### **GETTING REES FROM CFA – SOME SUGGESTED SOLUTIONS**

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Abbreviations			
CFA	Coal Fly Ash		
DES	Deep Eutectic Solvent		
IL	Ionic Liquid		
PGE	Platinum Group of Elements		
REE	Rare Earth Elements		
REY	Rare Earth Elements + Yttrium		

## 1. Introduction

Weaponizing of Critical Minerals has forced many countries to take crash actions to become self-sufficient in these minerals. After China has stopped export of REEs, the crisis of REEs, specifically in Indian automobile industry is glaring. Government of India has taken several steps to mine critical minerals. However, from policy making to providing industry-ready REEs and PGEs & other critical minerals – gestation period is too high. Immediate sourcing of industry grade REEs is the only imperative. Primary source of REY is monazite, xenotime etc. This article discusses getting REY from secondary sources.

Coal is the largest mining commodity produced in India. Indian coal is mainly drift origin – plant materials got transformed into coal. Such transformation process resulted in plant materials getting mixed with detritus minerals resulting in high ash content. This is considered a problem area for getting quality coal. This problem can be converted to a solution for obtaining REEs from CFA. Rutile (TiO<sub>2</sub>), Monazite-Ce [(Ce, La, Nd, Th)PO<sub>4</sub>] are found in Meghalaya Coal. Obviously, in Meghalaya coal, huge possibility of getting Critical Minerals and REE is there.

# 2. Sourcing of REEs from CFA

Researchers from Bhava Atomic Research Centre (BARC) have found several REEs in CFA and Coal samples of thermal power plants of different locations in India. They have found several REEs of varying quantities in those samples. The study has reported presence of Ce (Cerium) as high as 218µg/g in one of the CFA samples<sup>[1]</sup>. Cerium is used in Arc Lamps, colour TVs, Optical appliances for fine polishing of glasses etc.

Outlook Coefficients of REY found in CFA in three different studies are given below:

	Research paper	Outlook Co-efficient	
		For CFA	For Coal
1	Estimation of rare earth elements in Indian coal fly	≥0.7	NA
	ashes for recovery feasibility as a secondary		
	source <sup>[1]</sup>		
	(by P. Sandeep & others)		
2	Partitioning of Rare Earth Elements (REEs) from	0.1–1.2	0.3 – 4.5
	Coal to Coal Fly Ash in Different Thermal Power		
	Stations (TPSs) of India <sup>[2]</sup>		
	(by Sudip Maity & others)		
3	Distribution of trace elements and rare earth	0.8 – 1.0	NA
	elements in coal from the Bhalukasba Surni coal		
	block, Rajmahal coalfield, Eastern India <sup>[3]</sup>		
	(by Swasati Chakladar & others)		

Globally, CFA has been found to be a potential source of REY.

## 3. <u>Recovery of REY from CFA:</u>

Scientists and Engineers had used different methods and instruments while evaluating presence of REY in CFA. Those were mainly laboratory instruments. Besides heating system, microwave digesters (for making acid solutions) varieties of other instruments like, Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry (TQ-ICP-MS), Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), X-Ray Diffractometer (XRD machine) etc. are used. Commercial production of REE metals by laboratory instruments is not possible.

Processing of CFA for getting REE may produce toxic by-products, toxicity may be severe also. It is imperative to use a technology which will be safe, environment friendly and at the same time will give maximum yield. Following recovery methods are being proposed:

- (a) Magnetic separation technique can be used to separate iron-oxides from CFA<sup>[4]</sup>. For scalable production, vibratory feeder in conjunction with magnetic separator machine can be used. Magnetic portion of CFA may contain a good percentage of REY. Gadolinium (Gd), dysprosium (Dy), erbium (Er) and some other heavy REEs exhibit magnetic susceptibility. Industrial version of Energy Dispersive X-Ray Spectroscopy (EDS) in conjunction with use of any one or multiple application of screening by sieving, electrostatic separation, gravity concentrators need to be explored for extracting REY from magnetic portion and balance portion of CFA.
- (b) Dual Energy X-Ray Transmission Sensor Based Sorting technology working on the principle of Physics of Non-destructive Evaluation is employed for dry beneficiation of coal and minerals of copper, gold, molybdenum etc. In this

method, the sorting technology is similar to that employed in Airports for baggage checking. This technology requires huge data as the process involves Machine Learning and Data Computing. However, equipment based on this technology is working all over the world; improvisation and customization to the need is possible.

(c) Ionic leaching has been reported as one of most successful process for REE extraction. CFA is obtained in fine grained texture, thus grinding or sizing process is eliminated. It makes leaching of CFA in solvents easier. Possibility of high recovery rate of REEs from CFA in an environmentally friendly manner by using Ionic Liquid or Eutectic Solvent is there. DES has the potential for selective recovery of REEs.

Department of Science and Technology of Government of India has taken up a research project titled as:

"Extraction and separation of Rare Earth Elements from coal fly ash using lonic Liquids for multifunctional applications"

With a timeline of 2024 to 2027 under CSIR- National Physical Laboratory, New Delhi, Department of Science and Technology of Government of India has taken up a research project titled as: "Extraction and separation of Rare Earth Elements from coal fly ash using Ionic Liquids for multifunctional applications".

Regarding this project, it has been stated that "This project aims to use fly ash as an alternative to monazite minerals for REE extraction. Ionic liquids (ILs) are identified as green chemicals for REE extraction due to their large electrochemical window and ability to be functionalized according to element affinity. The feasibility study will use betainium bis- (trifluoromethylsulfonyl) imide [Hbet][Tf2N]'s ionic liquid for electrodeposition of REEs, as well as exploring imidazolium cation group with fluoride and chloride-based anions containing ILs. The project involves selecting fly ash from thermal power plants with high REE content, leaching fly ash with an alkaline solution, analyzing the concentration of rare earth elements, optimizing parameters for electrodeposition, analyzing yield and purity of electrodeposited REEs, stripping REE deposited on the cathode, regeneration of ionic liquid, comparisons with solvent extraction, and exploring other imidazole-based ionic liquids for electrodeposition."<sup>[5]</sup>

Possibility of expeditious completion of this project need to be explored.

# 4. Conclusion:

As on 30-Sept-2022, a total of 1677.30 million tonnes of CFA was in stock<sup>[6]</sup>. As such this is an excellent secondary source for REY. Besides, REY, CFA is source of several other metals also. It has been stated that from 100 million metric tons of CFA, about 10 million metric tons of iron and 10 million metric tons of aluminium could be recovered <sup>[7]</sup>. With the amount of REE contained in CFA, it becomes imperative that CFA should be treated

as a potential source of metals, including REY. More ways need to be explored to find out right CFA for any particular REE. More research bodies and private companies need to be involved to develop methodologies and technologies to obtain REEs from CFA with scalability to meet the growing need of industries.

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Glossary:			
Deep Eutectic Solvent:	Deep Eutectic Solvents are analogous to Ionic Liquid but not same. DESs are less toxic, highly degradable, biocompatible, contain large, nonsymmetric ions that have low lattice energy and hence low melting points. Mixture of choline chloride and urea is an example of DES.		
lonic Liquid:	Ionic Liquids are typically colourless viscous liquids. Ionic liquid is a type of salt at room temperature with a low melting point that is commonly used as a green solvent in chemical reactions. It is made up of organic cations and inorganic anions. It is characterized by low vapor pressure and minimal pollution. Imidazolium is an example of Ionic Liquid.		
Outlook Coefficient:	Outlook Coefficient provides information at the early stage of any study with a deposit grade of a REE present in that deposit and possible contribution of such deposits to output of that REE. It is given by the ratio of the relative amount of critical REE to the relative amount of excess REE: Outlook Coefficient: Outlook Coefficient provides information at the early stage of any study with a deposit grade of a REE present in that deposit and possible contribution of such deposits to output of that REE. It is given by the ratio of the relative amount of critical REE to the relative amount of excess REE: $K_{outt}$ = (Nd + Eu + Tb + Dy + Er + Y)/REE sum: (Ce + Ho + Tm + Yb + Lu)/REE sum. This is a measure of economic potential of a REE found in a deposit. Outlook Coefficient >0.7 is considered to have the potential of REY.		
REE:	Rare-earth Elements (REE) are a collection of 17 elements, namely, scandium (Sc), yttrium (Y) and all elements of lanthanides. Lanthanides are a group of 15 elemnts, namely, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu).		

REY:	Rare Earth Elements and Yttrium is abbreviated as REY. Yttrium is
	chemically similar to lanthanides. REY is used when Rare Earth
	Elements and Yttrium are discussed together.

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- 7. Same as 4.