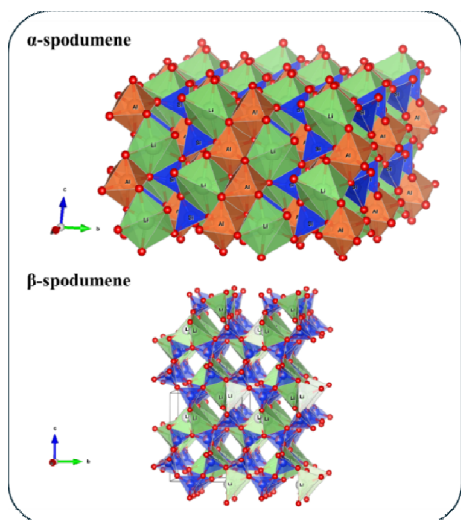


Fig.3. Crystal structure of α and β spodumene. Green, blue, orange and red spheres are Li, Si, Al and O, respectively. In β form, Si and Al occupy same site, Li site is partially occupied. (Drawn from crystallographic data reported in ICSD database, entries 9668 and 14235, respectively)

Lepidolite $[K(Li,Al)_3(Al,Si)_4O_{10}(F,OH)_2]$; monoclinic, $1M/2M_1$ polytypes; phyllosilicate]: The 2:1 (TOT) layer structure consists of two outward-facing tetrahedral $(Si,Al)O_4$ sheets sandwiching a central octahedral sheet in which Li^+ and Al^{3+} occupy M1/M2 sites; TOT layers are stacked along c and held together by interlayer K^+ cations.[27] Li resides inside the octahedral sheet, shielded on both faces by strongly bonded tetrahedral layers; aqueous H^+ must first displace interlayer K^+ and then penetrate the basal oxygen plane. Structural fluorine (F^- partially substituting OH^- in the octahedral sheet)[27] evolves as HF under acid conditions, requiring dedicated scrubbing. Zinnwaldite (the Fe^{2+} mica analogue relevant to Indian mica belt occurrences) contains Fe in octahedral sites and is therefore more acid-consuming in sulfuric-acid processing; however, it also offers potential value through co-extraction of Rb-rich interlayer alkali species.

Petalite ($LiAlSi_4O_{10}$; monoclinic $P2/a$; tectosilicate): All $(Si,Al)O_4$ tetrahedral corners are shared in a 3D framework with Li^+ in 4-coordinate framework cavities. The high Si:Al ratio (4:1) maximises Si–O–Si bridges and renders petalite thermodynamically stable toward hydrolysis at moderate temperatures. Conventional acid leaching requires additional mineralisation steps beyond those needed for β -spodumene.[28] Its

theoretical grade (4.50 wt% Li_2O vs. 8.03 wt% for spodumene) also makes it a lower-value primary feedstock.[12]

Eucryptite ($LiAlSiO_4$; trigonal; stuffed β -quartz): With the highest theoretical Li_2O (~11.8 wt%) of common silicates, eucryptite places Li^+ in hexagonal channels running along the c-axis of a β -quartz-derived $(Si,Al)O_4$ framework, conferring one-dimensional Li^+ mobility.[29] This channel geometry should allow topotactic H^+/Li^+ exchange under mild acid conditions without wholesale framework dissolution, offering a potentially energy-efficient extraction pathway. In practice, eucryptite occurs as an alteration product of spodumene rather than a primary ore mineral.[30]

Amblygonite/Montebrasite ($LiAlPO_4F/OH$; triclinic $P-1$; phosphate): Li^+ occupies a unique distorted 5-coordinate (trigonal bipyramidal) site within a 3D $AlPO_4$ framework. The decisive processing advantage is intrinsic chemical selectivity: sulfuric acid roasting produces water-soluble Li_2SO_4 and insoluble $AlPO_4$ as discrete phases, delivering 97.5% Li extraction with less than 2% Al co-extraction [31]. This also eliminates the expensive pH-adjustment Al-removal step. The practical limitation is abundance, since amblygonite rarely forms standalone ore bodies.

Table 2: Summary of major lithium minerals and their crystallographic structure.

Mineral	Crystal System / Class	Li^+ Site	Li theor. (wt%)
α -Spodumene	Monoclinic $C2/c$ Inosilicate (single-chain)	M2 octahedral (LiO_6)	3.73
Lepidolite	Monoclinic $1M/2M_1$ Phyllosilicate (2:1 TOT)	Octahedral in TOT sheet	3.56
Petalite	Monoclinic $P2/a$ Tectosilicate (3D)	LiO_4 in framework cavity	2.27
Eucryptite	Trigonal Stuffed β -quartz	Li in hexagonal channels (4-coord.)	5.53

Amblygonite / Montebrasite	Triclinic $P\bar{1}$ Phosphate (3D)	Distorted trigonal bipyramidal (5-coord.)	4.7
Zinnwaldite	Monoclinic Phyllosilicate (2:1 TOT)	Octahedral in TOT sheet	1.7

5. Primary Physical and Chemical Extraction Processes

5.1 Hard-Rock Comminution and Beneficiation

Processing of lithium-bearing pegmatites begins with conventional drilling and blasting, primary crushing followed by secondary/tertiary grinding with ball mills to liberate lithium silicate grains from the gangue matrix of quartz, K-feldspar, and muscovite. The Bond Work Index of spodumene (10.4 – 11.5 kWh t⁻¹[32]) is moderate; however, effective liberation requires ore to be ground below 150 µm because spodumene often has quartz-feldspar intergrowths.

Flotation is the dominant beneficiation technique for spodumene. The process exploits the preferential adsorption of long-chain fatty acid collectors (oleic acid, sodium oleate) or amine collectors at the spodumene surface as opposed to gangue, mainly feldspar and quartz. Gangue minerals are depressed using modifying agents including NaOH (pH control to 8.5–11.5), dextrin, quebracho tannin, and sodium hexametaphosphate. A well-designed circuit can produce spodumene concentrates of 5.0–6 wt% Li₂O at recoveries of 60–90%[33]. For lepidolite, the platy mica morphology causes high mechanical entrainment, and thus selectivity between lepidolite and muscovite becomes challenging.

5.2 Processing from spodumene

5.2.1 Thermal Treatment: The Critical $\alpha \rightarrow \beta$ Spodumene Phase Conversion

As discussed in section 4.4, natural α -spodumene is converted to the reactive β -polymorph before acid leaching by calcination:



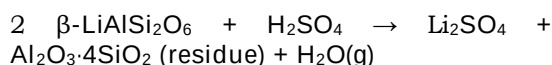
This reconstructive phase transition is accompanied by a volume expansion of

approximately 27–30%, causing decrepitation (spontaneous fragmentation) of the calcine, and that dramatically increases the surface area and porosity.[34] The resulting β -polymorph achieves almost complete Li extraction during H₂SO₄ roasting at 250°C.[35]

5.2.2 Hydrometallurgical Routes from Spodumene Calcine

5.2.2.1 Sulfuric Acid Roasting — The Dominant Industrial Route

Following calcination to β -spodumene, the most widely deployed commercial process involves roasting the calcine with H₂SO₄ in a rotary kiln or paddle mixer at 250°C[12]



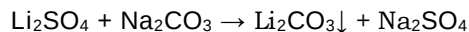
Aluminum is partitioned into an insoluble aluminosilicate residue, while Li is converted to water-soluble Li₂SO₄. The roasted clinker is water-leached at 60–80°C to dissolve Li₂SO₄ into a pregnant leach solution (PLS) containing Li at concentrations of 5–15 g L⁻¹. Subsequently, a multistep purification cascade is followed [36]:

(i) Al/Fe removal by pH adjustment to 6.0–7.5 with Ca(OH)₂ or NaOH precipitating Al(OH)₃ and Fe(OH)₃

(ii) Mg removal by Ca(OH)₂ at pH >10.5 precipitating Mg(OH)₂.

(iii) Ca removal by soda ash addition

The purified Li₂SO₄ solution is then converted to Li₂CO₃ by addition of hot Na₂CO₃ (soda ash) at 90–95°C:



Since Li₂CO₃ dissolution is exothermic in nature, it exhibits an inverted temperature-solubility relationship, i.e. solubility decreases from 13.3 g L⁻¹ at 20°C to 8.3 g L⁻¹ at 90°C[37]. Figure 4 illustrates this inverse solubility relationship and the operational rationale for hot precipitation. Thus, by conducting this reaction at high temperature precipitation yield is maximized. The resulting technical-grade Li₂CO₃ (typically 98.5–99.5 wt%) is filtered, washed, and dried. Figure 5 depicts a flowchart for production of battery grade lithium reagents from spodumene ore.

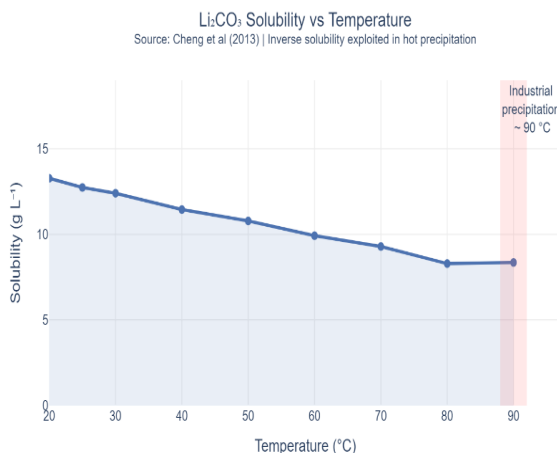


Fig.4. Temperature dependence of Li_2CO_3 solubility. The pronounced inverse solubility (13.3 g L⁻¹ at 20°C to 8.3 g L⁻¹ at 90°C) is exploited by conducting industrial precipitation at ~90°C (shaded region) to maximize yield.[37]

5.2.2.2 Alkaline Roasting Routes

An alternative to acid roasting is the limestone/soda ash calcination, where spodumene concentrate is co-calcined with CaCO_3 or Na_2CO_3 at 850–950°C. This avoids handling of concentrated H_2SO_4 and eliminates the large SO_4^{2-} effluent stream, but generates larger volumes of Ca-Si waste and yields lower Li recoveries (typically 70–80% for Na_2CO_3 roasting vs. 85–92% for acid roasting). [38]

5.3 Lepidolite

Lepidolite's phyllosilicate structure requires more aggressive leaching conditions than spodumene. Primary approaches include: roasting with Na_2SO_4 , K_2SO_4 or FeSO_4 at 800–900°C (achieving Li extractions of 90–95% and chlorination roasting.[39] Fluoride management is critical in all acid routes: lepidolite contains structural F^- which evolves as HF on acid treatment, requiring scrubbing and neutralisation. In mica belt deposits, lithium is primarily hosted in lepidolite or zinnwaldite, and in both the processing route must accommodate higher Fe (from zinnwaldite), Rb, and F contents.

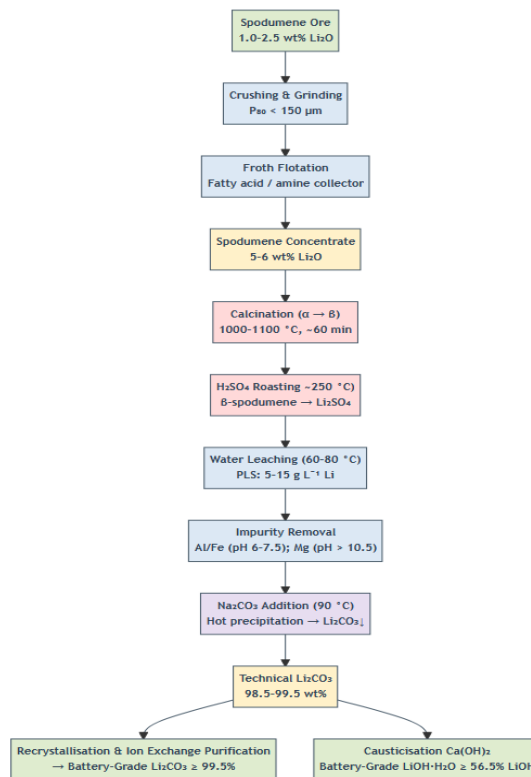


Fig.5. Full process flowchart for battery-grade lithium production from spodumene pegmatite ore, from mining through $\alpha \rightarrow \beta$ phase conversion, acid roasting, purification cascade, to final Li_2CO_3 and $\text{LiOH} \cdot \text{H}_2\text{O}$ products.

5.4 Brine Processing: Solar Evaporation

For high-grade Atacama brine resources, the dominant established process is the cascaded solar evaporation across large pond systems. Raw solar brine (typical Atacama composition: 2.1 g L⁻¹ Li; 119 g L⁻¹ Cl^- ; 51 g L⁻¹ Na^+ ; 38 g L⁻¹ SO_4^{2-} ; 24 g L⁻¹ K^+ ; 12 g L⁻¹ Mg^{2+})[40] is pumped from subsurface extraction wells and fed sequentially through ponds operating at progressively higher evaporative concentration. Over 12–24 months of solar exposure, the sequence of crystallisation is governed by the solubility phase equilibria of the Na–K–Mg–Li–Cl– SO_4 – H_2O system:

- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Halite (NaCl) crystallises first, significantly reducing Na^+ .
- Sylvite (KCl) and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) crystallise in intermediate ponds, the latter providing an important K co-product.

- Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) crystallizes at high concentration, partially reducing Mg^{2+} .

- The final 'Li brine' concentrate reaches approximately 4–6 wt% LiCl, with the Mg/Li mass ratio typically reduced to 1–3:1.

The concentrated brine is then processed chemically: lime treatment [$\text{Ca}(\text{OH})_2$ addition] precipitates residual Mg^{2+} as $\text{Mg}(\text{OH})_2$ and SO_4^{2-} as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Na_2CO_3 addition at 90°C precipitates Li_2CO_3 as described in section 5.2.2.1. Overall lithium recovery from salar brines via the evaporation route is ~50%, with losses to residual pore brine, crystallisation inefficiency, and processing.[41] India has no equivalent brine resource; however, KABIL's 2024 agreement with Argentina's state mineral company for five lithium brine blocks in Catamarca Province provides India with indirect access to Andean brine-type resources.[42]

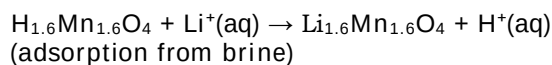
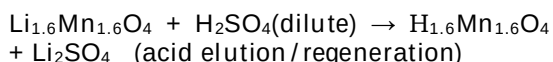
5.5 Direct Lithium Extraction (DLE)

Direct Lithium Extraction is an umbrella term for processes that selectively recover lithium from brines without the months-long evaporation step, typically returning the depleted brine to the aquifer. DLE encompasses three technology families, all of which are being used for commercial scale extraction.

5.5.1 Ion Exchange and Lithium Ion Sieves

Fixed-bed ion exchange has been applied to lithium recovery from dilute brine streams, with the most promising sorbent class being Lithium Ion Sieves (LIS) [43]—inorganic frameworks derived from lithium manganese oxide (LiMn_2O_4 or $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$) or lithium titanate (Li_2TiO_3 , expressed as H_2TiO_3 in the acid-activated form). The principle is topochemical: structural Li^+ is extracted by mild acid washing, leaving behind lattice vacancies of precisely the correct size and counter-charge environment to selectively re-admit Li^+ from dilute solution while excluding larger or differently charged cations.

For the manganese-based sieve, the adsorption/desorption cycle is:



The titanate-based H_2TiO_3 sieve is generally preferred industrially for its lower Mn dissolution during acid elution, comparable Li^+ selectivity over Na^+ and Mg^{2+} , and better mechanical stability. Reported Li^+ loading capacities range from 40 to 90 mg g⁻¹ sorbent, with Li/Na selectivity coefficients of 10–100 and Li/Mg selectivity of 50–200. [43]

5.5.2 Sorbent based solvent extraction

Solvent extraction of lithium from dilute aqueous solutions by means of chelating extractants, like crown ethers has been explored. This is more challenging than for most transition metals, owing to the high hydration energy of Li^+ (–520 kJ mol⁻¹) and its monovalent charge. Nevertheless, Crown ethers like 12-crown-4 (1.2 – 1.5 Å) with cavity diameter closely matching the ionic diameter of Li^+ (1.52 Å), provide intrinsic thermodynamic selectivity.[44] However, commercial applications are impeded by high extractant cost, slow kinetics, and limited loading capacity. Organophosphorus extractants (TBP, TOPO, Cyanex 923) extract Li^+ as neutral ion pairs from highly concentrated LiCl or Li_2SO_4 solutions, but selectivity over Mg^{2+} is limited. Solvent extraction is therefore not yet a primary industrial lithium purification step, though it may find niche application in the removal of specific impurities (e.g., B, Ca) from brine-derived Li solutions.[43]

5.5.3 Electrochemical DLE

Li^+ is intercalated into a LiFePO_4 or LiMn_2O_4 cathode from brine during a charging half-cycle, then deintercalated into a small-volume stripping solution during a discharging half-cycle, thereby leading to concentration of lithium into smaller volume solution. The process is highly selective (Li^+/Na^+ and $\text{Li}^+/\text{Mg}^{2+}$ selectivity ~100 in some systems) and energy-efficient at dilute brine concentrations.[45]

DLE represents a paradigm shift for brine-lithium economics since it eliminates the multi-year evaporation lag, reduces the water footprint dramatically, and enables recovery from lower-grade brines (including geothermal and oilfield brines previously considered sub-economic).

6. Purification and Preparation of Battery-Grade Lithium Products

6.1 Specifications and Impurity Limits

Table 5 provides a consolidated reference of battery-grade purity specifications for both Li_2CO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$, as per Chinese standards.

Table 5. Battery-grade Li_2CO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ purity specifications

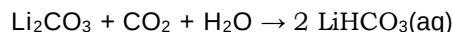
Parameter	Battery-Grade Li_2CO_3 (YS/T 582-2013)[46]	Battery-Grade $\text{LiOH}\cdot\text{H}_2\text{O}$ (GB/T 26008-2020)[47]
Li_2CO_3 / LiOH Content	≥ 99.5 wt% Li_2CO_3	56.5–58.5 wt% LiOH
Na	≤ 250 ppm (0.025%)	< 30 ppm
K	≤ 10 ppm (0.001%)	< 15 ppm
Ca	≤ 50 ppm (0.005%)	< 20 ppm
Mg	≤ 80 ppm (0.008%)	< 10 ppm
Fe	≤ 10 ppm (0.001%)	< 10 ppm
Al	≤ 10 ppm (0.001%)	-
SO_4^{2-}	≤ 800 ppm (0.08%)	< 100 ppm
Cl^-	≤ 30 ppm (0.003%)	< 10 ppm (D1 grade)
B	Not specified	0.5–100 ppm Annex A.
Moisture / CO_3^{2-}	$\leq 0.25\%$ moisture	-

Battery-grade lithium carbonate (Li_2CO_3 , ≥ 99.5 wt%) and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, ≥ 56.5 wt% LiOH) are the two-principal commodity-form lithium chemicals supplied to cathode precursor manufacturers. Technical-grade Li_2CO_3 (98.5–99.5 wt%) from the acid roasting route typically meets most of these limits, but may fail on Na (due to Na_2CO_3 carry-over from the precipitation step), Ca,

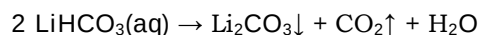
or SO_4^{2-} , necessitating further purification. It is mainly carried out by the following routes:

6.2 Recrystallisation

The most widely applied purification step for Li_2CO_3 is dissolution-recrystallisation, which exploits the inverse dependence of solubility on temperature. Technical Li_2CO_3 is dissolved in CO_2 -saturated water (forming soluble LiHCO_3):



Insoluble impurities and some co-precipitated metal hydroxides are removed by filtration of the bicarbonate solution. The filtrate is then heated to 90–95°C to drive off CO_2 , reprecipitating high-purity Li_2CO_3 :



Repeated cycles of dissolution-precipitation can raise Li_2CO_3 purity to ≥ 99.9 wt%, approaching the pharmaceutical and isotopic-separation grades.[48] The bicarbonate route is particularly effective at removing Ca^{2+} (which precipitates as CaCO_3 during the dissolution step) and Mg^{2+} (which precipitates as MgCO_3 or basic carbonate). Na^+ and K^+ contamination from Na_2CO_3 reagent can be minimised by using high-purity soda ash and careful wash liquor management.

6.3 Ion Exchange Purification

For the most demanding battery applications—especially high-nickel NMC811 and NCA cathodes where trace B, Cl^- , and SO_4^{2-} are particularly problematic—ion exchange polishing of the Li_2SO_4 PLS or dissolved Li_2CO_3 solution is applied.[49] Cation exchange (e.g., Purolite C100, Amberlite IRC86) removes residual Ca^{2+} , Mg^{2+} , Fe^{3+} , and Al^{3+} , and anion exchange (strong-base resins) removes SO_4^{2-} , Cl^- , and $\text{B}(\text{OH})_4^-$ while monovalent cation Li^+ passes unscathed. Chelating resins (iminodiacetic acid type) are particularly selective for Fe and Al at near-neutral pH. The ion exchange purification step is capital- and operating cost-intensive but essential for achieving the < 10 ppm Fe and Al specifications required by Tier-1 cathode manufacturers.

7. Key bottlenecks and process challenges

The $\text{Mg}^{2+}/\text{Li}^{+}$ Selectivity Problem: The separation of Mg^{2+} from Li^{+} is the defining technical challenge of lithium brine processing, and it is equally relevant—though in a different form—in the purification of hard-rock leach solutions. The chemical similarity of Mg^{2+} and Li^{+} arises from the fortuitous near-equality of their ionic radii (Mg^{2+} : 0.72 Å, Li^{+} : 0.76 Å in octahedral coordination), which causes them to exhibit similar partition behavior in many ion-exchange, solvent extraction, and precipitation systems. The Bolivian Uyuni brine, with a Mg/Li mass ratio of ~20:1[43], represents the extreme case: conventional lime treatment ($\text{Mg}(\text{OH})_2$ precipitation at pH > 10.5) would require enormous $\text{Ca}(\text{OH})_2$ consumption, generate massive waste, and risks co-precipitation of Li as LiOH or Li_2CO_3 given the high Li concentrations at late evaporation stages.

More effective Mg/Li separation strategies under active investigation include: nanofiltration membranes with $\text{Mg}^{2+}/\text{Li}^{+}$ selectivity >> 10; electrochemical intercalation using LiFePO_4 electrodes[45]; solvent extraction with D2EHPA, which preferentially extract Mg^{2+} over Li^{+} from sulphate media[50].

Conclusions

Lithium's journey from Arfvedson's 1817 discovery of an anomalous alkali in petalite to its present status as the defining critical mineral for zero-carbon energy transition encapsulates two centuries of advancing material science and engineering. The diversity of lithium's ore types—from dense pyroxene spodumene requiring high-temperature phase conversion and acid roasting, to platy lepidolite demanding more aggressive hydrometallurgical conditions, to dilute salar brines exploiting solar evaporation—demands a correspondingly diverse toolkit of techniques and processes for physical and chemical separations. No single process route dominates the future landscape; the choice is governed by ore mineralogy, deposit grade, geographic location, water availability, energy cost, and environmental regulations.

Across the global landscape, the most pressing research frontiers in lithium

separation science are: (i) energy-efficient $\alpha \rightarrow \beta$ conversion at reduced temperatures; (ii) DLE scale-up with durable, selective sorbents for brine and geothermal resource exploitation; (iii) $\text{Mg}^{2+}/\text{Li}^{+}$ membrane selectivity enhancement; (iv) economically viable Li recovery from end of life (EoL) lithium-ion batteries. The nascent EoL battery recycling sector creates an unusually concentrated and strategically aligned demand for separation science innovation.

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Separation of Zirconium and Hafnium: Challenges and Technological Approaches

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Introduction

Zirconium (Zr, atomic number 40) and Hafnium (Hf, atomic number 72) are transition metals in Group 4 of the periodic table, with Zr in Period 5 and Hf in Period 6. They exhibit almost identical atomic radii (160 pm and (159pm) respectively) and chemical properties due to [lanthanide contraction], where the filling of the 4f subshell in Hf causes poor shielding and stronger nuclear attraction, keeping its size similar to Zr. Due to their similar chemical properties (ionic diameter of Zr⁴⁺ and Hf⁴⁺ is 1.54 and 1.52Å respectively); they are commonly referred to as chemical isotopes. However, these metals have opposite nuclear characteristics. Zr is used in nuclear reactors as structural material and Hf having high neutron absorption cross section, is used as a control material in water-cooled nuclear reactors. About 90% of the total amount of Zr and Hf produced worldwide is consumed in the nuclear industry and it is considered as one of the major applications that required a hafnium-free zirconium component. Therefore, it is important to separate Zr and Hf prior to their transformation into pure metals due to their different use in nuclear industry [1]. Because of their similar chemical properties, it is very difficult and hence challenging to separate them from their aqueous solution. Both experimental and theoretical approaches were adopted to understand the fundamental nature of their interaction with different type of ligands and diluents to achieve the highest separation factor. Also, with the limited understanding of the chemical properties, many methods

were developed and adopted even in the industrial scale.

Experimental Approaches

Among various available experimental methods, the major separation processes which have been used for Zr and Hf separation either in large scale or semi large scale are described below.

The Methyl Isobutyl Ketone(MIBK) Process

The use of MIBK as organic extractant was pioneered by Voit [2]. In this process, the thiocyanic acid (HSCN) complexes of Zr and Hf in hydrochloric acid medium were separated with a fairly high separation factor (~5)[2] with the minor component, Hf was found to be concentrated in the organic phase. The presence of Hf in the solution was very small. Therefore, a ligand which selectively extracts Hf will be efficient and economically beneficial for the separation. This means that both elements (Zr and Hf) can be produced according to nuclear specifications. The organic phase (MIBK) itself was the extractant which exhibits a high load capacity and excellent disengagement characteristics. Point to be noted that the waste streams contain high concentrations of ammonium, thiocyanides, cyanides and organic products. The solvent itself is highly explosive and exhibits a solubility in water around 2%[3].

Although, MIBK-HSCN selectively extracts Hf over Zr, it has many disadvantages such as strong smell, inflammable and significant loss of extractant during extraction due to the low boiling point (115.7°C), low flashing point (13°C), and high solubility of MIBK in water (1.7% by

weight at 25°C). The Zr/Hf separation using MIBK homologues by replacing one side of C = O with either isopentyl, isohexyl, n-pentyl, n-hexyl or n-heptyl, while the other side are all methyl — were studied and compared with MIBK[4]. Effects of HSCN pre-extraction, HCl concentration, NH₄SCN concentration on Zr, Hf extraction and separation performance were investigated. Relationships between methyl alkyl ketone structure and their Zr/Hf separation performance were revealed. A new Zr/Hf separation system MNPK (methyl n-pentyl ketone)-HSCN was reported. MNPK has a higher boiling point (151°C), a higher flashing point (47°C) and a lower solubility in water (0.43% at 20°C) than MIBK. Compared to MIBK, it is safer, more friendly operation environments and less extractant loss during extraction. MNPK has as fast extraction kinetics as MIBK. It also has good anti-emulsification performance with a maximum separation factor (Hf/Zr) of 12.61. The loaded Zr and Hf in MNPK have very similar stripping behaviors with those loaded in MIBK by HCl and H₂SO₄ solutions, respectively. MNPK has now become the candidate of choice to replace MIBK from HSCN media in Zr/Hf separation industry. Though, the extraction of Zr and Hf in MIBK—HSCN system has been widely used in the production of nuclear-grade Zr and Hf in industrial scale, the extraction mechanism was not adequately studied. The extraction and stripping equilibrium of Zr and Hf in the MIBK-HSCN system was also reported [5]. The results showed that elevated HCl concentration can increase the distribution ratio of SCN⁻ and decrease that of Zr/Hf in the organic phase. In the stripping process, HCl concentration and the O/A phase ratio played important roles. The results indicated that SCN⁻ could be extracted into MIBK as HSCN•MIBK complex. Meanwhile, SCN⁻ could also be extracted into MIBK by complexing with metal (Zr or Hf). With the increase in the initial

concentration of HCl in the aqueous phase, the complexation molar ratios of SCN⁻ to Zr and Hf increased first and then decreased, and so do the extraction equilibrium constants, which might be due to the extraction competition of HSCN and metal complexes. In a recent study, a novel extraction system utilizing MIBK, HSCN, and glycine was exploited to enhance the separation of Zr and Hf[6]. Under optimized extraction conditions, the separation coefficient of Hf to Zr reaches 8.58, nearly double that of the traditional MIBK—HSCN system. Monitoring the flow direction of glycine reveals that it does not enter the organic phase; rather, glycine predominantly improves the separation coefficient by modulating the complexation of Zr and Hf in the aqueous phase, as evidenced by FTIR, Raman spectroscopy, and NMR analysis. The aqueous phase spectrum revealed that glycine forms a complex with metal ions in the aqueous medium. The complexes of Hf(OH)(SCN)₃ and Hf(OH)₂(SCN)₂ were formed upon the addition of glycine, while the complexation of Zr remains unchanged, resulting in an increase in the ratio of KHf to KZr from 1.4 to 18.2. The scrubbing process was also systematically analyzed, yielding a separation coefficient of 10. During the cleaning process, as the acidity of the washing solution increases, SCN⁻ in the oil phase becomes more difficult to enter the aqueous phase. Finally, a process comprising six theoretical stages of extraction coupled with six theoretical stages of scrubbing was designed based on a split-flow extraction model, achieving a purity and product yield of Hf exceeding 99%.

The Tri-Butyl Phosphate TBP Process

The use of TBP in nuclear industry is quite widespread. In this, TBP is diluted in kerosene as 60% of TBP v-v and sodium zirconate (Na₂ZrO₃) is used as the feed material. The organic solution is contacted with a nitric acid solution of 3N

where NaNO_3 (3.5N) is added as a salting out agent. The maximum metal content (Zr+Hf) of the liquor, below which third phase formation is avoided, was determined by Huré (1955) [7] to be 30 gm/L. Under these conditions, the separation factor was found to be 10. Unlike the MIBK process, the TBP process is selective to Zr, leading to the concentration of the major component (Zr) in the organic phase and thus high quality Hf could not be produced (usually 58% Zr / 42% Hf). The process was modified by utilizing 6N nitric acid with easy recyclability. A simplified flowsheet of the TBP process is displayed in Fig.1[2].

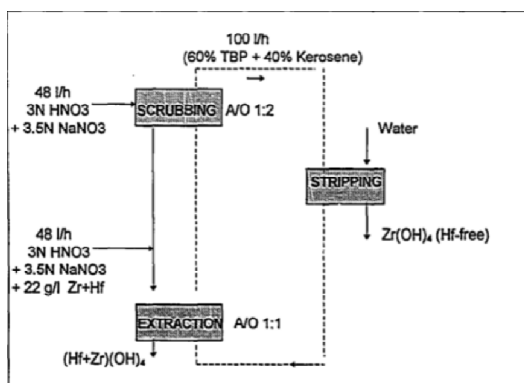


Fig.1. Schematic flowsheet of TBP Process

Earlier, the stoichiometric relation of Zr and Hf in the extraction process with TBP was studied [8] and reported the influence of the process variables on the distribution (D) and separation of Zr and Hf by TBP.

The production of nuclear zirconium oxide was demonstrated using TBP with a high acidity nitric acid [9] by conducting batch and continuous experiments in counter current mixer-settler circuits. The batch experiments indicated that an increase in nitrate concentration did not enhance the separation factor among Zr and Hf whereas acidity has a significant impact on the Zr/Hf separation. For aqueous/organic ratio of 1:1, 94% of the Zr was extracted and a separation factor of the 13.8 was obtained in one contact of the aqueous and organic phase. In the optimized continuous circuit, a product containing 99% of Zr and 0.03% of Hf was

obtained. The extraction of Zr with TBP in organic diluent was also studied [10]. The dependence of the distribution ratio of Zr on the TBP concentration in the organic phase and also the IR spectra of Zr-TBP extracts obtained at different concentrations of Zr and HNO_3 in the aqueous phase show that at least two kinds of extractable zirconium nitrate were formed. The solvate formed at HNO_3 concentration not exceeding 3M contains water molecules. The extractable species formed at higher nitric acid concentration in the aqueous phase was shown to be anhydrous zirconium nitrate. Further, in financial terms, the TBP process is twice as expensive than the MIBK process.

The CEZUS Process

In 1978, CEZUS company (Compagnie Europeenne du Zirconium), started a new industrial plant in France to produce Zr and Hf using the Besson's process (extractive distillation in molten salts). The success of this process was based on the elimination of several processing steps, associated with the MIBK and TBP. This process avoids the transition from anhydrous to aqueous system, for Hf separation by solvent extraction, and subsequent return to an anhydrous medium [11]. The Newham process (preferential reduction of zirconium tetrachloride) and extractive distillation in molten salts were considered the best possibilities. The distillation of ZrCl_4 and HfCl_4 in a molten salt bath was based on Besson's patent [12]. In CEZUS process, the operating pressure was kept one atmosphere with a temperature of around 400°C . This technology displays a separation factor of around 2 indicating that about 90 stages are required to achieve the desired separation. Both Zr and Hf were produced according to nuclear specifications. This process represents a shortcut between zirconite chlorination and the Kroll process, avoiding multiple steps of solubilization, solvent extraction, and

precipitation and calcination to produce ZrO_2 that will be chlorinated again. This process to promote the separation of Zr and Hf involves distillation of their solution in molten iron and aluminum chlorides at $400^\circ C$. Highly corrosion resistant alloys are required, as well as sophisticated technologies to pump and handle the various streams, while avoiding moisture contamination. Sehra [13]), in a way very similar to Skaggs, has reviewed various metallurgical processes for the separation of Hf and Zr. It stressed the importance of adopting the CEZUS process in India to replace the TBP technology presently used. As of now, about two thirds of all world Zr production are still produced by the MIBK process. Nevertheless, the environmental bill and an eventual increase in energy demand could push the nuclear industry into adopting more environmentally attractive technology.

The Amine Based Process (AP)

Amine-based extractants (such as Alamine 300, Alamine 308, Alamine 336, and Aliquat 336) are effective for separating Zr and Hf in both HCl and H_2SO_4 media. Octyl amine (specifically tri-n-octylamine or TOA is an effective, selective amine-based extractant for separating Zr from Hf, generally working best in sulfuric acid (H_2SO_4) media where it selectively extracts Zr over Hf. It was often used in the industrial-scale solvent extraction process [14]. Solvent extraction studies were also reported to investigate the selective extraction of Zr and Hf in hydrochloric acid medium [15]. For this purpose, several amine-based extractants were used at varying concentrations of extractants and HCl. Among the tested extractants, Alamine 336 showed good selectivity for Zr over Hf and led to the highest separation factor. A McCabe-Thiele diagram was constructed for the extraction of Zr with Alamine 336 in kerosene, and the tested batch simulation of counter-current extraction studies

showed that the extractions of Zr and Hf impurities were 98.5% and 12.5%, respectively. The coextracted Hf was scrubbed with dilute H_2SO_4 solution, and complete stripping of Zr was successfully achieved from the loaded organic phase by simple contact with 1M HCl solution. The Zr/Hf solvent extractive separation from sulfuric acid solutions using TOA as the extractant was studied at room temperature [16]. The Zr was shown to be extracted in the organic phase selectively with single-stage extraction rate of Zr of 61.23% and almost no extraction of Hf.

Mixed Ligand Based Process (MLP)

The extraction of Zr (IV) from aqueous HCl solution by TOA, Cyanex-921, and their binary mixture using kerosene as the diluent was reported [17]. The effect of some parameters on the extraction of Zr(IV) was investigated such as equilibration time, aqueous phase acidity, extractant molarity, chloride ion concentration, nature of diluents, and temperature. The extraction of Zr(IV) was found to be 99% from 7.5 M HCl using the mixture of extractants containing 0.1M TOA and 0.02M Cyanex-921 in kerosene. Kerosene was found to be the effective diluent for the extraction of Zr(IV). HNO_3 and Na_2CO_3 were shown to be the best stripping agents. Further, the extraction behaviour of Zr(IV) from sulfuric acid medium was studied with a binary mixture of TOA and Cyanex-923 (a mixture of four trialkyl phosphine oxides) in kerosene [18]. Quantitative extraction of Zr(IV) was studied by changing different parameters such as acid variation, extractant variation, effect of chloride ion concentration, effect of temperature, metal concentration variation, diluent effect, and pH effect. The percentage of extraction of Zr(IV) was found to be decreased when the concentration of Cyanex-923 and TOA was increased. The percentage of Zr was observed as 97.56% in a binary mixture of Cyanex-923 and OA. In another study, a new separation

procedure by solvent extraction was proposed. The method was based on using the mixture of TBP and Cyanex-923 as extractant in the organic phase [19, 20]. Several parameters including; TBP/Cyanex-923 volume ratio, extractant concentration in the organic phase, nitric acid and NaNO_3 concentration in aqueous phase were investigated and shown to be better than that of traditional TBP/ HNO_3 process. The advantage of this process was requirement of low acid concentration. The novel synergistic mixture of TBP and Cyanex-272 was used as the extractant in the hollow fiber renewal liquid membrane (HFRLM) technique for Zr/Hf separation [21]. The effects of the chemical and operational parameters such as HNO_3 concentration in the donor phase, NH_4F concentration in the acceptor phase, Cyanex-272 and TBP concentration in the liquid membrane phase, the lumen and shell side flow rates, and aqueous/organic volume ratio on the mass transfer and separation performance of HFRLM method were investigated. The obtained results reveal the intensification potential of proposed HFRLM technique for selective extraction of Zr over Hf with separation factor higher than 100. The HFRLM method provides two times higher mass transfer flux in comparison with hollow fiber supported liquid membrane (HFSLM). Also, the HFRLM method shows satisfactory stability for 700 min of continuous operation. The Zr ion transport through the LM phase follows the coupled co-transport mechanism and the diffusion in the renewal layer was recognized as the rate-controlling step in the HFRLM process. Next, the effect of various factors on the distribution of Hf ($\leq 5.60 \times 10^{-4}\text{M}$) between different acids and MIBK or TBP was studied by using Hf as a tracer, when the extraction was made from 7.5–11M hydrochloric acid with an equal volume of 1M TBP in benzene, Hf was extracted quantitatively (>99%) [22]. The Hf was stripped with 1–3M hydrochloric acid. A supported liquid

membrane system using hollow fiber membranes as supports (HFSLM) was studied for the separation of Zr and Hf. Also, TNOA and trioctylmethyl ammonium chloride (Aliquat 336) were used as carriers [23]. The effect on the transport and separation of Zr and Hf of HCl concentrations in the feed and stripping solutions, hollow fiber length, flow rate of aqueous phases was investigated..

Economic and environmental aspects for process selection

The MIBK process was considered to be the preferred route over TBP process for economic reasons as TBP method produced Zr at around twice the cost of that for MIBK's technology. The costs of the CEZUS' process were reported as even lower than those of the MIBK. The reasons for the French decision to replace the TBP process for an alternative other than MIBK technology was for the economic reasons, as well as the obnoxious odors generated in the MIBK process due to the formation of mercaptans, the high solubility of this solvent in water, and the fire risk concern (low flash point) [14]. In contrast, the USA has had huge industrial facilities, using the MIBK process, in operation for more than 40 years. According to the ideas discussed above, the ideal replacement for the present MIBK process is yet to come. The high cost to build a plant using the molten salt technology is a strong obstacle to its use in small scale or medium size plant. A solvent extraction process, simple in conception, with zero or low waste generation, could be a perfect solution that would change the production profile of Zr and Hf in the future. Recently, a review [24] article has described how Zr and Hf solution chemistry govern extraction and separation, offering strategic frameworks for identifying, amplifying, and exploiting solution chemistry disparities to advance separation efficacy at the atomic scale. This mechanistic perspective provided a novel and indispensable guide for the

rational design of next-generation separation technologies.

Zr and Hf was shown to be separable using 2-octanol ($C_8H_{18}O$) as an extractant in which the basic Zr carbonate was dissolved in HCl at concentrations ranging from 5-20% [25] in the presence of KF. The optimum conditions obtained for extraction were 10 wt% HCl in a 1.5M KF solution, a contact time of 15 minutes, and 100% 2-octanol resulted to a separation factor of 9.2 with a maximum extraction percentage of 96.58% of Zr. The optimum conditions for stripping of Zr were found to be 3 M H_2SO_4 as stripping agent, an A/O ratio of 1:1 and 40 minutes contact time. The McCabe-Thiele diagrams constructed from the experimental data indicated that four and five equilibrium stages were sufficient for the extraction and stripping respectively. A recovery of 97.25% of Hf was obtained using a mixture of oxalic acid and nitric acid as a stripping agent. A parametric study using solvent extraction was reported where pure Zr was recovered from zircon using 0.1mol/L Cyanex-923 solution in toluene [26] and showed that the rate of extraction of Zr is rationally fast. The distribution was found to be increased with increasing temperature, suggesting that the reaction is endothermic. The stability of Cyanex-923 against prolonged contact with nitric acid was checked and the regeneration capacity of the extractant was assessed.

In another study, the separation of Zr and Hf in nitrate medium using phosphine oxide based extractants (Cyanex-921, Cyanex-923, and Cyanex-925) in kerosene was also reported [27]. The rate of extraction of Zr and Hf was shown to be reasonably fast. Using HNO_3 (0.5M) as stripping agent, the recovery was found to be 97.5% and 10.2%, respectively after two stages. The extraction of Zr was about 90, 87.6, and 91.6% and separation factors were found to be 17, 21.4, and 40.7 for Cyanex-921, Cyanex-923, and Cyanex-925, respectively. Cyanex-925

was shown to be the more efficient compared to others.

Further, the effect of factors that influence Zr/Hf separation was reported by molecular level analysis [28], where, both Hf and Zr were shown to form an oxo-centered tetramer cluster with a core formula of $[OM_4(OH)_6(NCS)_{12}]^{4-}$ (OM_4-NCS , $M = Hf, Zr$). This structure was identified by single-crystal X-ray diffraction, as well as small-angle X-ray scattering. Zr was also shown to form (1) a large oxo-cluster formulated $[Zr_{48}O_{30}(OH)_{92}(NCS)_{40}(H_2O)_{40}]$ (Zr_{48}) and (2) NCS adducts of OZr_4-NCS . Zr_{48} was identified first by SAXS and then crystallized by exploiting favorable soft-metal bonding to the sulfur of NCS. While the large Zr_{48} likely cannot be extracted due to its larger size, the NCS adducts of OZr_4-NCS were also less favorable to extraction due to the extra negative charge, which necessitates coextraction of an additional counteranion (NH_4^+) per extra NCS ligand. Differentiating Zr and Hf coordination and hydrolysis chemistry adds to the growing understanding that these two elements, beyond simple solid-state chemistry, have notable differences in chemical reactivity.

Next, different organophosphorous ligands such as TBP, TOPO, Cyanex and many more have been employed in the solvent extraction studies of Zr^{4+} and Hf^{4+} [26, 29-36]. Solvent extraction processes are currently employed on a commercial scale to separate Hf^{4+} from Zr^{4+} ions using TBP-kerosene system [10, 29]. The major negative aspect of the TBP process is the low separation factor ($SF=DZr/DHf=10$) and third phase formation. On the other hand, in the MIBK process, the thiocyanate complexes of Hf and Zr ions get separated ($SFHf/Zr=7$) with the Hf complex getting enriched in the organic phase and the Zr complex in the aqueous phase [37]. The preferential extraction of Hf over Zr in MIBK process was opposite to the selectivity observed in the TBP process. This contrasting

selectivity trend at the molecular level is not clearly understood. Though the simultaneous production of pure Hf and Zr makes the MIBK process attractive and cost effective, the major disadvantage of this process is that the MIBK is water soluble and the waste streams contain toxic chemicals such as ammonium and cyanide salts. Also, the MIBK itself is highly volatile and explosive. Therefore, it is desirable to find out alternate extractants which can overcome the demerits of both TBP and MIBK by understanding the metal ion-extractant interaction. Similar limitations were observed for other type of ligands also. There is a continuing search for finding extractants which can outperform both TBP and MIBK. First-principles molecular modeling can be considered as an alternative route for the screening of the extractant.

Computational Approaches

Computational methods

The search by means of experiment alone is quite tedious and costly affairs because of trial-and-error approach. On the other hand, first principles based molecular modeling can be used to aid the experiment by finding the right candidate through quantum electronic structure calculations and molecular dynamics simulations. The study on the interaction of the Hf-Zr system with different type of ligands using a quantum chemical calculation is very limited in spite of its very useful application in the nuclear industry. Earlier study reported the interaction of Hf and Zr ions with acetone and tri methyl phosphate (TMP) at B3LYP= LanI2dz and BLYP=TZP levels of theory [38]. It is critical to focus on the quantum chemical study on the interaction of Hf-Zr with ligands to deliver a suitable ligand-solvent system for efficient separation of Zr from Zr-Hf mixtures or vice versa. Recently, the binding capability and selectivity of TBP, THPO, and Cyanex-925 with Hf and Zr

metal oxycations was reported [39]. Also, quantum chemical density functional theory-based study has been performed on the interaction of MIBK with Zr and Hf thiocyanate complexes [39]. Further, the structures and energetic parameters for the free ligand, hydrated metal ion and the metal-ion-ligand systems were computed using density functional theory (DFT) [40]. The systems of interest considered were alkyl phosphine oxide (MAPO) and mixed substituted alkyl phosphine oxide (MSAPO). Conductor like screening model (COSMO) solvation approach was used to account for the solvent effect in water-organic bi-phasic system. Bis (hexyl)-octyl phosphine oxide and (bis(2,4,4-trimethylpentyl) octyl phosphine oxide) were considered the major constituting species in the composition of MAPO and MSAPO. Hence, minimum energy structure of bis (hexyl)-octyl phosphine oxide (MAPO) and bis (2, 4, 4-trimethylpentyl) octyl phosphine oxide (MSAPO) and their complexes with Zr^{4+} and Hf^{4+} ions were optimized with generalized gradient approximation using BP86 functional employing split valence valence plus polarization (SVP) basis set as implemented in TURBOMOLE package [41]. Effective core potential (ECP) was used for both Zr and Hf where 28 and 60 electrons are kept in the core of Zr and Hf respectively [42]. BP86 functional consists of Becke B88 exchange functional [43] and Perdew P86 correlation functional [44] and was found to be successful in predicting various molecular properties. The free MAPO and MSAPO ligands and their complexes with metal ions were optimized without imposing any symmetry restriction. GGA based BP86 has the inbuilt limitation in the accurate energy predictions due to non-consideration of non-covalent interaction. Hence, single point energy calculation was further performed using BP86 optimized structures at B3LYP level of theory [45], which was known for its theoretical accuracy over simple GGA functional. Most of the metal ion

extraction takes place from the aqueous solution phase to the organic solvent phase aided by the ligand. Hence, the consideration of solvent effect on the complexation of the ligand moiety with metal ion in the QM calculation is thus indispensable. In order to study the aqueous and organic solvent effect, the optimized geometry obtained from BP86 level of theory was used for single point energy calculation using COSMO model [46]. The dielectric constant, ϵ of water and dodecane was taken as 80 and 2 respectively. The MOLDEN graphical program [47] was used for the visualization of various molecular geometry and structural parameters.

Structural parameters

Mostly metal ions are extracted from the aqueous environment, hence, hydrated Zr^{4+} and Hf^{4+} were optimized first and their structures are presented in Fig. 2. Both Zr^{4+} and Hf^{4+} ions are shown to be octa coordinated with Zr-O and Hf-O bond distance of 2.272Å and 2.270Å respectively. The very close distance of Zr^{4+} and Hf^{4+} ions is reflected in their similar chemical properties and thus poses a great challenge for their mutual separation.

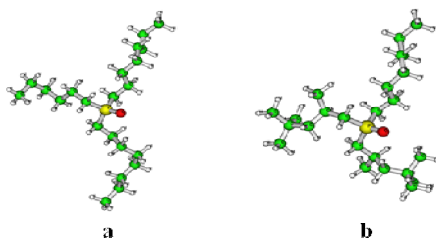


Fig.2. Optimized structures of hydrated (a) $Zr^{4+}(H_2O)_8$ and (b) $Hf^{4+}(H_2O)_8$ complexes

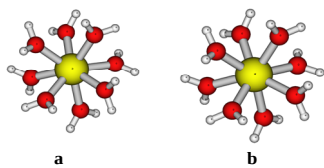


Fig.3. Optimized structures of (a) MAPO and (b) MSAPO.

The computed minimum energy structures of free extractants were displayed in Fig. 3. The P=O bond distance of MAPO and MSAPO was found to be 1.524Å and 1.525Å respectively. The optimized structures of complexes of Zr^{4+} and Hf^{4+} ions towards MAPO and MSAPO are presented in Fig.4. From figure, it is seen that both Zr^{4+} and Hf^{4+} ions are coordinated to the 4 nitrate ions and three extractants. Three nitrate ions are coordinated in mono-dentate fashion and one nitrate ion in bi-dentate fashion leading to eight coordination complexes. The M-O (phosphonic O) bond distance is shorter than that of M-O (O of Nitrate) bond distance indicates the stronger interaction with phosphine "O" atom. Further, the M-O bond distance for mono-dentate nitrate is shorter than that of bi-dentate nitrate ion.

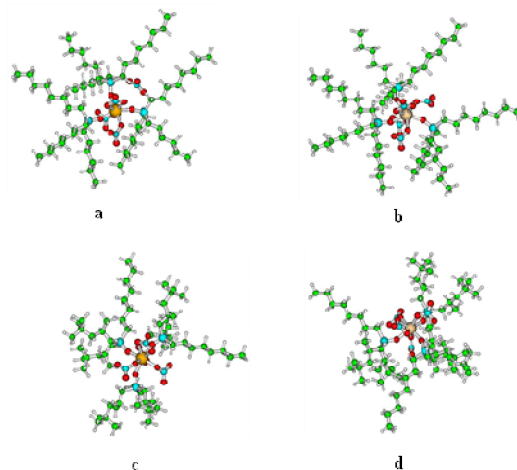


Fig.4. Optimized structures of nitrate complex of Zr and Hf with different extractants: (a) $Zr(NO_3)_4-(MAPO)_3$ (b) $Hf(NO_3)_4-(MAPO)_3$ (c) $Zr(NO_3)_4-(MSAPO)_3$ and (d) $Hf(NO_3)_4-(MSAPO)_3$. The green, cyan, red and grey sphere represents the C, N, O and H atom respectively. The dense and light-yellow sphere represents Zr and Hf atom respectively.

The Zr-O and Hf-O bond distances are very close to each other suggesting their similar interaction towards the ligands. After complexation with Zr^{4+} and Hf^{4+} ions, the P=O bond distance was found to be elongated for both MAPO and MSAPO. The P=O bond distance in MSAPO was changed to 1.565Å and 1.564Å after

complexation with Zr⁴⁺ and Hf⁴⁺ ions respectively, whereas the P=O bond distance was found to be lengthen to 1.582Å and 1.581Å with MAPO with Zr⁴⁺ and Hf⁴⁺ ions respectively. This elongation of bond length indicates the strong interaction of phosphonic O donor and the metal ion. Further, the elongation is higher with MAPO over MSAPO suggesting higher interaction for MAPO over MSAPO.

Metal-ligand binding energy (BE)

The calculated gas phase BE for Zr and Hf ions are listed in Table 1. The computed BE was found to be higher with MAPO compared to MSAPO. The higher BE for Zr⁴⁺ over Hf⁴⁺ ion indicated that Zr⁴⁺ ion will be preferentially extracted over Hf⁴⁺ ion. Next, the computed extraction energy (EE) was also found to be higher with MAPO compared to MSAPO with higher EE for Zr⁴⁺ over Hf⁴⁺ ion. The computed EE was found to be reduced compared to gas phase BE due to dielectric screening of the solvents. Higher EE for Zr⁴⁺ ion leads to preferential extraction of Zr⁴⁺ ion over Hf⁴⁺ ion. The theoretical separation factor (SF) was calculated by using the relation: $SF(Zr/Hf) = \exp(-\Delta E/RT)$, where R is the universal gas constant and T is the temperature ($\Delta E = (E_{Zr} - E_{Hf})$). The theoretical SF for Zr⁴⁺ and Hf⁴⁺ towards MAPO and MSAPO was found to be 57.23 and 41.54 respectively. The experimental SF was found to be 20 and 12.06 respectively. The calculated SF using DFT was found to be higher than that of obtained from experiments which might be attributed to limitation of theory as it cannot handle the large number of molecules and other practical parameters like experiments. Also, the thermodynamic correction was not done to the EE. Further, the selectivity factor for Zr⁴⁺- Hf⁴⁺ separation between two ligands was evaluated using the relation: $selectivity\ factor = SF(Zr/Hf)_{MAPO} / SF(Zr/Hf)_{MSAPO} = \exp(-\Delta E/RT)$. The calculated value of

selectivity factor was found to be 1.37 which is very close to the experimentally predicted value of 1.65 [39].

Table 1: Calculated extraction energy of Zr and Hf⁴⁺ with MAPO and MSAPO ligands using DFT [39].

System	Binding energy(ΔE) (kcal/mole)				$\Delta \Delta E$	$\Delta \Delta \Delta E$
	Gas phase		Solvent phase			
	Zr ⁴⁺	Hf ⁴⁺	Zr ⁴⁺	Hf ⁴⁺		
MSAPO	-974.3	-971.3	-81.0	-78.8	-2.2	-0.2
MAPO	-1002.0	-1000.1	-108.7	-106.3	-2.4	

Recently, MSAPO and MAPO were employed to determined distribution constant of Zr and Hf using dodecane and isodecanol as diluents in 80:20 ratio. The stoichiometry of metal ion extractant was found to be 1:3 for both Zr⁴⁺ and Hf⁴⁺ ions with MAP, whereas for MSAPO, it was 1:3 for Zr⁴⁺ ion and 1:2 for Hf⁴⁺ ion. The experimentally determined K_d values for MAPO and MSAPO are presented in Table 2.

Table 2: The values of experimental K_d for Zr⁴⁺ and Hf⁴⁺ with MAPO and MSAPO ligands [39].

Ligand	Feed (gpl)		K _d (Zr ⁴⁺)	K _d (Hf ⁴⁺)	SF (Zr/Hf)	Selectivity factor [SF _{(Zr/Hf)MAPO} / SF _{(Zr/Hf)MSAPO}]
	Zr ⁴⁺	Hf ⁴⁺				
0.1 M MAPO	1.2	0.6	12	0.6	20	1.65
0.1 M MSAPO	1.4	1.5	3.5	0.3	12.0	

The experimentally observed value was found to be in good agreement with the predicted EE. The experimental K_d for Zr⁴⁺ ion was found to be always higher than Hf⁴⁺ ion as predicted by the calculation. The theoretical SF was expressed in terms of the difference (ΔE) between the EE of Zr⁴⁺ ion (E_{Zr}) and Hf⁴⁺ ion (E_{Hf}), whereas experimentally, SF was determined from the ratio of K_d of Zr⁴⁺ ion and Hf⁴⁺ ion. The theoretical SF was found to be in good agreement with the experimentally observed selectivity of Zr⁴⁺ ion over Hf⁴⁺ ion. MAPO displayed higher selectivity over MSAPO for Zr⁴⁺ ion over Hf⁴⁺ ion. The structure and energetics of TBP, THPO and Cyanex-925 and their complexes with Hf and Zr oxycation at the BP86/TZVP level was reported earlier [48]. The calculated BE was shown to follow the order Cyanex-925>THPO>TBP>. The

calculated BE for Hf oxycation was found to be higher than that of Zr oxycation which was contradictory to the observed experimental trend. The experimental selectivity trend was recovered by inclusion of the second solvation sphere of the metal ion. Both the implicit and explicit solvation model was unable to predict the high selectivity of ZrO_2^+ with Cyanex-925 over TBP in the absence of nitrate anion. The presence of nitrate anion along with the second solvation shell ($n=24$ water molecules) around the oxycation, shows consistent results for selectivity as observed in the experiments. Further, the preferential selectivity of HfO_2^+ over ZrO_2^+ cation using MIBK-HSCN system was reproduced by DFT calculation. The experimental $\text{SF}[\text{SF}(\text{Zr}/\text{Hf} \text{ or } \text{Hf}/\text{Zr})]$ was found to be well correlated with the EE difference between two metal ions. In another study, the structures of Cyanex-925, TBP, and their complexes with Hf and Zr oxycations were optimized at the DFT/TZVP level of theory [49]. The effect of noncovalent interactions was examined by using the TPSSH and M06-2X density functionals. The free energy of extraction ΔG_{ext} was calculated by using the standard thermodynamic procedure in conjunction with the COSMO model. The calculated ΔG_{ext} , either with an implicit or explicit solvation model, fails to capture the experimentally reported preferential selectivity of ZrO_2^+ ions over HfO_2^+ ions in the absence of nitrate anions. The presence of nitrate anions along with the second solvation shell ($n = 6 + 1$ water molecules) around the oxycation shows consistent results with the calculated ΔG_{ext} as reported in the experiments. Different bonding analyses indicate the electrostatic nature of the interactions. The optimized structures are also displayed in Fig. 5. In both of the metal oxycation complexes, two ligand units are coordinated to the metal ion through O donor atoms of the P=O groups. The two ligands are far apart owing to the steric hindrance of the alkyl group. Both the

P=O and the M=O (Zr or Hf) bonds are lengthened owing to complexation with the metal oxycations. The increment in the P=O bond length was almost the same for both Hf and Zr and for both TBP and Cyanex-925 ligands. Both the Hf=O and Zr=O bond lengths are longer in Cyanex-925 than in TBP. The Zr–O (O of P=O) and Hf–O (O of P=O) bond lengths with Cyanex-925 and TBP are very close to each other. It is interesting to see the effect of nitrate anions on the structure and bonding parameters.

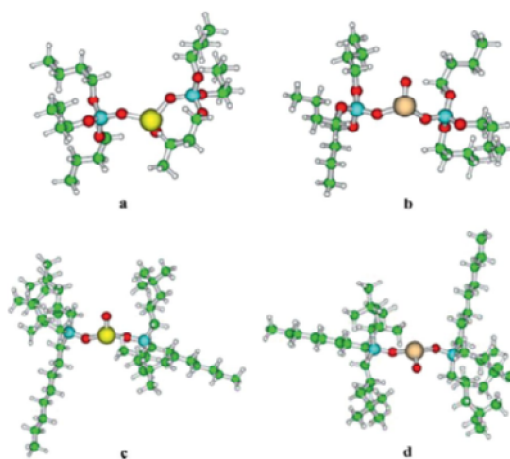


Fig.5. Optimized minimum-energy structures at the BP86 level of theory with the TZVP basis function for complexes of TBP and Cyanex925 with ZrO_2^+ and HfO_2^+ oxycations. (a) $\text{ZrO}_2^+(\text{TBP})_2$, (b) $\text{HfO}_2^+(\text{TBP})_2$, (c) $\text{ZrO}_2^+(\text{Cyanex925})_2$, and (d) $\text{HfO}_2^+(\text{Cyanex925})_2$. The red, green, and grey spheres represent O, C, and H atoms, respectively. The cyan sphere represents P atom.

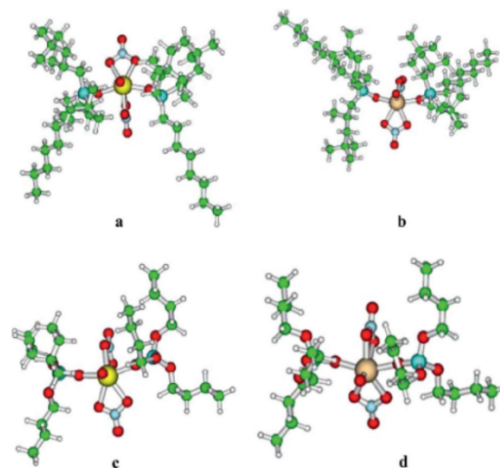
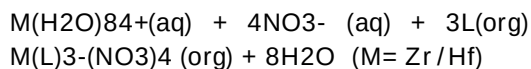


Fig.6. Optimized minimum-energy structures at the BP86 level of theory with the TZVP basis function for Cyanex925 and TBP and its complexes with ZrO_2^+ and HfO_2^+ oxycations with nitrate anions. (a) $ZrO_2^+(Cyanex925)_2$, (b) $HfO_2^+(Cyanex925)_2$, (c) $ZrO_2^+(TBP)_2$, and (d) $HfO_2^+(TBP)_2$. The blue spheres represent the N atoms. The key for all other atoms is as in Fig. 4.

The optimized structures with nitrate anions are presented in Fig. 6. There are no significant changes in the metal oxycation complexes of TBP and Cyanex-925 owing to the inclusion of nitrate anions. The nitrate anions are bonded to the oxycations in a bidentate fashion. There is a reduction in the P=O bond length for the oxycations and the ligands after inclusion of nitrate anions in the complexes. A larger reduction was in the Hf complexes than in the Zr complexes. Similarly, the reduction is larger with TBP than with Cyanex-925. The Hf=O and Zr=O bond lengths increase further owing to the presence of nitrate anions in the complexes. The Hf=O bond remains longer than the Zr=O bond. Similarly, the Hf–O and Zr–O bonds lengths increase further owing to the presence of nitrate anions.

Free energy of extraction using thermodynamic cycle

One of the key properties to be calculated in the metal– ligand complexation is the free energy of extraction (ΔG_{ext}). The metal–ligand complexation reaction was modeled as a 1:2 ($MO_2^+/2L$) stoichiometric reaction as follows:



$L=TBP/Cyanex-925$. The experimentally observed selective extraction behavior was explained with ΔG_{ext} using the thermodynamic cycle as given in Fig. 7.

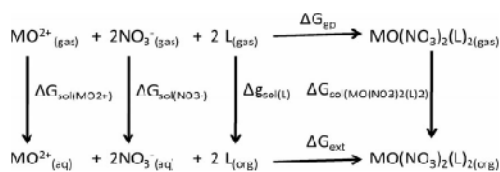


Fig.7. Thermodynamic cycle for the evaluation of the free energy of extraction of metal oxycations.

The values of ΔG_{ext} are presented in Table 3. The free energy of solvation for the ZrO_2^+ ion was lower than that for the HfO_2^+ ion with Cyanex-925 (L1) in the absence of nitrate ions, but after inclusion of nitrate ions the trend is reversed. A similar trend was also observed with TBP (L2). Although the presence of nitrate anions makes the value of ΔG_{ext} negative, the value is higher for HfO_2^+ than for ZrO_2^+ and makes $\Delta\Delta G_{ext}$ positive for the ZrO_2^+ ion with implicit solvation as shown in Table 3. However, the value of $\Delta\Delta\Delta G_{ext}$ is negative, which suggests the preferential selection of ZrO_2^+ over HfO_2^+ by Cyanex-925 over TBP. This implicit model fails to capture the higher selectivity of the ZrO_2^+ ion over the HfO_2^+ ion with TBP or Cyanex-925. Hence, the next explicit solvation with $n = 6$ water molecules (2A) was considered in the COSMO phase. The calculated values of ΔG_{ext} are negative for both ZrO_2^+ and HfO_2^+ ions for both TBP and Cyanex-925 but are more negative for HfO_2^+ ions than for ZrO_2^+ ions with TBP which leads to a positive $\Delta\Delta G_{ext}$ value and thus contradicts the experimental selectivity (Table 3). In combination with the high negative value of $\Delta\Delta G_{ext}$ with Cyanex-925, this leads to an overall negative value for $\Delta\Delta\Delta G_{ext}$. Therefore, explicit solvation with six water molecules fails to capture the experimental selectivity. In view of this, $n = 7$ water molecules (six in the first solvation shell and one in the second solvation shell, 2B) was considered. Although this model was able to capture the selectivity in terms of a negative value for ΔG_{ext} , $\Delta\Delta G_{ext}$, and $\Delta\Delta\Delta G_{ext}$, the individual value of ΔG_{ext} was abnormally high for both metal oxycations. Further, the effect of the second solvation shell on the free energy of extraction was examined by considering $n = 18$ water molecules (2C) surrounding both the cations. Here, the individual ΔG_{ext} values are more negative compared to those for $n = 7$ for both TBP and Cyanex-925 (Table 3). The value of $\Delta\Delta G_{ext}$ with L1 is positive, whereas with L2 it was

negative and led to a negative value for $\Delta\Delta\Delta G_{\text{ext}}$. In view of the inconsistent results with explicit first and second solvation shells, further calculations were performed with a cluster solvation model. The calculated values of ΔG_{ext} using a cluster with six water molecules (3A) for both ZrO_2^+ and HfO_2^+ ions towards TBP and Cyanex-925 are negative. The value of $\Delta\Delta G_{\text{ext}}$ with L1 is positive, whereas with L2 it is negative and leads to a negative value for $\Delta\Delta\Delta G_{\text{ext}}$. Next, the calculation was performed with a cluster of seven water molecules (3B), and the calculated values of ΔG_{ext} for both ZrO_2^+ and HfO_2^+ ions were negative as shown in Table 3.

Table 3. Calculated values of ΔG_{ext} [kcal/mol] with $\epsilon = 2$ at the BP86/TZVP level of theory (with NO_3^- ions).

	System	ΔG (calcd.)	$\Delta\Delta G$ (calcd.)	$\Delta\Delta\Delta G$ (calcd.)	$\Delta\Delta G$ (exp.)	$\Delta\Delta\Delta G$ (exp.)
1	$\text{ZrO}_2^+(\text{L1})_2$	-94.19	13.73	-4.72	-1.35*	-0.82
	$\text{HfO}_2^+(\text{L1})_2$	-107.92				
	$\text{ZrO}_2^+(\text{L2})_2$	-108.42				
	$\text{HfO}_2^+(\text{L2})_2$	-117.43				
2A	$\text{ZrO}_2^+(\text{L1})_2$	-115.16	0.59	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	-115.75				
	$\text{ZrO}_2^+(\text{L2})_2$	-129.39				
	$\text{HfO}_2^+(\text{L2})_2$	-125.26				
2B	$\text{ZrO}_2^+(\text{L1})_2$	-122.62	-0.08	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	-122.54				
	$\text{ZrO}_2^+(\text{L2})_2$	-136.85				
	$\text{HfO}_2^+(\text{L2})_2$	-132.05				
2C	$\text{ZrO}_2^+(\text{L1})_2$	-194.24	1.52	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	-195.76				
	$\text{ZrO}_2^+(\text{L2})_2$	-208.47				
	$\text{HfO}_2^+(\text{L2})_2$	-205.57				
3A	$\text{ZrO}_2^+(\text{L1})_2$	-7.50	0.59	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	-8.09				
	$\text{ZrO}_2^+(\text{L2})_2$	-21.73				
	$\text{HfO}_2^+(\text{L2})_2$	-17.60				
3B	$\text{ZrO}_2^+(\text{L1})_2$	-5.88	-0.08	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	-5.80				
	$\text{ZrO}_2^+(\text{L2})_2$	-20.11				
	$\text{HfO}_2^+(\text{L2})_2$	-15.31				
3C	$\text{ZrO}_2^+(\text{L1})_2$	58.07	1.59	-4.72		
	$\text{HfO}_2^+(\text{L1})_2$	56.54				
	$\text{ZrO}_2^+(\text{L2})_2$	43.84				
	$\text{HfO}_2^+(\text{L2})_2$	47.03				

The value of $\Delta\Delta G_{\text{ext}}$ with L1 as well as with L2 is negative, which leads to a negative value for $\Delta\Delta\Delta G_{\text{ext}}$. The results with a cluster of seven water molecules satisfy the correct criteria for the higher preferential selectivity of ZrO_2^+ over HfO_2^+ ions, as ΔG_{ext} , $\Delta\Delta G_{\text{ext}}$, and $\Delta\Delta\Delta G_{\text{ext}}$ are all negative, and their magnitudes also seem to be reasonable. The experimental selectivity is reproduced after consideration of nitrate ions as is evident from the values of $\Delta\Delta G_{\text{ext}}$ (-0.08 kcal/mol for TBP and -4.80 kcal/mol for

Cyanex-925) and $\Delta\Delta\Delta G_{\text{ext}}$ (-4.72 kcal/mol). The calculated $\Delta\Delta\Delta G_{\text{ext}}$ values are 8.72 kcal/mol and -4.72 kcal/mol in the absence and presence of nitrate anions [experimental $\Delta\Delta\Delta G_{\text{ext}} = -0.82$ kcal/mol from $\text{SF} \approx \exp(-\Delta\Delta\Delta G_{\text{ext}}/\text{RT})$]. It is interesting to study the effect of a cluster of 18 water molecules (3C) on the free energy. The calculated values of ΔG_{ext} for both ZrO_2^+ and HfO_2^+ ions towards TBP and Cyanex925 are positive (Table 3). The value of $\Delta\Delta G_{\text{ext}}$ with L1 is positive, whereas with L2 it is negative, which leads to a negative value for $\Delta\Delta\Delta G_{\text{ext}}$. Therefore, from the above analysis with different water cluster sizes considered, it was found that a cluster of seven water molecules (3B) captures the correct selectivity trend as reported in the experiments. Another point to be mentioned is that the value of $\Delta\Delta\Delta G_{\text{ext}}$ was found to be independent of any solvation model for the oxyanion. The dielectricity of the solvent also plays an influential role in the selectivity of the metal ions. To investigate the solvent effects, the $\Delta\Delta G$ values were computed to study the selectivity of ZrO_2^+ ions over HfO_2^+ ions over a wide range of dielectric constants ($\epsilon = 2-40$), and the results are presented in Fig. 8. Interestingly, the value of $\Delta\Delta G$ with Cyanex-925 is the highest (-4.8 kcal/mol) with a solvent of $\epsilon \approx 2$, it then decreases to -4.32 kcal/mol with a solvent of $\epsilon = 10$, and after that it remains almost constant, whereas the value of $\Delta\Delta G$ with TBP was lowest (-0.08 kcal/mol), increased to -0.15 kcal/mol with a solvent of $\epsilon = 10$, and after that it remained almost constant. The value of $\Delta\Delta\Delta G$ was the highest at $\epsilon = 2$ or less, which indicates that long-chain alkanes such as kerosene would be suitable solvents for the extraction.

HOMO-LUMO analysis

The relatively higher BE with Cyanex-925 over TBP was explained by the energy gap between highest occupied molecular orbital (HOMO) and the lowest

unoccupied molecular orbital (LUMO) and the dipole moments of the ligands. The HOMO–LUMO energy gap for Cyanex-925 (5.70 eV) is lower than that for TBP (6.70 eV), and the dipole moment is higher for Cyanex-925 (3.70 D) than for TBP (3.40 D). The smaller the HOMO–LUMO energy gap, the higher the reactivity of the ligand; hence, there are more interactions with Cyanex-925 than with TBP.

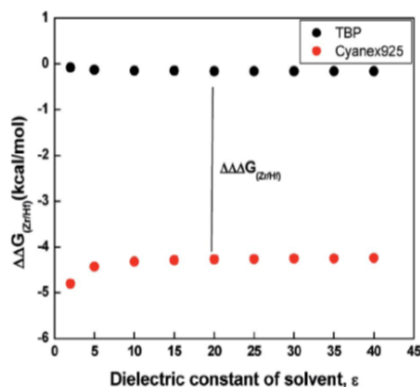


Fig.8. Calculated values of $\Delta\Delta G_{ext}$ and $\Delta\Delta\Delta G_{ext}$ for the ZrO_2^+/HfO_2^+ by L1 and L2 vs. dielectric constant.

Similarly, as the interactions are dictated by the ion–dipole interaction, the ligand with a higher dipole moment (here, Cyanex-925) interacts more than the ligand with a low dipole moment (TBP). According to the hard and soft acids and bases (HSAB) principle of Pearson,[50] hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. The Cyanex-925 and TBP ligands with oxygen donor atoms act as hard bases, as is evident from their large HOMO–LUMO energy gaps. Similarly, both the doubly charged Hf and Zr oxycations act as hard acids owing to their large HOMO–LUMO energy gap. The energies of the HOMO and the LUMO are a measure of electron-donor and electron-acceptor capacity, respectively, and consequently determine the donors and acceptors in charge-transfer interactions. The smaller the numerical value of the HOMO (a positive number), the better the molecule is as an electron donor, as the small number indicates that less energy is required to remove an electron from it.

Likewise, the smaller the magnitude of the LUMO (a negative number), the more stable the orbital for the incoming electron, which favours electron-acceptor characteristics. Thus, by examining the numerical values of the HOMO and LUMO of a pair of molecules, one can often decide which compound will be the donor and which the acceptor. The calculated HOMOs and LUMOs of Cyanex-925 and TBP are displayed in Fig. 9.

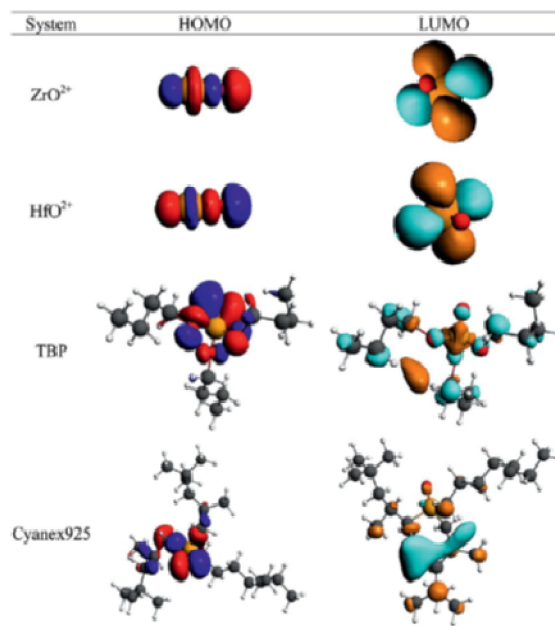


Fig. 9. Calculated HOMOs and LUMOs of metal oxycations, TBP, and Cyanex925.

Population analysis

It is interesting to explain why the Hf oxycation showed higher interactions than the Zr oxycation in the gas phase. To understand this, HOMOs and LUMOs of the Hf and Zr oxycations and the charge transfer on the metal ion in the respective complexes were calculated by using natural population analysis (NPA). The calculated NPA charges and orbital occupancies are listed in Table 4. It is seen that there are negligible charge populations in the f orbitals, which indicates their nonparticipation in the complex formation; however, significant charge populations were observed for the

s and d orbitals which indicates the presence of covalency in the bonding.

Table 4. Calculated values of NPA partial charges (Q) and orbital (s, p, d, f) occupancies at the BP86/TZVP level of theory.

	s	p	d	f	Q ^[a]
ZrO ²⁺					2.52(2.28)
ZrO ²⁺ (L1) ₂	2.09	5.97	1.85	0.007	2.07(1.91)
ZrO ²⁺ (L2) ₂	2.08	5.97	1.87	0.007	2.05(1.88)
HfO ²⁺					2.62(2.33)
HfO ²⁺ (L1) ₂	2.10	5.96	1.65	0.006	2.26(1.96)
HfO ²⁺ (L2) ₂	2.13	5.97	1.70	0.006	2.17(1.81)
ZrO(NO ₃) ₂					1.99(1.88)
ZrO(NO ₃) ₂ (L1) ₂	2.18	5.98	1.83	0.008	1.98(1.94)
ZrO(NO ₃) ₂ (L2) ₂	2.19	5.99	1.79	0.008	2.01(1.90)
HfO(NO ₃) ₂					2.11(1.79)
HfO(NO ₃) ₂ (L1) ₂	2.22	5.99	1.68	0.007	2.09(1.85)
HfO(NO ₃) ₂ (L2) ₂	2.22	5.99	1.65	0.007	2.11(1.81)

[a] Calculated values of Mulliken partial charges (Q) at the M06-2X/TZ2P level of theory in parentheses.

The charge transfer is larger for Zr than for Hf for both the TBP and Cyanex-925 complexes. The NPA charge is higher on the Hf center than on the Zr center in all of the complexes, which indicates that the Hf oxycation complexes have less covalent character than the Zr oxycation complexes. Similar observation can be drawn from the LUMO values. The calculated energy of the LUMO in HfO²⁺ (−17.494 eV) is smaller than that for ZrO²⁺ (−18.139 eV), which suggests that HfO²⁺ is a better acceptor than ZrO²⁺ and thus forms the more stable complexes.

Old practices in plant

There are many established processes for the production of reactor grade Zr. Two companies, M/s Teledyne Wah Chang and M/s Western Zirconium of USA use MIBK-thiocyanate SX system whereas M/s CEZUS, France uses extractive distillation of chlorides and M/s Nippon Mining, Japan operates the plant using amine sulphate route. At NFC, India TBP-Nitrate process is being practiced [51]. At NFC, hafnium free (Hf < 50 ppm) Zr is being produced regularly on tonnage scale since 1971 from nitrate media using TBP as the solvent. In this process, Zr/Hf separation is the most critical step which

involves extraction of Zr from crude zirconyl nitrate solution using TBP diluted with kerosene (30:70) with Zr/Hf separation factor of 10. The acidity plays an important role in the extraction, scrubbing and stripping steps. The major problem in the extraction of Zr has been that of third phase formation possibility during the extraction of Zr mainly due to silica. If the solubility of solute-extractant complex in diluent is exceeded, troublesome third phase formation takes place. The highest separation factor for Zr/Hf is achieved at ~ 4.5 molar free acidity.

Liquid-liquid extraction equipment

The most important part is the equipment for any liquid-liquid extraction technique is the contactors in which the two immiscible phases are mixed together. The purpose of the contactors is to mix intimately the two phases to provide sufficient interfacial area across which the transfer of the required solutes takes place. Over the years different solvent extraction contactors have been developed for use in the mineral processing industry these include mixer-settlers, pulsed columns and centrifugal extractor[52].

Mixer-settler (MS)

The mixer-settler is a simple stage wise liquid-liquid contactors which consists two parts, namely a mixing chamber where the aqueous phase and the solvent phase are intimately mixed together, and a settling chamber into which the two-phase solution are allowed to separate by gravity due to the difference in their density. The Fig. 10 shows a typical flow diagram of mixer-settler unit. Each mixer-settler unit provides a single stage extraction. In this case of multi-stage mixer-settler, multiple mixer-settler units are connected in counter-current manner [53, 54]). The mixer-settler becomes the most commonly used contactor because it is a proven

technology; simple to construct, operate and maintain; able to process high throughput volumes and simple to assess its performance [55, 56].

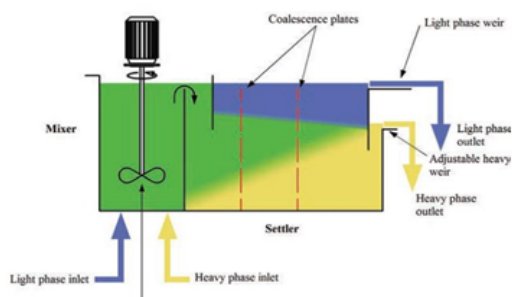


Fig.10. A typical Flow diagram of a mixer-settler unit consisting mixing chamber and settling chamber.

Pulsed column (PC)

The pulsed column is a contractor without individual extraction stages in contrast to mixer-settler. The pulsed column is basically an enclosed vertical column containing either perforated plates in the case of a sieve-plate pulsed column as shown in Fig. 11, or a series of rings and donuts in the case of the proprietary Bateman pulsed column, and a pulsing mechanism at the bottom of the column [57]. The solvent (light phase) entered at the bottom and travelled from the bottom to the top whereas the aqueous solution (heavy phase) flowing in counter-current. Owing to the difference in density between the solvent and the aqueous phase, the latter will settle to the bottom and the solvent will rise to the top. The aqueous phase, which disperses in droplets, is immiscible with the solvent. To generate and maintain this emulsion, the liquids are moved back and forth to create turbulence as they encounter obstacles positioned along the column. The obstacles are usually referred to as perforated trays. [52]. The efficiency of liquid-liquid contractors depends on the degree of turbulence imparted to the system and the interfacial area available for mass transfer[58]. Therefore, in pulsed columns, rate of mass transfer can be increases by pulsation to liquid phase

that decreases the size of the droplets. One of the advantages of pulsed columns is the absence of moving parts to make proper contact between dispersed and continues phases in entire column that causes a decrease in maintenance costs and finally a decrease in total costs[59].

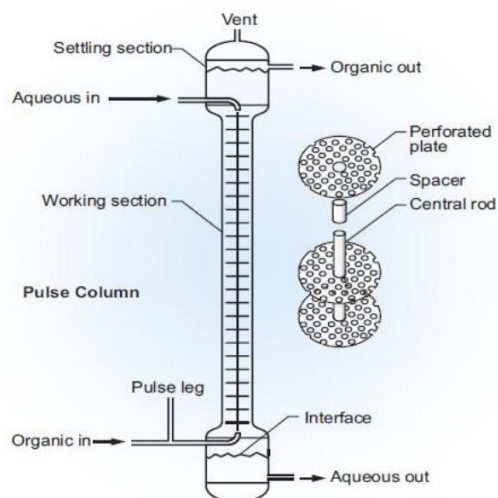


Fig.11. A schematic diagram of pulsed column (McKetta and Weismantel, 1998[60]).

Centrifugal extractor (CE)

The centrifugal extractor, also known as annular centrifugal contactors, is ideal for a system in which the density difference between the two phases is small. In this extractor system, two immiscible liquids with different densities, are fed to separate inlets and are mixed in the annular space between the spinning rotor and the stationary housing. The mixed phases are directed towards the centre of the rotor by radial vanes in housing bases (see Fig. 12). As the liquids enter the central opening of the rotor, they are accelerated towards the wall. The mixed phases are accelerated to rotor speed. The separation takes place as the liquids are displaced upwards[61, 62]. The separated phases exit the extractor by overflow and underflow weirs, almost similar to those in mixer-settlers. [61]. The main advantage is the compact footprint which indicates that maintenance operations can be performed using appropriate

shielded containments[52]. They also present other advantages such as short residence times, low holdup volumes, flexible phase ratio, and centrifugal acceleration settling. However, as centrifugal extractors are finely machined, they tend to be the most expensive type of extractor in capital investment terms[63]. The performance of centrifugal extractor is characterised by the following parameters: flooding, holdup, pressure, back-mixing and efficiency. Their compact nature also means that liquid hold-up is very small, ensuring that chemical equilibrium is attained rapidly[52].

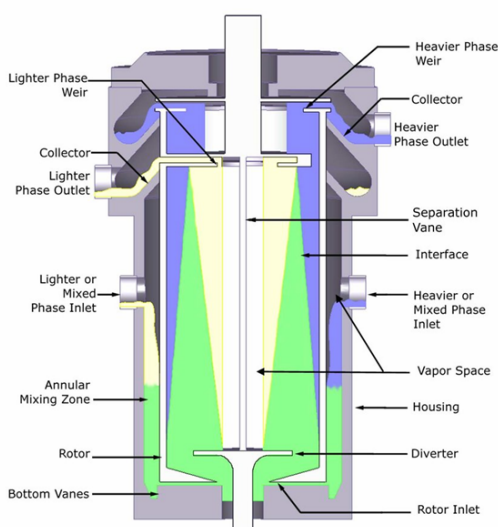


Fig.12. A schematic diagram of centrifugal extractor, also known as annular centrifugal contactors.

For large-scale industrial production, the pulsed column is preferred over the other two contractors but the required height of pulsed column becomes inconveniently high due to higher number of theoretical stages. Again, the mixer – settler stays ahead when the operational flexibility, stage reliability and handling dirty liquid are in concerns. Hence, mixer-settlers were selected for solvent extraction operations as it is better for experimental optimization.

Advanced chemical processes

The conventional extraction process using TBP was not suitable to recover Hf value

which is lost in low acidic lean stream. Also, presence of high concentration of silica poses additional challenge. Recently, a high separation factor for Zr over Hf using a novel alkyl phosphine oxide-based (APO) ligand was demonstrated [64]. The developed process was successfully applied in five stage mixer settlers set up in counter current mode with zirconium nitrate as the scrubbing agent and oxalic acid as the strippant. The reported research work was quite effective in achieving complete extraction of the Hf as well as recovery of the metal as a concentrated solution ~ 10 g/L with 95% purity. The Zr value was also recovered during stripping and can be considered for use in Zr purification plant for value recovery of the Hf and Zr from raffinate waste. It has been observed that high amount of silica in zirconium nitrate solution causes the formation of emulsion in mixer-settler. In order to avoid this drawback of mixer settler, recently, pulsed stirred column (PSC) was explored for selective extraction of Zr[65]. In the reported literature, most of the columnar contactors use either stirring or pulsing for generation of liquid-liquid dispersion. The stirring speed is generally high in mixer settler whereas it is quite low in PSC. PSC has several advantages over MS. PSC requires smaller foot-print area, low organic inventory, minimum instrumentation, and can work in presence of solids in the aqueous phase.

Technical Challenges

There are many technical challenges listed below which are to be addressed in the present practices.

- i. Zr and Hf have nearly identical radii and electronic configurations, making selectivity difficult. Many conventional extractants, like acid extractants (e.g., DEHPA), fail to provide a high enough separation factor.
- ii. Conventional systems like MIBK-HSCN suffer from low boiling points, high flammability, and high solubility in

- water, leading to significant solvent loss and also hazardous in nature.
- iii. The presence of silica in the feed stream, typical in zirconium production, causes emulsion formation, hindering separation efficiency in the settler, demanding, requiring prep-steps like flocculation and ultrafiltration.
 - iv. Optimal separation requires a carefully designed, multi-stage counter-current process (e.g., typically 5 or more stages) for extraction, scrubbing, and stripping. Optimized flow sheet is still evolving.
 - v. Distribution coefficients are non-linear, dependent on aqueous-phase acid concentration and organic loading, making it difficult to maintain peak efficiency in each stage simultaneously.
- d. Effective waste valorization. Modern processes, including those using MAPO, can now treat raffinate slurry waste to recover 95% pure Hf, producing it as a concentrated solution and reducing waste volumes.
 - e. Intensification of separation by process modelling using CFD. Utilizing CFD-PBM (Computational Fluid Dynamics and Population Balance Model) strategies enables optimized agitation, decreasing the required organic-to-aqueous ratio and improving energy efficiency.

Opportunities & Optimization

There are multiple opportunities and scope in the scientific and technological aspects for the development of an efficient and cost-effective technology for Zr-Hf separation which comprises:

- a. Development of alternative and advanced extractants. Using solvents such as Tri-iso-amyl Phosphate (TiAP) or mixtures like TBP and Cyanex 923 offers better separation, lower acid concentration requirements, and improved Zr/Hf ratios. Mixed Alkyl Phosphine Oxide (MAPO) has shown superior performance in extracting Hf from lean solutions (waste streams).
- b. Molecular Modelling tools can be adopted for identification of next generation extractant with high distribution coefficient and high Zr-Hf separation factor.
- c. Development of improved setup configuration with counter-current operation concept. Using 5-12 stage counter-current setups optimizes the extraction efficiency. Designing for specialized agitation that avoids excessive turbulence in the settling zones prevents re-emulsification.

Conclusions

The preferential extraction of Zr^{4+} ion over Hf^{4+} ion or vice versa followed by their high purity product for different technological application is continuously evolving. As of now, the major equipment used for the separation are mixer-settler, centrifugal extractor or pulse column using the solvent extraction principle. Additionally, separation can be achieved using column chromatography by suitable adsorbent. The next generation solvent system for efficient cost effective Zr-Hf separation can be achieved by extensive use of molecular modeling comprising DFT, MD and AIMD in conjunction with machine learning and artificial intelligence for the identification of the best extractant, diluent, adsorbent and strippant. On the other hand, using the next generation solvent system, pulse column-based extractor can be designed as an alternative equipment to mixer-settler and centrifugal extractor for recovery of high purity Zr and Hf depending on the content and type of impurities in the feed solution.

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Processing of Critical Minerals: Studies on Midstream Activities of Selected Elements in Mineral Processing Division

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Introduction

Critical minerals are strategically important raw materials essential for modern industries, clean energy technologies, defense systems, and hightechnology manufacturing, but are often susceptible to supply disruptions due to limited domestic reserves and heavy import dependence. In the Indian context, critical minerals such as lithium, cobalt, nickel, graphite, niobium, tungsten, and rare earth elements (REEs) have gained significant importance with the country's growing focus on electric mobility, renewable energy deployment, semiconductor manufacturing, and advanced defence systems. To address mineral security concerns, the Government of India has identified a list of critical minerals and initiated several policy measures, including exploration reforms, auction of critical mineral blocks, overseas mineral asset acquisition, and development of downstream processing and value-addition infrastructure under initiatives such as the National Critical Mineral Mission and Atmanirbhar Bharat[1]. The Department of Atomic Energy (DAE), India [2,3], plays a crucial role in the exploration, beneficiation, extraction, and utilization of critical minerals required for nuclear energy and other strategic sectors. Within DAE, the Atomic Minerals Directorate for Exploration and Research is primarily responsible for exploration and resource assessment, while the Materials Group of Bhabha Atomic Research Centre undertakes process flowsheet development and extraction technology research for recovery of these minerals from indigenous resources, which includes both midstream and downstream activities. Commercial scale production and downstream utilization are further supported by industrial units under DAE, thereby contributing to India's self-reliance in strategic mineral supply and sustainable industrial growth.

The development of process flowsheets for the recovery of critical mineral values from ores is highly challenging due to their low-grade occurrence and complex mineralogical characteristics. These challenges arise from the fine dissemination of target minerals, their occurrence in multiple mineral phases, and their association with refractory mineral matrices in many instances. Critical minerals such as lithium, rare earth elements, cobalt, niobium, tantalum, and tungsten are commonly associated with gangue minerals, silicates, oxides, or sulfides, thereby necessitating multiple stages of beneficiation, selective leaching, impurity removal, and downstream purification for efficient recovery. The refractory nature of mineral values often demands intensive pre-treatment methods such as roasting, cracking, or alkali/acid digestion to liberate the valuable phases. Such aggressive treatment schemes increase process complexity, reagent consumption, and energy costs. In addition, the presence of penalty elements and chemically similar impurities complicates selective separation, all of which demand complex separation and purification circuits with tight process control. Variability in ore composition across deposits further limits the development of universally applicable flowsheets, necessitating site-specific optimization. Therefore, sustainable recovery of critical minerals requires integrated flowsheet design that balances metallurgical efficiency, environmental compliance, waste minimization, and economic viability.

This paper discusses and showcases studies conducted in Mineral Processing Division of BARC on the process flowsheet development for the recovery of some critical minerals / metals like REE, Li, Nb, Zr, Hf, Mg, Ni, Co, Cu, Re, Rb, Cs and W from primary as well as secondary resources such as coal fly ash of Indian

origin Critical minerals are strategically important raw materials essential for modern industries, clean energy technologies, defense systems, and hightechnology manufacturing, but are often susceptible to supply disruptions due to limited domestic reserves and heavy import dependence. In the Indian context, critical minerals such as lithium, cobalt, nickel, graphite, niobium, tungsten, and rare earth elements (REEs) have gained significant importance with the country's growing focus on electric mobility, renewable energy deployment, semiconductor manufacturing, and advanced defence systems. To address mineral security concerns, the Government of India has identified a list of critical minerals and initiated several policy measures, including exploration reforms, auction of critical mineral blocks, overseas mineral asset acquisition, and development of downstream processing and value-addition infrastructure under initiatives such as the National Critical Mineral Mission and Atmanirbhar Bharat[1]. The Department of Atomic Energy (DAE), India [2,3], plays a crucial role in the exploration, beneficiation, extraction, and utilization of critical minerals required for nuclear energy and other strategic sectors. Within DAE, the Atomic Minerals Directorate for Exploration and Research is primarily responsible for exploration and resource assessment, while the Materials Group of Bhabha Atomic Research Centre undertakes process flowsheet development and extraction technology research for recovery of these minerals from indigenous resources, which includes both midstream and downstream activities. Commercial scale production and downstream utilization are further supported by industrial units under DAE, thereby contributing to India's self-reliance in strategic mineral supply and sustainable industrial growth.

The development of process flowsheets for the recovery of critical mineral values from ores is highly challenging due to their low-grade occurrence and complex mineralogical characteristics. These challenges arise from the fine dissemination of target minerals, their occurrence in multiple mineral phases, and their association with refractory mineral matrices in many instances. Critical minerals such as

lithium, rare earth elements, cobalt, niobium, tantalum, and tungsten are commonly associated with gangue minerals, silicates, oxides, or sulfides, thereby necessitating multiple stages of beneficiation, selective leaching, impurity removal, and downstream purification for efficient recovery. The refractory nature of mineral values often demands intensive pre-treatment methods such as roasting, cracking, or alkali/acid digestion to liberate the valuable phases. Such aggressive treatment schemes increase process complexity, reagent consumption, and energy costs. In addition, the presence of penalty elements and chemically similar impurities complicates selective separation, all of which demand complex separation and purification circuits with tight process control. Variability in ore composition across deposits further limits the development of universally applicable flowsheets, necessitating site-specific optimization. Therefore, sustainable recovery of critical minerals requires integrated flowsheet design that balances metallurgical efficiency, environmental compliance, waste minimization, and economic viability.

This paper discusses and showcases studies conducted in Mineral Processing Division of BARC on the process flowsheet development for the recovery of some critical minerals / metals like REE, Li, Nb, Zr, Hf, Mg, Ni, Co, Cu, Re, Rb, Cs and W from primary as well as secondary resources such as coal fly ash of Indian origin

Rare Earth Elements

India possesses significant REE resources about 8.2 million tonnes (REO), mainly hosted in monazitebearing beach placer deposits along the coasts of Kerala, Tamil Nadu, Odisha, Andhra Pradesh, and parts of West Bengal. Besides beach sands, recently hard rock deposits such as Ambadongar, carbonatite in Gujarat and alkaline complexes in Siwana Ring Complex (SRC), Rajasthan have been explored[4]. The major strengths of Indian REE resources include large monazite reserves which are rich in Nd-Pr. However, there are several limitations and challenges associated with these resources. Most Indian deposits are enriched predominantly in light rare earth elements (LREE) except

SRC deposits, while heavy rare earth elements (HREE), which are more critical and valuable for advanced technologies, occur in comparatively lower concentrations. In addition, the ores are often low grade and mineralogically complex, making beneficiation and separation difficult and expensive. The occurrence of radioactive thorium in monazite poses significant environmental, regulatory, and material handling challenges during its mining and downstream processing operations. Currently, India produces about 3000 tonnes of REO annually by exploiting monazite of beach sand origin[5]. To mitigate the issue of low HREE and radioactivity, efforts are in place to explore the potential of REE in secondary resources such as coal fly ash, phospho-gypsum and red mud etc. Studies carried out on various hard rock REE resources and coal flyash of thermal power plants are discussed in following sections along with scheme on capturing the associated by or coproducts.

REE and Mg recovery from carbonatites of Ambadongar, Gujarat

The Ambadongar REE deposit, located in the Chhota Udepur district of Gujarat, India, is one of the country's important carbonatite-hosted REE resources associated with alkaline igneous activity. The deposit is primarily composed of carbonatites enriched with bastnäsite, parisite, synchysite, and other fluorocarbonates minerals containing LREE, particularly cerium, lanthanum, neodymium, and praseodymium. The deposit is considered strategically significant because it represents a non-beach placer source of REE in India and has the potential to support domestic supply for clean energy and advanced technology sectors due to vast resource potential of 1.2 million tonnes of REO with average grade 0.94 wt. %[4,6]. The REE are hosted in three different lithologies namely ankerite, breccias and sovite, where ankerite assay highest concentration of REO up to 4 wt. %. Sovite and breccia are lean grade in REE in the range of 0.3-1.0 wt. %. In addition to REE, the Nb, Sr and Mg are potential by-products. Interestingly, ThO₂ content in this deposit is nearly 15 times lower compared to monazite of Indian beach sand origin per unit of REO. However, the high ferruginisation of the mineral phase and the ultrafine (2-15 µ)

and acicular shape of REE bearing minerals makes it challenging to design a beneficiation and hydrometallurgy processes for the recovery of REE. The gamut of study conducted on this ore sample covers 22 bore hole and 3 composite samples and a comprehensive process scheme was designed to recover REE values as well as Mg as a by-product. A simplified process flowsheet is given in [Figure 1](#).

Process flowsheet was designed to recover the REE in a sustainable manner with minimum acid dosage and recycling of reagent and minimising the liquid and gaseous effluents. The technology developed was transferred to Gujarat Mineral Development Corporation for testing at pilot scale and adoption at commercial scale once successfully demonstrated at pilot scale. The overall recovery of the REE stands about 55% with purity of the product Rare Earth Double Sulphate >90%. The recovery of Mg was 30 & 80% depending on the choice of the sequence of certain processes with purity of the product >95%.

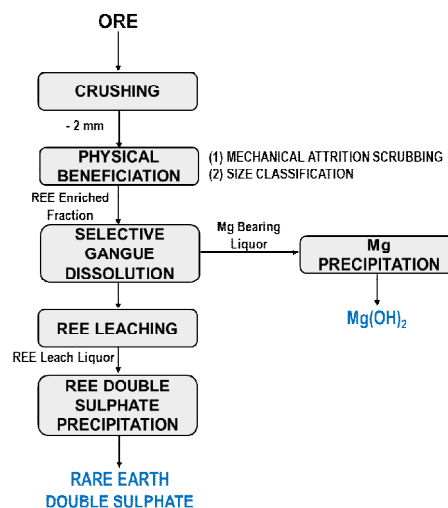


Figure 1: Simplified Process flowsheet for the recovery of REE and Mg from the Ambadongar ore

REE, Nb, Zr and Hf recovery from hard rock type ores of Siwana Ring Complex, Rajasthan

A new REE prospect belonging to the hard-rock category has recently been identified by the AMD in the Siwana Ring Complex (SRC) located in the Balotra

district (Earlier in Barmer till 2023) of Rajasthan, India. The Neoproterozoic peralkaline rocks of the complex have shown encouraging concentrations of HREE along with rare metals such as Nb, Hf and Zr. These metals are hosted in lithologies including alkali granite, microgranite (hypabyssal equivalent of granite), tuffaceous pyroclastic rocks, and alkali rhyolite. The Siwana Ring Complex represents a well-preserved caldera within the Malani Igneous Suite and is predominantly composed of acid volcanic rocks and intrusive ring-dyke granites. The complex covers an area of approximately 800 km² and exhibits a characteristic nearcircular outcrop pattern typical of calderarelated magmatic systems. Several localities within the complex show significant enrichment of REEs, including Gudanal, Bhatikhera, Meli, Phulan, Golia-Gungrot, Mamajikawala, Maylawas, Ludrara, Ramaniya, Indrana, Dantala, Mawri, Magreswar, Nal and Buriwara. Exploration in these areas is still in progress but as per initial approximation, the reserves combined from these deposits may go beyond 1 million tonnes of REO with cut of grade at 0.2% [4,7,8]. The REO grade in these deposits assayed between 0.35-0.50 wt.%. Although the concentration of total REE is low in SRC deposits compared to Ambadongar but nearly 40% of the REE are contributed from HREE, which have high economic and strategic importance. Besides REE, these deposits contain significant quantity of Zr, Nb and Hf. The ratio of concentration of these metals stands approximately fixed at $Zr = 2 \times \text{total REE} = 20 \times Nb = 40 \times Hf$ in all these deposits, making SRC a very attractive group of deposits. Like Ambadongar, SRC deposits too, contain nearly 4-5 times less ThO₂ content compared to monazite of beach sand origin with per unit of REO. In last 5 years, comprehensive process flowsheets for Bhatikhera, Dantala and Ramaniya has been developed for the recovery of REE, Nb, Zr and Hf. The gamut of study conducted on these samples includes detailed chemical and mineralogical analysis, physical beneficiation, leaching, purification using solvent extraction employing ionic liquid and precipitation. Following REEbearing minerals have been identified in Electron Probe Microscopic Analysis (EPMA): monazite, bastnaesite, allanite, rhabdophane and pyrochlore along with

complex REEbearing phases (hydrated Mn-Pb-Ce-Si complex, Fe-Mn-Ce rich complex, hydrated REE silicate, hydrated LREE phosphate, Fe-Ti-Nb-REE silicate and Ca). The Zr and Hf bearing phases are zircon and gittinsite. The silicate gangue minerals analysed were aegirine, quartz, arfvedsonite and K-feldspar. Physical beneficiation using gravity separation gave a scope of about recovering 60% REE in 30 wt.% with similar recovery other associated by-products[9]. Due to the intrinsically refractory nature of REEs, Nb, Zr, and Hf, the ore sample was subjected to sulphuric acid baking at 250–300 °C, followed by water leaching to solubilize the metal values. Nb, Zr, and Hf were selectively extracted from the leach liquor using an ionic liquidbased solvent extraction system and subsequently stripped using an HCl–NaCl mixture.

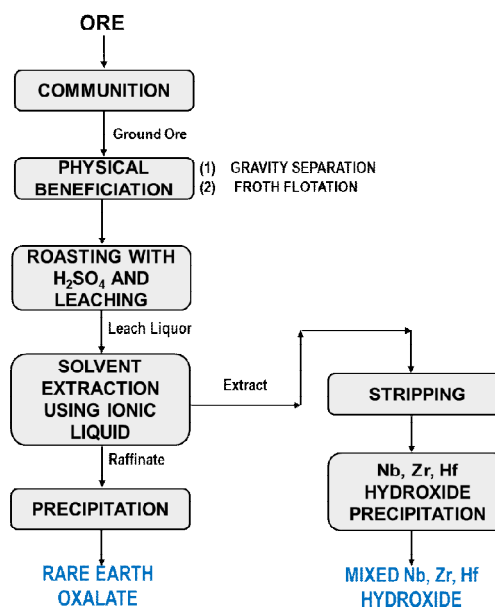


Figure 2: Simplified Process flowsheet for the recovery of REE, Nb, Zr and Hf from Bhatikhera, Dantala ore sample of Siwana Ring Complex

The stripped metal values were precipitated as their respective hydroxides through neutralization. REEs remaining in the raffinate were recovered by oxalate precipitation using oxalic acid. The ionic liquidbased solvent extraction circuit enabled effective and selective separation of Nb, Zr, and Hf. A simplified process flowsheet for the recovery of REE, Nb, Zr and Hf is depicted in [Figure 2](#).

The precipitate obtained after solvent extraction circuit for Nb, Zr and Hf was assaying about 40% Zr, 5% Nb and 1 % Hf with product purity >98%. Interestingly, REE concentration in the product was <0.01%. Similarly, mixed REE oxalate obtained after precipitation using oxalic acid from the raffinate was completely devoid of Nb, Zr and Hf. REE oxalate purity was >95% with <0.1% of Nb, Zr and Hf combined. The integrated process flowsheet designed gave a scope for recovering about 88-90% of REE, 70-75% Nb, 60-65% Zr/Hf values.

Recovery of REE from coal fly ash

As discussed in the previous sections, the commercial exploitation of primary REE resources is constrained by two major challenges: the relatively low abundance of HREE and the associated radioactivity arising from the presence of thorium (Th), uranium (U), and their daughter products. To address these limitations, increasing attention has been directed toward the evaluation of secondary resources such as coal fly ash (CFA), red mud, and phospho-gypsum as alternative sources of REE. Among these, CFA has emerged as the most promising resource owing to its comparatively higher HREE content and relatively simpler extraction pathways.

In India, several research laboratories have undertaken studies to evaluate the occurrence of REE and other critical metals in CFA generated from different thermal power plants. Although these investigations have not yet been systematically coordinated, they have identified several promising sources, notably the CFA generated from the thermal power stations at Neyveli. Detailed characterization of Neyveli CFA samples collected over different time intervals indicated total REE concentrations in the range of 1000–2200 ppm, with a relatively consistent HREE:LREE ratio of approximately 25:75. The major chemical constituents of the CFA were found to be SiO₂ (40–50%), Al₂O₃ (15–25%), Fe₂O₃ (7–15%), CaO (5–18%), and MgO (1–4%).

Various process routes employing H₂SO₄, lactic acid, deep eutectic solvents, and HCl have been investigated for REE recovery from Neyveli CFA[10–12]. Among

these, the hydrochloric acid route was identified as the most suitable due to its lower reagent cost, operational simplicity, and fewer process steps. In this process, REEs were leached using dilute HCl (1.0–1.5 M) and subsequently precipitated as crude mixed REE oxalates. Purification of the crude oxalate was achieved through a two-stage refining process to obtain highpurity mixed REE oxides (>99%). Initially, the crude REE oxalate was calcined at 600°C and dissolved in dilute HCl, followed by neutralization of the solution to pH 8 to selectively precipitate REE as hydroxides while retaining calcium in the barren liquor. The precipitated REE hydroxides were then redissolved in dilute HCl, re-precipitated as oxalates, and calcined to produce the final mixed REE oxide product. The resulting oxide assayed >99% total rare earth oxides (REO), with approximately 26% comprising HREE oxides. The combined impurity content, including SiO₂, Al, Fe, Ca, and Mg, was maintained below 1%, demonstrating the technical feasibility of producing highpurity REE products from coal fly ash.

An MoU have been set up between BARC and NLC India Ltd to set up a pilot to demonstrate the process flowsheet developed. A succinct process flow diagram for the recovery of REE from the CFA of Neyveli is depicted in [Figure 3](#).

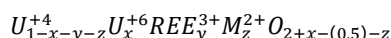
Recovery of critical minerals from uranium ore deposits

It is very well known that uranium ore deposits are formed in the reducing environments and require the presence of sulphide minerals or carbonaceous matter to reduce the hexavalent mobile complex of uranium to make a deposit in mixed +4/+6 state. It's not only the uranium which have good affinity towards sulphur but also many other weak acidic metals e.g., Zn, Cu, Co, Ni, Mo, Re, Ag, Au etc. In many places ore deposits of Cu and uranium have been found in vicinity due to sulphide minerals. In Indian U ore deposits too, the trend is same. The existing mine of Jaduguda, contains significant concentration of some of the critical minerals like Ni, Mo and Re besides other important non-fuel energy element Cu. M/s. UCIL operated By-product Recovery Plant during 80's to early 2000 for recovering the three important minerals – Cu, Ni and Mo, based on the process flowsheet developed by Mineral

Processing Division (then Ore Dressing Section). The process scheme essentially involves multiple stages of flotation using both cresylic acid-cresote oil and pine oil which was later supplemented with alkyl xanthates. The plant was closed due to steady depletion of the byproduct contents in the blended uranium ores fed to uranium mill. However, with renewed interest in non-fuel energy minerals the uranium ore of Jaduguda alone chemically analysed for its byproduct values. The ore assayed about 1000 ppm of Ni, 150 ppm of Cu, 120 ppm of Mo and 40 ppm of Co in 2025. A flotation circuit using sodium isopropyl xanthate as collector was designed consisting of 4 stages of rougher flotation and 8 cleaner stages. The assays of Cu, Mo, Ni and Co elements in the final cleaner float was 18, 8, 33 and 1 wt.% respectively. Interestingly, the molybdenite in Jaduguda is associated with porphyry type copper deposition. Such Mo mineral accommodates good concentration of another important critical metal namely rhenium (Re). The Re content of MoS_2 was about 270 ppm in Moly concentrate assaying Mo 45% [13]. Work is presently in progress to assess the Re potential of new ore samples collected.

Similarly, in the metasomatite type uranium ore of Rohil – Ghateswar, Sikar district, Rajasthan occurrence of Cu and Mo was confirmed. The ore sample assayed about 0.04% U_3O_8 , 0.14% Cu, 0.024% Mo with total S of 4.3%[13]. The majority of the S is contributed from pyrrhotite FeS and pyrite FeS_2 with concentrations nearly 10 and 1% respectively. Froth flotation scheme was designed to recover the Cu and Mo from this ore sample too and up to 20 times enrichment were achieved using sodium isopropyl xanthate as collector. Although FeS , pyrrhotite minerals are not critical minerals but due to their magnetic nature the mineral values can be easily separated using low intensity magnetic separation with field intensity of 3 k Gauss[14]. This mineral can be used to generate H_2SO_4 in situ upon oxidative pressure leaching with O_2 at elevated temperature. The H_2SO_4 generated from pyrite cinders can be used in the leaching of the uranium and other critical metals in the same plant.

Besides, Cu, Mo, Ni and Co, co-existence of REE is also established from petro-mineralogical studies of Mineral Processing Division. Uraninite can host many elements with ionic radii similar to U^{4+} in eight-fold coordination. This applies particularly to Th^{4+} , the rare-earth elements (REE^{3+}), and Y^{3+} [15].



Besides, REE occurrence have been observed in discrete minerals such as allanite, monazite and bastnaesite. All the lattice substituted ions are released into leach liquors during hydrometallurgical processing their ores using H_2SO_4 . Although dissolution of refractory discrete phases is not feasible under mild acid conditions adopted for uranium but the REE existing in uranium phases gets incidentally dissolved during leaching. The U sample of Naktu, UP; SingridungriBanadungari, Jharkhand and Geratiyon ki Dhani, Rajasthan were assayed about 200, 1200 and 500 ppm of REE respectively. The leachability of the REE under the conditions adopted for U were 70, 30 and 55% respectively from these ore samples. Since REE exist in cationic nature in sulphate media at pH 1.5-2.0 and U exist as uranyl sulphate anion, their separation becomes quite easy. Uranium from the leach liquor is purified and concentrated using anionic resins

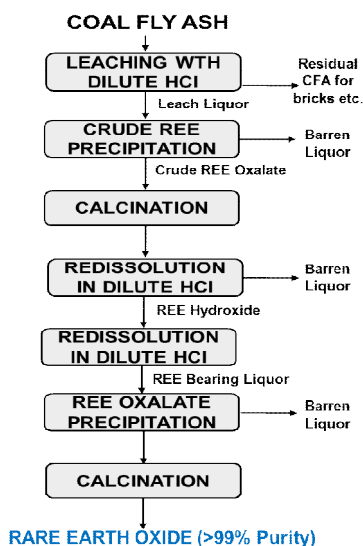


Figure 3: Simplified Process flowsheet for the recovery of REE from the coal fly ash of Neyveli, Tamilnadu

leaving REE in the barren liquor. The REE from barren liquor were recovered by precipitation using Na_2SO_4 and oxalic acid as precipitation reagent to recover them as REE double sulphates and REE oxalate respectively. The purity of the products obtained was >80%. Such single step recovery of REE from the uranium barren liquor avoids lengthy process flowsheets adopted for the recovery of REE from primary resources. Extraction of all the co-existent metal ions of valuable nature is essential for multiple reasons chiefly for upholding sustainability goals.

Lithium and associated byproducts - Rb and Cs

Lithium is one of the most important critical minerals for India because of its essential role in manufacturing rechargeable batteries used in electric vehicles, mobile phones, laptops, and large-scale energy storage systems. With India rapidly expanding renewable energy capacity and promoting electric mobility, demand for lithium is increasing significantly. India is highly dependent on imports from countries such as Australia, Chile, and China, creating supply chain vulnerabilities. Process schemes were developed for the recovery of Li as its hydroxide monohydrate from these mineral concentrates. For spodumene of Li_2O grade of 5.35%, decrepitation was carried out at 1000 °C to change the chemically inert alpha phase to the relatively permeable beta phase. The beta spodumene was treated with H_2SO_4 at 250 °C for the ion exchange reaction which replaces Li in the beta spodumene with H^+ of acid. This reaction also brings out some unwanted metal ions into the liquor, which were separated by an impurity removal step and subsequently Li was precipitated as its carbonate and converted to hydroxide monohydrate of purity >99% in separate step. In the case of lepidolite mineral direct salt roasting with $\text{CaSO}_4 + \text{Na}_2\text{SO}_4$ at 1000 °C followed by aqueous leaching gave release and solubilization of Li values. Besides lithium, the mineral concentrate assayed two other important metals viz., Rb and Cs up to a concentration level of 0.76% and 0.19% as Rb_2O and Cs_2O respectively. Although Rb and Cs are not listed in the critical mineral list of 2023 MMDR act but their economic values are very high. Recovery of valuable metals associated with critical metal can help in

design of economic process flowsheet for the recovery of critical metal from a low-grade ore deposit. About 90% Li, 85% leaching efficiency of Rb and Cs could be achieved using salt roasting and water leaching. An integrated process flowsheet which can yield Li, Rb and Cs has been developed in the Division.

Beneficiation of Tungsten ores

Tungsten is a strategically important critical mineral due to its exceptional physical and chemical properties, including the highest melting point among metals (3422°C), high density, hardness, corrosion resistance, and excellent wear resistance. These properties make tungsten indispensable in sectors such as defense, aerospace, electronics, mining tools, cutting and drilling equipment, superalloys, catalysts, and clean energy technologies. Tungsten carbide is extensively utilized in hard metals for the manufacture of cutting tools, as well as liners for crushing and grinding equipment. Tungsten-based alloys are also employed in armourpiercing ammunition, radiation shielding, and high-temperature applications owing to their superior mechanical and thermal properties. Due to its limited global production, geographically concentrated supply chain, and increasing demand in advanced manufacturing sectors, tungsten has been designated as a critical mineral by several countries, including India.

India's total tungsten ore resources, as per NMI data (1st April 2020) under the UNFC classification, are estimated at 89.43 million tonnes containing 1,44,650 tonnes of WO_3 , all categorized as Remaining Resources[16]. Worldwide resources of tungsten stand at 4.5 million tonnes. China leads in both the production as well as in the resources accounting nearly 80% and 50% respectively[5]. In India, these resources are primarily concentrated in Karnataka (41%), Rajasthan (27%), Andhra Pradesh (17%), and Maharashtra (11%), while the remaining 4% occurs in Haryana, Tamil Nadu, Uttarakhand, and West Bengal. Important tungsten occurrences are reported from several deposits, including Degana, Rajasthan, where WO_3 grades range from 0.09%–1.62%, and Balda, Sirohi, with average grades of 0.24%–0.48%. Other deposits in Sirohi

district such as DewaKaBera and Udwaya contain 0.03% and 0.27% WO_3 , respectively. In Bankura, West Bengal, the deposit averages 0.1% WO_3 . The KuhlKhabana-Agargaon belt in Maharashtra shows grades ranging from 0.01%–0.48% WO_3 across different blocks. Additionally, scheelitebearing gold ore and tailings at Kolar Gold Fields and Mysore mines in Karnataka are considered potential secondary tungsten sources, containing 0.01–0.05% WO_3 [16].

In the Degana deposit of Rajasthan, primary wolframite mineralization occurs in three distinct modes: (i) as disseminated crystals of varying sizes within well-defined quartz veins or pegmatites cutting across granites and adjoining phyllites; (ii) as eluvial and graveltype placer deposits; and (iii) as disseminations within granite and phyllite, locally concentrated in stockwork zones. At present, quartz-vein type wolframite deposits are mainly exploited through manual hand-picking methods. To enhance tungsten recovery, process flow sheets for the mechanical beneficiation of such ores have been developed by the mineral processing division (MinD) of BARC. The developed flow sheet involves crushing followed by classification at 28#, with the coarse and fine fractions treated separately using jigs and shaking tables, respectively. Final upgrading to obtain a marketable concentrate includes tabling for silicate gangue removal, flotation for sulphide mineral separation, lowintensity magnetic separation to remove pyrrhotite, and highintensity magnetic separation for final concentrate purification. The process flowsheet developed could enrich the low-grade ores of grades varying between 0.02%–0.2% WO_3 to 1.2% to 50% WO_3 based on the different recovery. At 1.2% WO_3 recovery was 60%, whereas at recovery reduced to 20% at 25% WO_3 and further grade improvement to 50% WO_3 was achieved at 10% recovery[17]. Beside W, good concentration of zinnwaldite was observed which is a good source of lithium and can host up to 7% of Li_2O values. MinD also developed process flowsheets on other promising W deposits mentioned in the previous section using combination of gravity – magnetic – flotation separation techniques. The schemes were efficient enough for recovery of both the W minerals like wolframite and scheelite.

Other activities related to critical minerals

MinD also studied exhaustively beneficiation of tin values from two of the most well-known deposits of the country Bastar in Chattisgarh and Tosham of Haryana. It also made detailed investigations on exploiting the cobaltiferous pyrite of Kalyadi copper deposit, Karnataka, adopting sulfation roasting for capture of contained Co values. Besides above-mentioned critical minerals, Division is presently actively working on mapping and tapping of coal, coal fly ash and zinc plant samples from different parts of country for assessing the potential for Ge and Ga values.

Conclusions

The studies undertaken in the Mineral Processing Division of BARC demonstrate a comprehensive and strategic approach toward strengthening India's capabilities in the midstream processing of critical minerals required for nuclear energy, clean energy technologies, and defence applications. The process flowsheets developed for the recovery of rare earth elements, lithium, niobium, zirconium, hafnium, magnesium, and tungsten from both primary and secondary resources highlight the division's multidisciplinary expertise in mineral beneficiation, hydrometallurgy, solvent extraction, and product purification. Considerable progress has been achieved in developing sustainable and integrated extraction routes for complex indigenous resources, including Ambadongar carbonatite, Siwana Ring Complex hardrock deposits, uranium process liquors, coal fly ash, spodumene, lepidolite, and tungstenbearing ores.

The investigations effectively address several challenges associated with Indian critical mineral resources, such as low ore grades, refractory mineralogy, fine dissemination, associated impurities, and radioactivity. The developed process schemes emphasize selective metal recovery, reduced reagent consumption, recycling of process streams, minimization of effluent generation, and recovery of multiple value-added byproducts, thereby enhancing overall resource efficiency and process economics. Collectively, these

studies provide a strong technological foundation for the indigenous development of critical mineral processing capabilities and contribute toward achieving longterm resource security and strategic self-reliance for the country.

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Dr. Ram Karan is a researcher specializing in process flowsheet development for uranium, rare earth elements (REEs), and other critical minerals/metals. His expertise includes mineral beneficiation, hydrometallurgy, and chemical processing of primary and secondary resources. He has contributed significantly to beneficiation and extraction studies on complex REE deposits at Ambadongar (Gujarat) and Siwana Ring Complex (Rajasthan), and secondary resources such as Neyveli coal fly ash. His work has led to innovative and scalable recovery flowsheets for REEs, niobium, zirconium, hafnium, and associated metals, with technology acceptance by GMDC and NLC India Limited. He also works on green extraction technologies using biodegradable organic acids and Deep Eutectic Solvents.



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Dr. T. Sreenivas was former Head of the Mineral Processing Division, BARC Hyderabad, with extensive expertise in recovery of strategic and critical mineral values from primary and secondary resources. His areas of interest include mineral beneficiation, hydrometallurgy, surface chemistry and geometallurgy. Over the years he contributed significantly towards translational research particularly in respect of uranium and rare earth ores exploitation and also on concepts of comprehensive extraction or maximum use of mined material. Presently, he is serving as the DAE-Homi Sethna Chair. Dr. Sreenivas has authored and co-authored numerous technical papers and has actively contributed to national scientific and technological initiatives in the minerals sector. He was recipient of DAE-Homi Bhabha Science and Technology Award and also National Geoscience Award from Ministry of Mines.

Separations and Purification of Tellurium

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Abstract

Tellurium, a relatively less explored element of the periodic table that scarcely comes upon in a typical discussion about critical elements, is a strategically important chalcogen element that can play a prominent role in the technological growth and sustainability [1]. Be it energy generation, semiconductor devices, metallurgy, optical materials or even various chemical methodologies, the unique metalloid properties of tellurium have made it indispensable to our modern life and technology in more ways than most people are typically aware of [1-3]. Apart from its application-oriented demands, the other factor that makes it a critical mineral in a geopolitical context is its relative rarity on earth, having an abundance in earth crust that is hundreds of times lesser than even thulium, the rarest stable member of so-called rare earth elements [3]. Due to the strict requirements of the physical properties for many of the advanced technologies, many applications of tellurium call for the need of very high purity form of the element. Such preparation of high purity tellurium requires efficient separation and purification techniques because naturally occurring tellurium is usually associated with many elemental impurities that, even at ppb levels, can adversely affect the properties and performance of the desired end-material [4]. This article presents a modest review on the technological relevance of tellurium and strategies for its separation and purification.

Introduction

Despite being a common element in the whole of the universe, tellurium represents one of the rarest elements in the earth crust. The contrast between abundance of tellurium in the universe and its scarcity on Earth is one of the most striking "disappearances" in nature. The mystery is

explained by some simple facts of chemistry. During the early, hot stages of Earth's formation, the free hydrogen rich conditions of the solar nebula led to the formations of hydrides of tellurium, which were highly volatile and lost into deeper space as gas before the planet could fully solidify. Most of the remaining tellurium that did not escape likely dissolved into the molten iron due to its siderophilic nature and sank into the core, leaving the crust depleted. This led to a scarce abundance of the metal, comparable to that of platinum (~ 1 µg/kg) [3]. However, unlike platinum, which is found in its native state, tellurium is reactive and its rare occurrence in earth's crust is often found in a disguised form via bonding to other metals like gold, silver, or copper, producing what are typically referred to as tellurides [5]. The combination of its rarity and the reactivity meant that the world had to wait for the birth of modern analytical chemistry in the late 18th century to properly identify and isolate it [6].

Before we delve deeper into the complexities of the science behind the isolation and the refining of tellurium from its mineral sources, it is appropriate to discuss and get some insights into its geochemical distribution throughout the earth. As already mentioned, while tellurium is exceptionally rare in the earth's crust, its occurrence in native form is even more infrequent [7]. The native occurrence of tellurium is almost exclusively observed in hydrothermal ore veins [8]. These are cracks in the earth's crust, where hot, mineral-rich fluids have circulated and deposited their contents as they cooled. In the native state, tellurium is a metalloid mineral with silvery white appearance. Although the crystal structure of native tellurium has trigonal symmetry, it is more often found in massive irregular or granular forms because of its chaotic growing conditions [9]. Because of tellurium's chemical affinities, native tellurium is rarely alone. It is usually found alongside

native gold, bismuth, and sulfide minerals[5]. In fact, the initial discovery of tellurium in the late 18th century was in an ore from a gold mine in Romania, by an Austrian mineralogist Franz-Joseph Müller von Reichenstein [10]. Although the naming of the element was done by Martin Heinrich Klaproth after the Latin 'Tellus' meaning Earth [11].

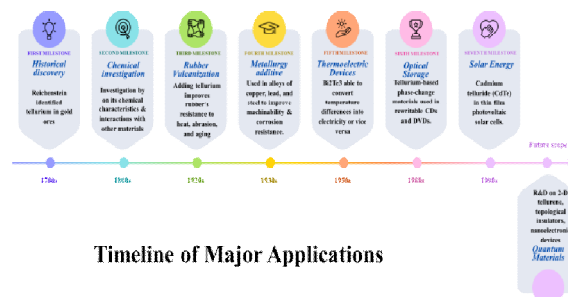


Figure-1. Timeline of major applications[18-24].

Due to the high reactivity tellurium is more frequently encountered in a combined state. This chemical nature, in particular affinity for noble metals such as gold, silver, copper and other elements such as lead and bismuth, has given rise to a distinctive class of minerals known as tellurides, famous in the mining world. Most common mineral tellurides include Calaverite (AuTe_2), Sylvanite ($(\text{Au}, \text{Ag})\text{Te}_2$), Petzite (Ag_3AuTe_2), Hessite (Ag_2Te), Krennerite (AuTe_2), Altaite (PbTe) etc. Interestingly, in the Australian gold rush of late 1800s, miners often discarded the calaverite in their search of gold, mistaking it for some pyritic material. Later, its proper identification as a telluride of gold sparked a second gold rush for its mining from the discarded materials. It was from the mineral calaverite, that the chemist Klaproth isolated tellurium form, just before assigning its name [11]. Despite the geological importance of such tellurides, the most dominant useable sources of tellurium worldwide in modern times are the anodic slimes produced during the electrolytic refining of copper [12]. A combination of factors is responsible for this, among them the primary factors are economics, concentration and availability. The rarity of tellurium in earth crust makes the tellurium ores too small in quantity to mine profitably by themselves. In contrast, the refining of copper, which is done globally in gigantic quantities as a common metal, produces leftover anodic slimes in which the concentration of tellurium is thousands of times higher than normal

rocks [12]. Being a chalcogenide, tellurium tends to occur dispersed in sulfide ores of gold, silver, lead and more importantly copper, in very low concentrations. Despite the low concentration, the total amount becomes significant because of the massive scale of copper mining, compared to the smaller scale of gold mining for example. This makes the extraction of the metal as a byproduct of copper refining, while using the existing infrastructure for copper, more efficient economically. Apart from that, some amount of tellurium is also extracted from refinery residues of lead, gold and selenium, but usually in smaller scales [13].

Tellurium also occurs in oxidized forms called tellurites (TeO_3^{2-}) and tellurates (TeO_4^{2-} or TeO_6^{6-}), which typically form in the oxidation zones of telluride ore deposits near Earth's surface [14]. Although these oxidized minerals are generally rarer than tellurides, these are chemically and geochemically interesting. These secondary minerals are typically formed during weathering when oxygenated groundwater alters primary tellurides such as Calaverite and Hessite. Geochemically, tellurides contain Te in reduced oxidation states (usually -2), while tellurites contain Te(IV) and tellurates contain Te(VI), the highest oxidized state.

Belonging to the group 16 of the periodic table, the chalcogenide tellurium is chemically similar to Sulfur and Selenium. However, the large difference in ionic radii between sulfur and tellurium makes the presence of the latter very low in common sulfide minerals, lower than the amount of selenium in these minerals.

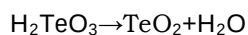
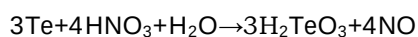
Physical & Chemical Characteristics:

Since the extractive metallurgy and purification techniques of all metals are strictly based upon their physical and chemical characteristics, the understanding on these properties guides for appropriate and economic mode for their extraction and purification. Also, the understanding on these properties enlightens their application prospects. The silvery-white metalloid possesses unique metallic and nonmetallic physical, chemical, and engineering characteristics that make it valuable in modern electronics, metallurgy, and energy technologies.

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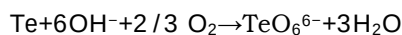
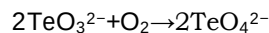
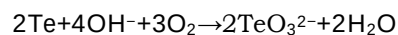
Tellurium is an intrinsic p-type semiconductor with a narrow band gap of approximately 0.35 eV at room temperature [15]. Its electrical conductivity is highly anisotropic and increases slightly upon exposure to light, a characteristic of photoconductive material. Its thermal conductivity is also low compared to metals, typically around 2-3 W/mK. It is also anisotropic, meaning heat flows differently along certain directions depending on alignment of atoms in those directions. It has a melting point of 449 °C, making it significantly volatile compared to other semi-metals or transition metals. It is also prone to sublimation at high temperatures, particularly in vacuum or inert gas or hydrogen flow [16]. This behaviour is utilized in purification techniques like vacuum distillation. While the pure element requires heat to vaporize, many of tellurium's chemical compounds organotellurium compounds, hydrides and halides are highly volatile even at room temperature [28]. Its oxide, TeO₂, is also more volatile than the metal itself; however, the volatility of its fellow chalcogenide oxide, SeO₂ is significantly more. This fact can also be utilized in the separation of Te and Se [17]. The metalloid tellurium is highly brittle in solid form, with low hardness and mechanical strength. This feature is often utilized to make structural alloys more machinable with minute tellurium addition [18].

Tellurium is stable in air and water, and oxidises when heated in air to form TeO₂, with +4 being the most stable oxidation state. Additionally, it also shows highest oxidation state of +6 and lower states like -2, +2 in highly oxidizing & reducing conditions [30]. Tellurium is chemically inert to mild non-oxidizing acids like HCl, dil. H₂SO₄, because its reduction potential is relatively high. However, with strong oxidizing acidic conditions like with conc. HNO₃ or hot conc. H₂SO₄, it is easily oxidized to Te (IV) compounds like H₂TeO₃ or TeO₂[19].

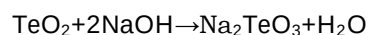
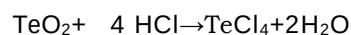


Similarly, the metal is chemically inert to mild bases, but with strong alkalis like

NaOH or KOH in oxidizing conditions, it reacts vigorously to form tellurites (TeO₃²⁻) and tellurates (TeO₄²⁻ or TeO₆⁶⁻).



Tellurium dioxide (TeO₂) is insoluble in water, and it is amphoteric in nature, meaning it reacts and dissolves with both acids and bases. This amphoteric property forms the basis for selective dissolution and purification strategies in purification. Among the metal tellurates/ tellurites, the alkali salts are highly soluble in water while the heavy metal salts are insoluble. These ionic groups are more stable in alkaline media while some precipitation can take place in acidic media. The reactivity of tellurium with metals is also significant at high temperatures, forming tellurides as discussed earlier (-2 oxidation state)[19].



Applications and Importance:

The combination of several of these physicochemical properties make tellurium highly valuable for advanced technological applications [1,17-21]. The increasing importance of tellurium as a strategic material arises from its unique role established in the several fields and some of them are briefed below:

➤ Thin-Film Solar Photovoltaics:

Approximately 70% of the world's refined tellurium is consumed by the solar energy sector, specifically in Cadmium Telluride (CdTe) thin-film solar cells. CdTe is the primary commercial alternative to traditional silicon-based solar panels, yielding more energy than silicon panels under real-world conditions. CdTe panels perform exceptionally well in high-temperature, humid, and low-light environments, and are highly favored for massive, utility-scale solar farms [18].

➤ Thermoelectric Energy Harvesting & Cooling:

Tellurium-based compounds, most notably Bismuth Telluride Bi₂Te₃)

and Lead Telluride (PbTe), are the industry gold standard for thermoelectric devices. These devices provide silent, vibration-free, highly precise cooling in computer microprocessors, portable refrigerators, laser diodes, and laboratory instrumentation by the Peltier effect (creation of temperature gradient upon passage of electric current). Conversely when subjected to a temperature gradient, they generate electricity (Seebeck effect). These are used to capture waste heat from industrial machinery and automotive exhausts to improve overall energy efficiency. Such conversion of heat into electricity has also been used in Radioisotope Thermoelectric Generators (RTGs) to power deep-space probes where solar energy is unavailable. These use PbTe to convert the heat of decaying plutonium directly into electricity [20].

- **Infrared detectors and optical devices:** Tellurium is alloyed with mercury and cadmium to produce Mercury Cadmium Telluride (HgCdTe), an incredibly sensitive semiconductor used to manufacture state of the art infrared (IR) sensors to be used in night-vision goggles, thermal imaging cameras, and missile guidance systems. Its ability to detect tiny variations in heat signature makes it irreplaceable in modern aerospace and defense engineering [21].
- **Alloying additives in metals:** Addition of minute quantities of tellurium (0.02% to 0.1%) in steel and copper drastically improves the machinability of these materials, meaning that the metals can be sliced, drilled, and shaped with minimal wear on industrial cutting tools [35, 36]. In addition, tellurium is added to lead plates to improve their mechanical strength, vibration resistance, and chemical durability against sulfuric acid in lead-acid batteries, extending the lifespan of industrial batteries used in telecommunications and power grids [22].
- **Electronics and phase change memory materials:** Chalcogenide glasses containing tellurium (such as GeSbTe) are capable of switching

rapidly between amorphous (disordered) state and a crystalline (ordered) state upon electrical or optical impulse. These are used to write binary code (1 and 0) in non-volatile Phase-Change Memory (PCM) chips [23].

- **Rubber vulcanization:** Synthetic rubber vulcanized with tellurium exhibits mechanical and thermal properties that are superior to sulfur-vulcanized materials in many ways. The function of Te is closely similar to that of sulfur.
- **Other applications:** Some oxides of Tellurium serve as components of commercial oxidation catalysts that are used for the manufacture of acrylonitrile in polymer industry. While some Te bearing compounds act as specialized pigments for ceramics. Even in radiopharmaceuticals, Tellurium is used as a precursor in the production of ^{131}I , a diagnosis as well as treatment tool in cancer.

Thus, the applications of the element are multitude and its major uses have evolved since the time of its discovery. It is demonstrated in Figure-1. At the same time, the global demand and consumption of tellurium has steadily climbed over the years. In current times use is distributed differently among different technological sectors [1,23,24]. Apart from these established uses of the element, modern scientific research is still exploring newer ways in which tellurium can play a critical role in societal advancements. Tellurium is emerging as a "chalcogen cathode" for next-generation aqueous Zinc-ion batteries. It offers high electrical conductivity and high volumetric capacity compared to traditional sulfur-based cathodes. In recent years, Tellurium has gained significant attention in nanotechnology and quantum-material research due to its unique electrical and optical properties. Tellurium-based materials, such as tellurene and topological insulators, are being investigated for applications in flexible electronics, quantum computing, spintronics, and next-generation electronic devices [25].

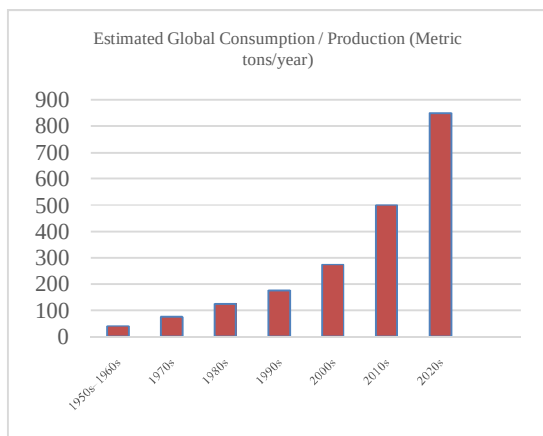


Figure-2. Estimated global production of Te over the years.[34,35]

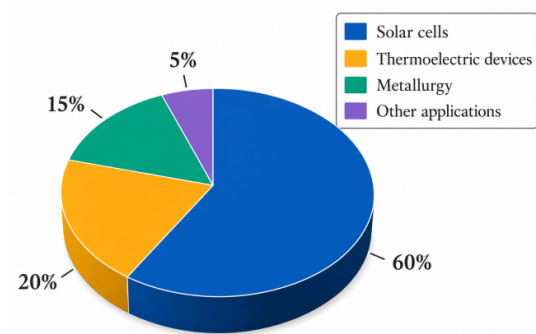


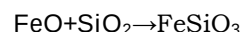
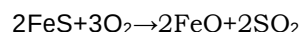
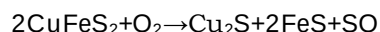
Figure-3. Te utilization in different sectors [24].

Many of these applications require tellurium of very high purity, typically in the range of 99.99% to 99.9999% [20]. The preparation of high purity tellurium requires efficient separation and purification techniques because naturally occurring tellurium is usually associated with many impurities such as selenium, sulfur, copper, lead, gold, silver, bismuth etc. Trace impurities, even at ppm or ppb levels, significantly influence electrical conductivity, thermoelectric efficiency, crystal growth behavior, and optical performance [20,21,22]. Consequently, separation science plays a crucial role in transforming crude tellurium-bearing intermediates into ultra-high purity products. We will be discussing important aspects of these separation techniques in the following sections.

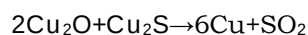
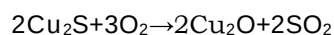
Sources of tellurium for extraction:

Considering the fact that Tellurium recovery is tightly connected to the electro-refining of copper, it is essential to mention

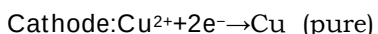
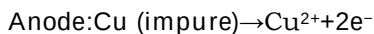
the typical process adopted for Cu extraction. The industrial extraction of copper from its sulfide ores mainly involves a sequence of steps. Mineral ores like chalcopyrite (CuFeS_2) is crushed after mining and concentrated by froth floatation, where the powdered ore is mixed with a solution of frothers in water and bubbling of air produces bubbles to which the hydrophobic sulfide particles attach and float. The concentrate from the froth is then heated in air, in a process similar to partial roasting. In the controlled oxidation, the more thermodynamically favorable reaction of FeS to FeO takes place, while the copper remains largely as a sulfide. This also removes moisture, organic matter and volatile impurities like As, Sb in the process. The oxide FeO formed has high reactivity with silica. This is utilized in the following smelting processing where the mixture is heated over 1200°C with a silica flux (pyro-metallurgical smelting). As a result, iron oxide reacts with the silica flux to form a lightweight, glassy molten slag at the top (FeSiO_3), which is skimmed off and discarded, while the bottom layer contains the molten pool of copper sulfide and some remaining iron sulfide ($\text{Cu}_2\text{S} \cdot \text{FeS}$), together referred to as copper matte.



This is followed by the process called Bessemerisation, in which high-pressure air or oxygen is blown through the molten matte. In this process the remaining reactive iron sulfide is oxidized to slag (FeSiO_3) to be poured off, and the oxygen reacts directly with the copper sulfide, driving off the sulfur as sulfur dioxide gas and leaving behind metallic copper called blister copper because escaping SO_2 creates surface blisters (~98.5% pure). Then, the blister coppers are melted in an anode furnace with oxygen blowing to remove remaining sulfur. This step is followed by a heat treatment with a reducing agent like natural gas or green wood logs to remove excess oxygen (pyrotechnic refining). This produces thick rectangular plates called copper anodes (~99.5% pure).



Finally, in the electrolytic refining step, the cast copper anodes are suspended in large concrete tanks filled with an acidic copper sulfate (CuSO_4) electrolyte. Alternating between them are thin starter sheets of pure copper (the cathodes). An electric current is turned on, and the copper ions are released from the impure anode and migrate to cathode and deposited as 99.99% pure copper. Soluble base metals (like nickel, iron, and zinc) dissolve into the liquid and stay there. Noble metals like gold, silver, and platinum cannot dissolve at this voltage. As the surrounding copper matrix pulls away, they slide off the face of the anode plate and settle. Insoluble tellurides and selenides remain and fall to the bottom.



The pure copper cathodes are pulled out while the heavy, muddy residue at the bottom of the tank is pumped out, filtered, and processed as anodic slime to extract precious metals. These insoluble anodic slimes, called copper anodic slime (CAS), typically contain gold, silver, Pt group metals, lead, bismuth compounds, selenium, and tellurium, the element of current discussion. Tellurium in the anodic slime mainly present as tellurides, like Cu_2Te , Ag_2Te , AuTe , etc. This is mainly because of their low solubility, and oxidation resistant, and hence not easily oxidized under electro-refining conditions [26].

The purification of tellurium presents several scientific and technological challenges on account of several factors. They include:

- The difficulty in separation from other chalcogenides, particularly selenium, which behave chemically identically during refining.
- Association of Te with noble metals and heavy metals such as Cu, Ag, Au, As, Sb, Bi, Pb in the anodic residues.
- Presence of multiple oxidation states of Te.
- Volatility of tellurium compounds.
- Environmental constraints related to toxic emissions.

- Requirement of stringent impurity control etc.

Extraction of Tellurium of CAS:

The general strategy for the extraction of tellurium from the copper anodic slimes (CAS), collected from the bottom of the copper refining tanks, involves a highly specialized chemical journey. This process has also gone through many changes as time has passed. Tellurium (Te) is a minor but incredibly valuable component of these slimes, usually making up anywhere from 1% to 10% of the dried mud [27].

Because tellurium chemically behaves as a metalloid, its extraction relies on carefully altering pH and using selective reduction. Two broad classes of techniques, namely, pyrometallurgical and hydrometallurgical processes, have been primarily used for the recovery of tellurium from copper anode slimes (CAS).

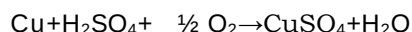
Pyrometallurgical methods include acid baking, oxidation roasting, soda roasting, chlorination, and vacuum distillation, whereas hydrometallurgical approaches involve alkali leaching, oxidative acid leaching, and high-pressure alkali/acid leaching [28]. Presently, an integrated pyro-hydrometallurgical recovery route, which combines the processes based on efficiency, is used as common practice for the industrial tellurium recovery in [29]. In addition, emerging techniques such as microwave- and ultrasonic-assisted processes have also shown considerable potential for enhancing tellurium recovery efficiency [30].

The combined pyro-hydrometallurgical process can be broken down into the following steps:

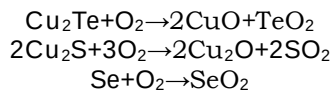
Acid leaching: Before targeting tellurium, the massive amount of residual copper left in the slime (CAS) is recovered. The wet anodic slime is treated with dilute sulfuric acid (H_2SO_4) while air or oxygen is blown through the slurry. The copper dissolves completely into the solution as copper sulfate (CuSO_4) and is recycled back to the copper refinery. The tellurium, along with gold, silver, and selenium, remains in the solid residue. This is primarily due to the precious metals (especially gold and silver) having incredibly high chemical stability and very low electrode potentials, their respective telluride compounds like

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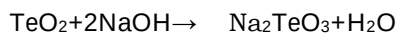
compounds like Ag_2Te and AuAgTe_4 are highly resistant to be dissociated apart by simple sulfuric acid.



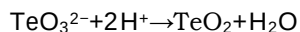
Oxidative Roasting: The roasting step acts as a critical chemical separator of Te and Se of the anodic slime. The dried anodic slime is heated strongly in the presence of air or oxygen, usually at temperatures of about 300–700°C. Under these oxidizing conditions, tellurium compounds (like CuTe) are converted into oxides of tellurium (TeO_2) and Copper (CuO). Selenium is volatile at these temperatures and gasifies as SeO_2 , allowing for an initial separation of selenium from tellurium. Similarly sulfur also volatilizes as SO_2 . Other non-volatile oxides remain in the solid.



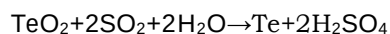
Alkali leaching: To separate tellurium from the noble metals (gold and silver), the residue must be chemically transformed so the tellurium becomes soluble. This is usually done using an alkaline baking/leaching process. The roasted material is leached using a strong sodium hydroxide (NaOH) solution. Tellurium dioxide reacts with the base to form soluble sodium tellurite (Na_2TeO_3), while leftover selenium converts to sodium selenate or selenite. The sodium tellurite and selenium compounds dissolve completely into the liquid, leaving gold, silver, and platinum-group metals as well as copper oxide behind as a solid residue, which are separated.



Neutralization and Precipitation of TeO_2 : The tellurium in the liquid filtrate is then isolated from other soluble impurities. Sulfuric acid (H_2SO_4) is carefully added to the sodium tellurite solution to neutralize it around the pH 5.5–6.5. Tellurium dioxide thus produced has amphoteric nature and possesses minimum solubility in this specific pH window. It precipitates out of the solution as a clean, hydrated tellurium dioxide cake often called "tellurium mud".



Final Reduction to Tellurium Metal: The purified TeO_2 cake is reduced to elemental tellurium. Common reducing agents include SO_2 /hydrazine/glucose etc. The reduction stage separates tellurium from oxygen chemically and produces recoverable metallic tellurium suitable for industrial use.



Melting and Casting: The elemental tellurium powder are collected, thoroughly washed with demineralized water to remove salts, and dried. The material is then melted in a graphite crucible under a protective inert atmosphere (or a flux cover), at temperatures above its melting point (450°C) and cast into commercial ingots or sticks, typically yielding a commercial purity of 85% to 95%.

Although there are many industrial processes that utilise some varieties and alternates procedures to achieve the individual steps, the above steps represent a widely used procedure for the extraction of tellurium from copper anodic slimes [12,29,30]. Apart from copper refineries that makes around 90% of the global tellurium supply, there are also secondary sources like lead refinery residues, gold processing residues, metallurgical residues of bismuth, nickel, zinc extraction streams, electronic waste recycling streams, which also serve as minor sources (~10%) of global tellurium production.

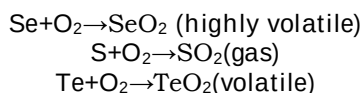
Purification of Tellurium

It should be mentioned here that the crude tellurium produced still contain some minute amounts of Se, Cu, Pb, Bi, Ag, S etc., and hence needs further purification techniques to be of use in modern technologies. A variety of refining techniques are used to obtain the ultra-pure tellurium from the crude tellurium, we will look in some of these processes. These processes mainly include oxidative refining, vacuum distillation, zone refining, electrolytic refining etc. [31]

Oxidative refining

This method is based on the difference in oxidation behaviour of tellurium compared

to the impurities present in the crude metal. Some impurity elements oxidize at different rates while some form oxides with different volatilities. The crude tellurium is melted in a refining furnace beyond the melting point of tellurium (449°C) and air or oxygen is passed through the melt. In this process, Selenium is oxidized to SeO_2 , which is highly volatile, and escapes from the melt with furnace gases. Similarly, sulfur present escapes as SO_2 . Metals like copper, lead and bismuth are easily converted to oxides and are removed as slag. Since these impurities have greater affinity for oxygen with faster oxidation rates, the controlled temperature, oxygen supply and duration of airflow is carefully controlled to minimize the formation of TeO_2 . Even after conversion of small amount of Te to TeO_2 , it remains in the molten mass or the slag instead of escaping with SeO_2 or SO_2 due to relatively less volatility. The oxide can later be recovered from the molten mass or slag by chemical treatment like reduction, thus minimizing the metal loss. After oxidative refining, the purified tellurium from the melt shows an increase in purity to about 95% to 99% Te. This purity is often sufficient for ordinary metallurgical uses, however, for electronic or semiconductor applications, a much higher purity is required. Such purity is achieved by the subsequent techniques.



Vacuum Refining

After oxidative refining, small amounts of impurities previously mentioned is still remaining in the metal. Further refining is achieved by using the difference in vapor pressure of different constituents of the starting material. The starting material is placed in a vacuum furnace and air is evacuated using vacuum pumps. Upon heating the materials, tellurium vaporizes more easily compared to the less volatile impurities. Under vacuum, even in the temperature below its boiling point (988°C), tellurium vaporizes more readily because reduced pressure increases evaporation and lowers the temperature required for boiling. The less volatile impurities like Cu, Pb, Bi remain in the residue while Se has very high volatility and separates earlier than Te in many cases. The tellurium vapor moves to a cooler region and is collected to

obtain the metal of purity around 99.5% to 99.9%. This amount of purity is also suitable for manufacture of alloys, industrial chemicals or thermoelectric materials. However, for semiconductor grade purity, further refinement is needed.

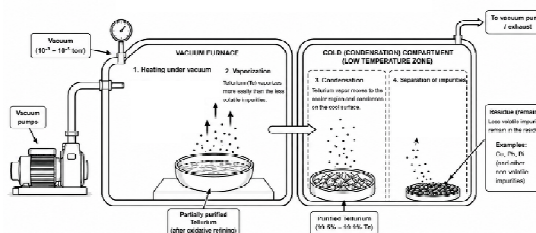


Figure-4. Vacuum refining of Te.

Electrolytic refining:

This method uses electrolysis to separate tellurium from the trace amounts of remaining impurities. Electrolytic refinement utilizes an anode made of impure tellurium and a thin starter sheet of pure tellurium as a cathode material. Under the application of electric potential, impure tellurium dissolves at the anode and pure tellurium deposits at the cathode. Typical electrolyte used is acidic salt solution of tellurium containing Te^{4+} ions. At the anode, where positive electric potential is applied, impure tellurium metal loses electron and dissolves into the electrolyte solution. The Te^{4+} ions thus produced migrate through the electrolyte towards the cathode. At the cathode, where negative potential is applied, tellurium ions undergo reduction by gaining electrons and deposit as pure tellurium metal. Noble metal impurities like Au, Ag, Pt etc. do not oxidize or dissolve from the impure anode and settle below the anode as anodic slime, while, more reactive elements like Cu and Fe do dissolve into the electrolyte solution but do not deposit easily on the cathode under the controlled conditions. Selenium behaves chemically similar to tellurium, making separation difficult. Careful control of voltage and electrolyte composition helps minimize the selenium deposition at the cathode. The metal obtained after electrolytic refining has a purity in the range of 99.9% - 99.99%. This is a significant purity for many high-end applications of the metal, however still not preferred for the semiconductor applications.

Anode: $\text{Te (impure)} \rightarrow \text{Te}^{4+} + 4\text{e}^-$

Cathode: $\text{Te}^{4+} + 4\text{e}^- \rightarrow \text{Te (pure)}$

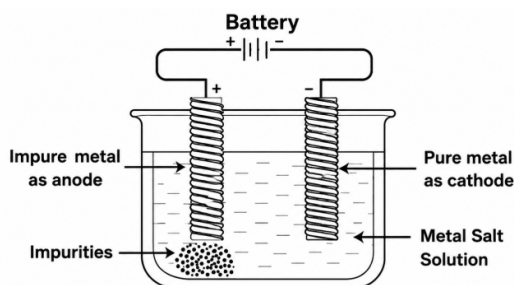


Figure-5. Typical electrolytic metal purification process.

Zone refining

Even after oxidative refining, vacuum distillation and electrolytic refining, minute traces of impurities are still remained, and they also make them unsuitable for high end applications. For semiconductor and some other electronic applications, even ppm level impurities are harmful. Hence, a further purification step is required that can obtain tellurium of purity 99.999% (5N) to 99.9999% (6N) or even higher, which is suitable for such high-end applications. Zone refining is the final ultra-purification step used to obtain extremely pure crystalline tellurium. The highly sophisticated method is based on the different solubility of impurities in molten tellurium compared to solid phase. In principle, when a molten metal begins to freeze, a metallic crystal starts to grow that prefers to bond with atoms of its own kind. Because foreign impurity atoms typically have a different atomic radius or valency, they don't fit easily into the crystal structure and are physically rejected back into the remaining liquid pool. Thus, when a rod of tellurium, obtained as a product of the previous refining stage, is heated in a narrow section of its body beyond its melting point by a heating element, a narrow small molten region develops. The heater then slowly moves from one end of the rod to the other, thereby moving the molten region. As the molten region moves, the impurities go from the newly crystallized solid section to the newly developed liquid phase, and these impurities tend to accumulate at the moving molten zone. Finally, after the molten zone reaches the end most of the

impurities get collected at this region and the end is cut off and discarded. Repetition of this process significantly improves the purity while reducing the rod length to some amount. The entire process is carried out under vacuum or inert atmosphere to prevent the oxidation of the tellurium piece. Thus, the slow process can produce tellurium of extreme high grade.

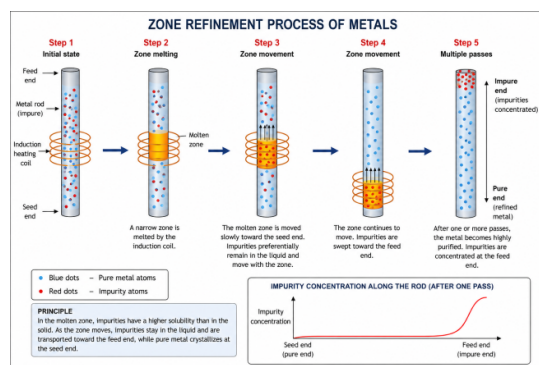


Figure-6. Typical zone refining process for metal purification.

Global production and supply of tellurium

Regarding the production of tellurium, the supply chains remain extremely concentrated, with China. The roughly 70–75% of refined tellurium of world supply is produced and supplied by China. Several other producers include Japan, Russia, Sweden, Canada, and a few copper-smelting economies where tellurium is recovered as a by-product from copper anode slimes [24]. Recent estimates indicate that China alone produced around 750 tonnes of refined tellurium in 2024, far ahead of all other countries combined. This concentration has made tellurium strategically sensitive, especially after China introduced export controls on several critical minerals including tellurium and its compounds [32]. The metal is increasingly viewed as essential not only for clean-energy technologies such as cadmium telluride (CdTe) solar panels, but also for aerospace alloys, memory chips, thermal imaging systems, radar electronics, and next-generation defence systems. India has therefore started treating tellurium as a strategic and critical mineral under its broader critical minerals and energy-security policy. The country currently depends heavily on imports because domestic tellurium resources are limited and refining capacity is still developing.

Indian companies are attempting to recover tellurium from copper refinery by-products, especially through integrated copper smelting and precious-metal recovery operations [33]. India's production scale is still very small compared with China, Japan, or Russia, and high-purity refining capability remains limited.

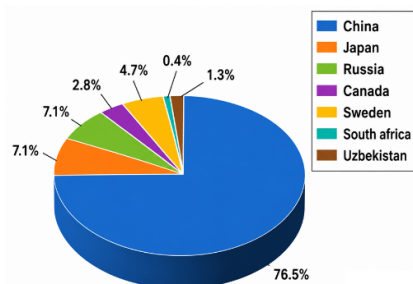


Figure-7. Estimated global Te production by country [24].

India's recoverable tellurium output is estimated to be only a few tonnes per year, often considered less than 5 tonnes annually [33]. However, notable domestic recovery initiatives have been taken by Hindustan Copper Limited at Ghatsila, Jharkhand; and Hindalco Industries through copper refining operations at Dahej. India is gradually building such purification capabilities through metallurgical R&D and refinery upgrades, but the country is not yet a major supplier of ultra-high-purity tellurium at global scale. Nevertheless, India's push for solar manufacturing, semiconductor fabrication, electronics, and defence self-reliance is driving stronger policy attention toward tellurium and other critical metals. As India expands domestic photovoltaic manufacturing and strategic technology sectors, tellurium is increasingly being recognized alongside lithium, cobalt, gallium, germanium, and rare earths as a critical mineral necessary for long-term industrial and national security resilience.

Conclusion

Preparation of high purity tellurium is a technologically sophisticated process involving multiple separation and purification stages. Because tellurium occurs mainly as a by-product in complex metallurgical systems, effective separation science is essential for obtaining high

purity material suitable for advanced technological applications. A combination of pyrometallurgical and hydrometallurgical techniques is generally employed. Among these, solvent extraction, ion exchange, electrorefining, vacuum distillation, and zone refining represent the most important technologies for achieving ultra-high purity grades. Modern developments increasingly emphasize environmentally sustainable processing, energy efficiency, recycling integration, and high selectivity purification systems. Future progress in advanced materials, green chemistry, membrane technology, and process automation will continue to improve the efficiency and economics of tellurium purification. Given the growing global importance of photovoltaic materials, thermoelectrics, semiconductor devices, and quantum materials, high purity tellurium will remain a strategically critical material. Continued research in separation science and technology will therefore play a pivotal role in supporting the expanding demand for ultra-high purity tellurium.

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ASSET Bulletin on "Separations in preparation of high purity critical elements"

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Separation for high purity rare earth oxides from primary resources

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Introduction

Rare earth elements (REE) are a group of seventeen elements, in particular lanthanides (atomic number 57-71) as well as scandium and yttrium. Scandium and yttrium are considered REE since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. REE have wide applications in various areas due to their special physical and chemical properties. The applications of REEs is categorized into the traditional and the high-tech areas. The traditional areas include the industries of metallurgy and machinery, glass and ceramics, petroleum and chemical industry. During the last four decades, there has been an explosion in the applications of REE in high-tech areas, which include the industries of phosphors, permanent magnets, batteries (hydrogen storage material, NiMH) and nuclear industry, as well as superconductive materials and magnetorestrictive materials. The traditional applications of REE require in mixed rare earth metals, alloys, oxides or salts whereas the high-tech areas need high purity single rare earth oxide (REO). So, REE are also referred as the "Vitamins of Modern Industry". At present, some of the REEs (neodymium, europium, terbium, dysprosium and yttrium) are considered as "critical metals" due to projected supply risks and their importance to clean-energy technologies [1].

The largest use compiled for the year 2025 was in: magnets, followed by catalysts, polishing, glass, phosphors, batteries and others shown in Fig. 1 [2]. Individual RE usage by application is shown in Fig. 2. It is impossible to maintain modern life without REE [3-5]. REE receive their name, not because they are rare in the earth's crust, but because they rarely exist as individual native metals such as gold, copper and silver. Due to their reactivity they exist in association with ore/minerals [6]. They are classified into light rare earth elements-LREE (La, Ce, Pr, Nd), middle rare earth elements-MREE (Sm, Eu, Gd) and heavy

rare earth elements-HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu) based on group separation by organic solvents. The close chemical similarity of all the rare earth elements is, first of all, displayed in their occurring together in nature and further by the fact that it took nearly 160 years of effort by many great names in science to isolate and identify them. Now separating these rare earths from other type of elements are more or less established to the date, whereas partitioning of the intra group elements is still posing a challenge. In last few decades, the separation of REEs has attracted great attention due to their potential industrial and economical significance in addition to the increased demands of REs of high purity.

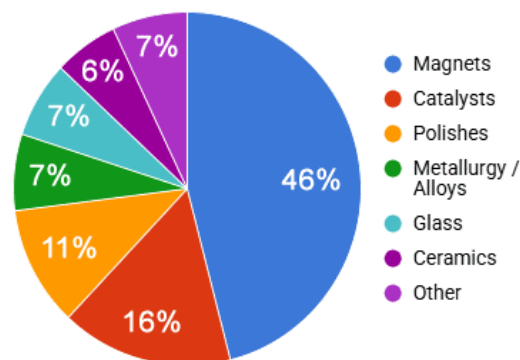


Fig.1. Uses of Rare Earth Elements

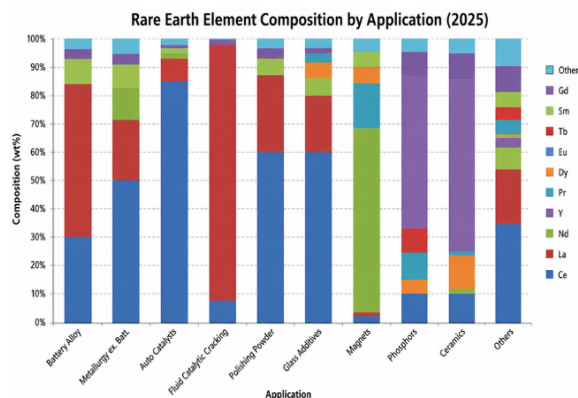


Fig.2. Rare Earth Element composition by Application

Rare Earth Minerals, Occurrences and Resources

Over 250 RE minerals occur in various geological environments; however, nearly 95% of commercially important RE resources are concentrated in three minerals: bastnaesite, monazite, and xenotime [2]. Bastnaesite and monazite are rich in light rare earth elements (LREEs), whereas xenotime contains higher proportions of heavy rare earth elements (HREEs), particularly yttrium. Major global REE reserves are in China, the United States, Brazil, Vietnam, Russia, and India. Important carbonatite-hosted deposits include Bayan Obo (China), Mountain Pass (USA), Mt. Weld (Australia), and Araxá (Brazil) [7]. India mainly possesses monazite-bearing beach placer deposits, along with some hard rock deposits associated with carbonatites and peralkaline granites. Ion-adsorption clays, predominantly found in China, are another major source of HREEs. China accounts for over 90% of global rare earth oxide (REO) production [8].

Considering the growing demand and strategic importance of rare earths (REs), India holds significant potential due to its large monazite reserves in the beach sands of Kerala, Odisha, and Tamil Nadu, estimated at ~7.23 million tonnes of rare earth oxides. In Gujarat and Rajasthan, 1.29 million tonnes of in-situ REO resources have been identified in hard-rock areas [8]. The export restrictions imposed by China since 2010 have accelerated global efforts to develop alternative REE supply sources. Secondary sources such as e-waste, phosphogypsum, ocean bottom sediments, red mud, deep sea sediments and coal fly ash are emerging as important alternatives, particularly for HREs like yttrium, dysprosium, erbium, ytterbium and lutetium [9-13]. Indian coal fly ash contains significant quantity of REE and Anand Rao et al. reported a leaching process for recovering mixed rare earths from the coal fly ash [14].

Rare earth ore Beneficiation and Hydrometallurgical Processing

Prior to individual REE separation, the rare earth (RE) ore undergoes a series of physical beneficiation steps to concentrate

the RE minerals, followed by hydrometallurgical processing to bring the RE values into solution for subsequent individual separation. Different types of ores require different processing routes, as detailed below.

Monazite

Monazite is a phosphate-based rare earth ore with composition $(\text{REE})\text{PO}_4$ and constitutes a major component of carbonatite-related rare earth deposits. It is characterised by a dominance of LREEs and the presence of radioactive elements, predominantly thorium and some uranium. Monazite exists mainly in placers, especially coastal placers. Many other minerals such as Magnetite, Ilmenite, Garnet, Zircon, Rutile, Quartz are commonly found in monazite placers. The separation of monazite from coastal placers is a complex process involving gravity separation, floatation, magnetic separation, electrostatic separation followed by chemical separation. In chemical separation, monazite is treated by sulfuric acid or by alkali like sodium hydroxide. The sulfuric acid method had been used most extensively in the United States [15]. With this method, depending on the acid/ore ratio, temperature and concentration, either thorium or the rare earths can be selectively solubilized or both thorium and rare earths totally solubilized [16]. Rare earths and thorium are subsequently recovered from the solution. The process of rare earth recovery based on rare earth double sulfate precipitation was largely developed and has found industrial application [17].

The alkali route is lucrative because the phosphate content of the ore is recovered as a marketable by-product, trisodium phosphate, at the beginning of the flowsheet, and this has been a major attraction for the commercial use of this process [18]. Indian Rare Earths Ltd. plant uses the caustic soda treatment for the decomposition of monazite sands [19], which include: (a) Reaction of finely ground monazite sand with hot concentrated aqueous caustic soda solution, to convert the rare earth and thorium contained in the ore into the irrespective hydroxides. (b) Separation of the insoluble hydroxides from the dissolved phosphate and excess caustic

soda. (c) Recovery of trisodium phosphate from filtrate, and (d) Selective dissolution of REEs in 30% HCl, 70°C and at pH~3,2, leaving thorium and uranium (insolubles). Iron is precipitated by oxidizing it to the ferric and lead by precipitation with sulphide.

Bastnaesite

Bastnaesite is the most industrially important rare earth mineral, containing 67-73% Rare Earth Oxide (REO). It is the major source of LREE. Well known Bastnaesite deposits are Mountain Pass and Bayan Obo. A bastnaesite deposit is relatively easy to concentrate. Floatation is the most common concentration process. Kruesi and Duker [20] of Molycorp developed the process to produce rare earth chloride from bastnaesite as follows: . (a) The bastnaesite concentrate (70% REO) is leached with hydrochloric acid followed by removal of lead sulfate, and then excess sulfate precipitation by barium chloride.

Xenotime

Xenotime is a rare earth phosphate mineral with its major component yttrium orthophosphate (YPO_4). It is one of the most important source of HREE. Occurring as a minor accessory mineral, xenotime is found in coastal placers, pegmatites and igneous rocks. Yttrium is the major REE in the xenotime. The total REO is higher than 42% and yttrium accounts for 50-70% of this. The separation of xenotime uses a combination of gravity separation, electrostatic, magnetic separation and floatation. It is converted to water soluble sulfates by leaching with conc. H_2SO_4 at 250–300°C for 1–2h [21-22]. Such leaching was uneconomical for concentrates containing less than 10% xenotime. These are treated by wetting the solids with sufficient acid and heating the mass at 300°C followed by water leaching. About 80–90% of the rare earths are solubilized. The recovery of rare earths by processes such as double sulfate precipitation is not possible because yttrium and the heavy rare earth sulfates are quite soluble. The sulfate solution is directly taken for separation. In the alternative process, the fine ground xenotime is treated by fusing it with molten caustic soda at 400°C or by mixing it with sodium carbonate and

roasting at 900°C for several hours [23]. After leaching out the phosphates, the hydroxide residue is dissolved in a minimum amount of hydrochloric acid and filtered from impurities such as silica, cassiterite, etc. The rare earths are recovered by precipitation as oxalates.

Ion-Adsorbed type rare earth deposits

Ion-adsorption clays are deposits which contain rare earth ions adsorbed physically to the clay minerals surface, mainly kaolinite and halloysite. Weathering of igneous rock, primarily granite, that contains specific rare earth-bearing minerals results in their formation. These deposits typically exhibit an enrichment in HREEs, particularly dysprosium and terbium, and are widely reported across southern China. The REEs present in ion adsorption clays are not soluble in water or hydrolyzed in water but follow ion-exchange laws [24]. The separation process is relatively simple, including leaching, precipitation and calcination.

Secondary sources of Rare earth and its' exploitation

For the countries with minimum primary rare earth sources, focus is also on recycling for the sustenance of the modern civilization. REE use is expected to increase due to global transition to a greener future. Growing volumes of discarded EV motors, wind turbines, and e-waste offer major future opportunities. Currently, most recycled supply comes from manufacturing scrap in China, but Improved recycling technologies and supportive policies are expected to further boost rare earth recycling worldwide. It can relieve some pressure on primary supply and can be a more cost-effective, environmentally friendly alternative to opening new mines. However, REs extraction from these end-of-products remains uncommon compared with REs extraction from primary resources. For instance, it has been estimated that <1% of REs were recycled from permanent magnets in 2009 [9].

Phosphate rocks are an alternative source of REs since they generally contain a non-negligible amount of REs. In recent years, attention has been paid to phosphate

deposits as a potential source of REs because: (i) the mining and processing of phosphate rocks is already financed by the fertilizer industry, (ii) there is a great demand of these metals, and (iii) if these elements are not recovered, they would be lost and ultimately accumulate in soil. Therefore, these factors encouraged researchers to develop efficient methodologies for recovering these metals from phosphate rocks.

On the other hand, hard coal fly ashes (CFAs) have been estimated to contain 445 ppm REE on an average global basis. There have been many reports of CFAs with REE contents that far exceed the world average (0.1–1.0 wt%). The estimation and exploitation of the resources and the recovery of the REE as a by-product from coal deposits may thus be considered as a promising way for obtaining REE [14].

Separation of individual rare earth oxides

The rare earth produced from different ores or solutions is a mixed product containing various individual REE. To separate them to individual elements presents one of the most challenging separation tasks in hydrometallurgy. In comparison to lengthy processes such as fractional precipitation and crystallization, solvent extraction, also called liquid-liquid extraction, offers a more flexible approach for production of individual REO at required purities and quantities. Separation is enabled by the gradual decrease in ionic radii across the lanthanide series (lanthanide contraction), which creates subtle differences in ligand coordination behavior, allowing separation of REE. Solvent extraction (SX) is currently the dominant technology for REE separation and purification. A basic solvent extraction process includes extraction, scrubbing/washing and stripping. In SX, the extractant is the active component responsible for the transfer of the metals from the aqueous solution to the organic phase. In the extraction stage, the desired and undesired metal is extracted depending on the distribution coefficient of metal ions. Scrubbing stage is essential to remove undesired elements from the organic solution. Scrubbing solution may contain a relatively high amount of valuable metal. For this reason it

is normally recycled back to extraction stage and mixed with the feed aqueous solution. Stripping is the reverse operation of extraction. The valuable metal is stripped from the organic solution and is concentrated in the stripping solution. The organic solution is reused for extraction. The metal in the stripping solution is recovered as the final product. To achieve the targeted purity of individual REE, multistages of extraction are often used due to similar distribution ratio for all REE. The commonly used rare earth extractants are 2-ethylhexyl phosphonic monoester (EHEHPA, P507), PC88A and Ionquest 800, di-(2-ethylhexyl) phosphoric acid (D2EHPA, P204) [25–27].

Development of solvent extraction processes for separation of Rare Earth oxides

Solvent extraction (SX) is the backbone of the rare earth industry and the most widely used technique for separating rare earth elements (REEs) with very similar chemical properties. The mixed RE chloride solution obtained from monazite processing is fractionated into light rare earths (LRE), middle rare earths (MRE) and heavy rare earths (HRE) fractions by solvent extraction. Only two organophosphorous solvents D2EHPA and PC88A are used in large scale separation of rare earths. Though D2EHPA is an efficient extractant for rare earths, the difficulty is back extracting them from the solvent phase, resulting in high consumption of acid [15].

SX process flow-sheets based on PC88A involving multistage counter current extraction, scrubbing and stripping was developed at Materials Group, BARC to separate individual high purity rare earth oxides namely Dy_2O_3 , Gd_2O_3 , Sm_2O_3 , Tb_4O_7 , Y_2O_3 , Nd_2O_3 , Pr_6O_{11} at Kg scale. The general scheme followed is to first separate yttrium oxide from HRE concentrate which generates a by-product of Dy concentrate (~70%). This is further purified to high purity dysprosium oxide in another SX process which generates a Tb rich by-product. Tb purity is further enhanced in another SX circuit [28]. These developed SX processes are described below. IREL has successfully implemented BARC technologies, through its in-house R&D, to tonnage scale.

Solvent extraction process flow-sheet for the recovery of high purity (99.9%) Y_2O_3 from monazite mineral

There are many yttrium separation and purification systems. Regardless of the extraction system, they all utilize the position shifting of the yttrium distribution coefficient to achieve yttrium separation from other REE. Naphthenic acid is used in separation of yttrium (>97%) from chloride solution [29]. In naphthenic acid system, additives like alcohols, petroleum sulphide and ethers are used. These additives lead to dissociation of polymers due to the formation of hydrogen bond between naphthenic acid and alcohol. In turn it results in decrease of rare earth extraction by naphthenic acid. To circumvent, quarternary amine based solvent was successfully used in our lab for yttrium separation from monazite. The feed for yttrium purification by SX employing two cycles using PC88A and Aliquat336 (quaternary ammonium salt) was HRE concentrate of monazite analyzing 50-60% Yttrium oxide. Under optimized conditions, PC88A extracts most of the heavy rare earths excluding Dy. Loaded organic is back extracted and the strip solution is used as feed to second cycle SX circuit with Aliquat336 as extractant. Aliquat336 as extractant in thiocyanate medium gives preferential separation of other HRE over yttrium which behaves like lighter rare earths. The crude concentrate of yttrium ranging from 80 to 93% Y_2O_3 can be used for its purification in the second cycle. The second cycle is comprised of 20-stages extraction (20% Aliquat 336-1% isodecanol-0.5M NH_4SCN -kerosene), 8-stages scrubbing (2M NaCl), 4-stages stripping (acidic water, pH=3) and 2-stages for regeneration of Aliquat336 for re-use. The phase ratio (O/A) for extraction, scrubbing and stripping cascades is kept at 1, 10 and 4 respectively. The out-going streams are analyzed for total oxide and individual rare earth to check purity, recovery and material balance. The purity of yttrium oxide obtained was > 99.9% in the raffinate with > 98% recovery. The overall process is shown in Fig. 2. The second cycle also renders a by-product rich in erbium value (40%) and this has been upgraded to 80% Er_2O_3 in another SX process [30]

Development of a solvent extraction process flow-sheet for the recovery of high purity (99.9%) Y_2O_3 from xenotime mineral

Xenotime is a complex phosphate mineral of heavy rare earths which contains 60% Y_2O_3 apart from other rare earths and host of impurities including Si, Fe, Ca, Mg, U, Th etc. A robust integrated hydrometallurgical process was developed for xenotime wet hydroxide cake received from OSCOM, IREL. A two cycle SX circuits (PC88A and Aliquat 336) developed and demonstrated. The overall hydrometallurgical process steps consisting of leaching with HCl, silica removal by flocculent, impurities removal by selective precipitation at controlled pH. The above mentioned two cycle PC88A and Aliquat336 counter current solvent extraction process was adopted to separate high purity Y_2O_3 .

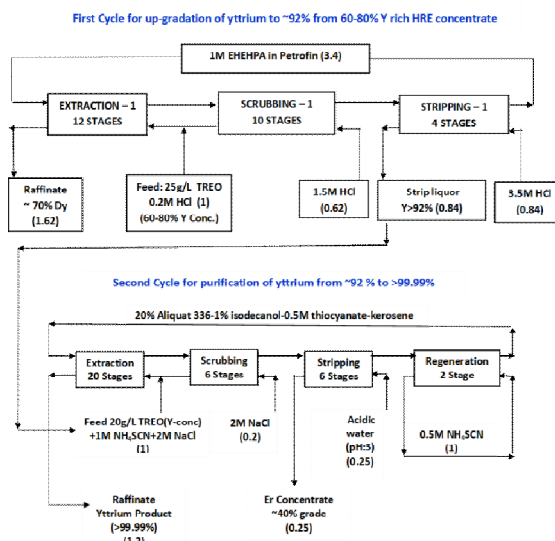


Fig.3. Dual Cycle solvent extraction process flow-sheet for production of yttrium oxide

SX process for separation of high purity neodymium and praseodymium oxides

Separation of adjacent REE such as Nd and Pr is a technically challenging task. The primary parameter governing the separation between Nd and Pr in the SX process is the equilibrium separation factor, defined as the ratio of distribution ratio of Nd to that of Pr. The process was developed to separate Nd from Pr from feed containing 38%La, 10%Pr, 35%Nd and 17%Sm using 30% saponified PC88A extractant and scrubbing with pure Nd solution at reflux ratio of 70-80%. The purity of Nd 99% could be achieved in 18

stages of extraction and 40 stages of scrubbing with dilute solution of neodymium chloride which is mildly acidic. The scrub solution thus obtained is re-circulated to the extraction section by mixing with the aqueous feed solution. Most of the Pr, Ce and La co-extracted are scrubbed out in this step thereby purifying Nd. The scrubbed extract flows into another six stage mixer settler unit and Nd is recovered from the extract by stripping with dilute HCl. Nd is precipitated as Nd-oxalate, and converted to oxide. Pilot plants of capacity 1T/Y are setup by IREL based on BARC technology [32] and Nd_2O_3 and Pr_6O_{11} produced at RED, Alwaye

SX process flowsheet for production of >99% Gd_2O_3 :

A two cycle solvent extraction process based on PC88A as an extractant for the separation and purification of nuclear grade gadolinium from a crude concentrate of rare earths has been developed and demonstrated successfully. Gadolinium concentrate (~70%) was processed in two cycle solvent extraction using PC-88A solvent. In the first step, Gd, Sm, Nd and Pr are separated from Tb and other HRE. In the second step, Gd with 99.9% purity is separated from other LRE. Optimized condition was arrived at by computer simulation using mathematical models and was validated by mixer settler runs. Kilogram quantity of Gd_2O_3 with 99.5 %purity has been produced. The resultant gadolinium nitrate was produced from Gd_2O_3 obtained by the solvent extraction process developed by us was found to be suitable for its use in PHWR power reactors [33]. Gadolinium oxide is converted to nitrate form ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) which meet the specifications for PHWR applications. 150 Kg of gadolinium nitrate was supplied to TAPS, Tarapur and in another campaign 250 Kg supplied to KAPP-3 for its application in PHWR. Based on BARC developed technology, pilot scale facility for Gd_2O_3 production at 1T/Y has been setup at Alwaye, IREL. Large scale facility at IREL has been setup to produce nuclear grade gadolinium nitrate to meet larger quantity requirement by NPCIL.

SX process flowsheet for separation of >99% pure dysprosium oxide:

The separation and purification of dysprosium from HRE fraction ($\text{Y}_2\text{O}_3 \sim 60\text{-}67\%$, $\text{Dy}_2\text{O}_3 \sim 20\text{-}25\%$, $\text{Gd}_2\text{O}_3 \sim 4\%$, $\text{Tb}_4\text{O}_7 \sim 4.0\%$, $\text{Ho}_2\text{O}_3 \sim 3\%$, $\text{Er}_2\text{O}_3 \sim 3.0\%$, $\text{Sm}_2\text{O}_3 \sim 1.06\%$) successfully accomplished by adopting a dual cycle of solvent extraction scheme based on PC88A only. Taking the advantage of the extraction order of rare earths and yttrium with PC88A, yttrium including heavy rare earth fractions are separated in the product strip solution, while dysprosium is concentrated in the raffinate solution along with terbium, gadolinium etc in the first cycle. In the second cycle dysprosium is purified to the extent of >99.5% with respect to other rare earth impurities from the dysprosium concentrate obtained in the raffinate of first cycle. Under optimized conditions of process parameters continuous operations of mixer settler can yield ~99% pure Dy_2O_3 with >98% recovery. The integrated process flow-sheet with optimized process variables to produce dysprosium oxide is shown in Fig.3. In addition to Dy_2O_3 product, this process also produces two concentrates namely yttrium (>93%, 1st cycle) and terbium (>54%, 2nd cycle). Process details were shared with IREL for commercial production and IREL has set up a plant of 1T/Y capacity for production of Dy_2O_3 from monazite concentrates to meet strategic requirement [34].

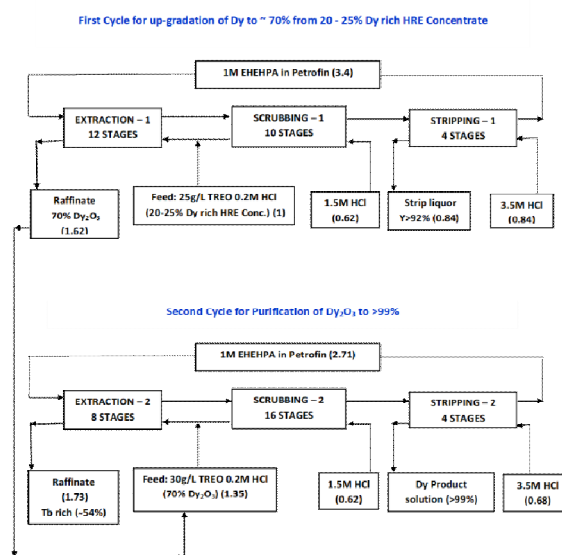


Fig.4. Solvent extraction process flowsheet for separation of dysprosium oxide

Development of SX process flowsheet for production of >99% pure terbium oxide:

High purity terbium finds applications in phosphors, magnets and other high technology areas. Indian monazite contains 0.4% terbium. During fractionation, a heavy rare earth fraction assaying 60% Y₂O₃ is produced where terbium gets concentrated to 5%. Further processing yield 14% Tb in Dy concentrate. Terbium concentrate assaying Tb₄O₇ - 70%, Dy₂O₃ - 28%, Gd₂O₃ - 1.3% and Y₂O₃ - 0.3% is obtained in the Dy SX purification circuit. A process has been developed to obtain grade >99% Tb₄O₇ by SX using 1M PC88A [35]. In the first cycle of SX by PC88A terbium purity is raised to >90% in the first cycle by selectively extracting heavy rare earths than terbium in the organic phase leaving terbium rich RE mix product in the raffinate. This terbium rich mixed RE is again processed under optimized conditions in the second cycle comprising 8 stages extraction, 8 stages scrubbing and 4 stages stripping of mixer settlers. The strip solution obtained is >99% pure Tb₄O₇ with >93% recovery while producing a Tb-Gd rich product at raffinate end as shown in Fig.4.

Conclusion

High-purity rare earth elements are indispensable for advanced materials and emerging technologies, and solvent extraction continues to be the most effective and widely employed route for the separation and purification of individual rare earths from primary resources. Multistage counter-current solvent extraction circuits have been designed and optimized for the processing of monazite and xenotime mineral concentrates, enabling the efficient production of individual rare earth oxides with purities exceeding 99%.

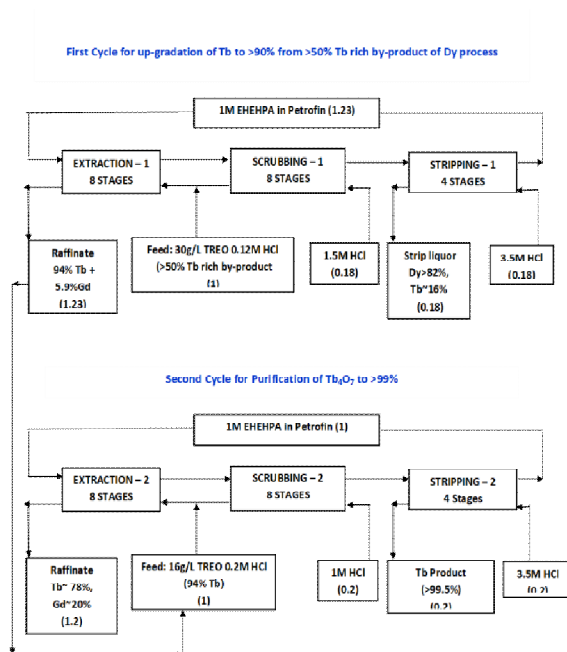


Fig.4. SX Flowsheet for separation and purification of terbium oxide

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