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Recovery of Rare Earth Elements from Spent Hard Disc Drive Magnets- Urban Mining Suitable for Developing Countries.

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ABSTRACT: *Rare Earth Elements (REE) are strategic metals essential to the development of innovative high- tech. industries particularly those associated with green energy like wind power, electric vehicles, Nickel Metal Hydride batteries (Ni-MH), robots, atomised industrial machines and Hard Disc Drive (HDD). HDD magnets are made of an alloy of three elements mainly Neodymium (REE), Iron and Boron (NIB) with an approximate formula of* $Nd_2Fe_{14}B$*. Recycling of REEs from secondary materials by urban mining compliments the traditional mining of REEs from primary ores. There has been growing interest in the industry to develop feasible processes of recycling the magnet materials due to environmental concerns and natural resources reserves. This paper presents extraction of Nd & Fe and their separation besides, further enrichment of mainly Nd. Complete conversion of Neodymium sulphate in to Neodymium oxalate is studied by IR spectroscopy. Characterization studies of REE oxides obtained by the thermal decomposition of Neodymium oxalate have shown the recovery of Nd- 93.66%, Pr- 5.878%, Tm- 0.2778%, Lu- 0.147%, and Er-317.7 ppm. TGA presented explains the thermal stability of REE oxalates and REE oxides. Strategic oxides of REEs so produced by urban mining can be reused in the production of magnets and Iron sulphate obtained as by product has several other applications.*

Key words: *HDD, Lanthanide Contraction, Neodymium, Rare Earth Elements, Urban Mining*

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I. INTRODUCTION:

Humanity's progress since the industrial revolution has been underpinned by fossil fuels such as oil, natural gas, metals like iron, copper and aluminium In the modern Periodic Table two sets of fourteen elements each placed at the bottom are called, inner transition or sub transition or 'f' block elements. Elements from Lanthanum-57 to Lutetium-71 are called Lanthanides or lanthanons or now popularly known as Rare Earth Elements (REEs).With increasing population, greater quantities of these resources are needed to deliver prosperous life styles in emerging economics. In cities with high population density, quantities of metals such as gold, silver, platinum and REEs are hidden in the waste electrical, electronic equipments (WEEE or E-Waste) and the term 'Urban mine' is referred to these resources. In the present work recovery of REEs from spent HDD magnets is demonstrated. Energy efficient air conditioner and HDDs used as data storage assembly inside the computers are best examples of low-carbon foot print products. Reclaiming metals and non metals from E-Waste in an environmentally sound way for a sustainable society is now popularly known as Urban Mining or Surface mining or Green Metallurgy. Urban mining helps reduce emission of carbon dioxide, conserve natural resources and preservation of ecosystems in addition to employment generation. In this direction, all over the world recycling and recovery of metals from E-waste is gaining importance.

Neodymium one of the more critically scare rare metals is used in sustainable technologies. Recycling of REEs that can be extracted from spent HDDs has become an important research area due to the issues of declining natural resources. Many well documented reports have presented processes, like leaching with inorganic acids, organic acids, solvent extraction, use of hydrogen to separate and recycle NIB type magnets, process etc. Waltron *etal* (2013), have reported the use of hydrogen as a processing agent to decrepitate sintered Nd-Fe-Boron contained within the hard disk drives in to demagnetised hydrogenated powder [1]. But the use of hydrogen to separate and recycle Nd-Fe-Boron type magnets from electronic waste is not economically viable for the developing countries, because hydrogen being combustible gas poses serious problems during storage and transportation. Jiro Kitagawa (2017) presented wet process using inorganic acids to leach out metals is associated with the problems of safe discharge of waste solutions. The waste acid recyclability is critically dependent on efficient extraction of the constituent elements of the magnet from the used acid [2].Ho-Sung Yoon *etal* (2014) have presented leaching kinetics of Neodymium in Sulphuric acid from E-scrap of NdFeB permanent magnets.Concentration of Sulphuric acid 3M, pulp density and temp. range for optimum leaching of Nd has been reported[3]. Marino Gergoric *etal* (2018) have reported the recovery of Nd, Pr, and Dy from Nd-Fe-B magnets waste powder using leaching and solvent extraction. The goal was to determine potential selectivity between the recovery of REEs and other impurities in the material. Citric acid and acetic acid were used as leaching agents, while di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used for preliminary solvent extraction tests[4]**.** Organic reactions being molecular in nature are slow; leaching of metals from NdFeB magnets is not practically feasible, further there is not enough literature on the use of organic acids as leaching agents. Jelle H. Rademaker *etal* (2013), have investigated characterisation and leaching using (tetraoctyl-diglycolamide) and solvent extraction for the recovery of REEs. Use of Solvent extraction method TODGA (tetraoctyl-diglycolamide), iron can be dissolved along with other elements during leaching or co-extracted during solvent extraction. In this work, extraction of REEs with from a real leachate, obtained by neodymium magnet powder dissolution in nitric acid, was studied. The goal was to selectively extract the REEs from other elements in the solution. TODGA was used as the extracting agent due to its selective extraction properties for REEs and other f-block elements. The influence of the diluents on the overall extraction and the selectivity of the extraction w as studied in order to determine application feasibility of future processes [5]. Nour-Eddine Menad *etal* (2017) have reported the use of tetralin (a hydrogen-donor solvent) use of a specific catalyst containing charcoal, under vacuum at 700^0C to isolate REEs from Iron of the magnets[6]**.** S.T. Abrahami *etal* (2014) have investigated on REEs recovery from post consumer HDD wherein shredding, thermal demagnetisation, grinding, treatment with sulphuric acid, followed by conversion of REEs into their fluorides and finally fluorides reduced to REEs using Magnesium as reducing agent. Use of fluorine needs extra caution, special infrastructure, should not involve the use of glass wares and therefore convenient to practice only by developed countries [7]**.**C. Joseph *etal* (1998) have investigated the precipitation REEs as oxalates. Study revealed that precipitation of Neodymium of NIBs alone as oxalate is not possible. Due to the remarkable similarities in the ionic radii, both Neodymium and Praseodymium together get precipitated as their oxalates-$NdPr(C_2O_4)_3.10H_2O$.Study has also reported the TGA and thermal decomposition of Nd and Pr and st oxalates and stability of oxides at various temperatures [8]**.** Koen Binnemans *etal* (2013) have underlined the importance of 'Balance problem' REE recycling is recommended in view of the so-called "balance problem". For instance, primary mining of REE ores for neodymium generates an excess of the more abundant elements, lanthanum and cerium. Recycling of Neodymium can reduce the total amount of REE ores that need to be extracted. REE recycling can reduce the environmental challenges associated with REE mining and processing. 'Balance problem' supports the need for Urban Mining [9]. Kenji Baba *etal* (2013) have reported an environmental vision that designates the sustainable society as the goal of its environment management and its pursuing activities aimed at the prevention of 'global warming' conservation of resources and prevention of ecosystem. As a part of Hitachi's resource recycling initiatives, these activities also include the recycling of REE magnets.REE magnets are a key material in energy saving and digital equipment such as HDD, high efficiency air conditioners, hybrid vehicles and wind power generators [10].'Balance problem' is primary mining of REE ores for Neodymium generates an excess of the more abundant elements, such as Lanthanum and Cerium. Recycling of Neodymium can reduce the total amount of REE ores that need to be extracted. This can only be realised by developing efficient, fully integrated routes [11]. The objective of this paper is to address the issue of 'balance problem', conservation of natural resources, reduce dependence on developed countries for the supply of REEs, to lower the price of REEs and related products, recycling of HDD magnets is the best option. When the developed countries are making all out efforts in recycling of REE magnets, E-Parisaraa being India's premier approved E-waste Recycler is committed to innovative methods towards sustainability and disseminate research data for the benefit of developing countries. Materials required for the present paper and data generated was all from Urban Mining Research Centre of E-Parisaraa functioning in Bangalore.

II. MATERIALS

Magnets recovered by manual dismantling and segregation of HDD of CPU and Laptops (Fig.1)

Fig.1 Dismantling of HDD

Fig.2 Exploded view of HDD

Fig.3 Demagnetised magnets

III. METHODOLOGY

HDD magnets are an alloy of REE, Iron and Boron. Alloy cannot be just melted and metals cannot be separated by physical techniques. Each magnet recovered from CPU of a Desk-top has an average weight of 15g and that from laptop weighs 3g. To ensure reproducibility of the results, several 'batch experiments' have been carried out taking 15 kg of magnets for each batch. Physico-chemical principles followed for the recovery of REEs and also Iron from magnets have been presented below.

III (i) Demagnetisation

Magnets recovered by manual dismantling of HDD were heated to Curie temperature (350^{o}C).Demagnetised magnets were used for the recovery of REEs. The composition of the demagnetised magnet was checked using EDXRF spectrophotometer (Fig.11).

III (ii) Removal of Outer Protective Nickel Layer

Thin layer of Nickel coated over the magnet to protect Nd and Fe from undergoing oxidation was removed by controlled oxidation using about 5% Hydrogen peroxide followed by treatment with very Dil. Sulphuric acid. In about 5-10 minutes Nickel layer was leached out as Nickel sulphate. This was filtered out, filtrate was concentrated, crystallised to get Nickel Sulphate crystals (Fig.6a)

III (iii) Dissolution of Nickel Free Magnets in Sulphuric Acid

Nickel free magnets were crushed to smaller pieces and treated with 3 M Sulphuric acid at about 60^{0}C taking care for proper exhaust. Nd and Fe content of the magnet completely leached out as sulphates in about 30-48 hours.

$$Nd_2Fe_{14}B + 17H_2SO_4 \longrightarrow Nd_2(SO_4)_3 + 14FeSO_4 + 17\,H_2 + B$$

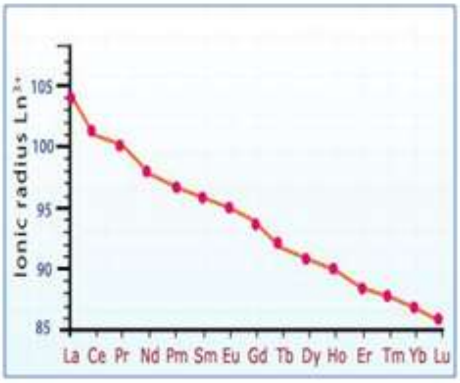
It was observed that most of Boron of the magnet converted in to its oxide and a small amount released sulphur dioxide gas as shown in the equation

$$2B + 2H_2SO_4 \longrightarrow B_2O_3 + 3SO_2 + 3H_2O$$

Care was taken to use stoichiometric quantities of Sulphuric to avoid discharge of remnants at the end.

III (iv). Separation of Neodymium Sulphate from Iron Sulphate

Leachate was filtered; solid unreacted Boron and Boron trioxide were separated from Sulphates of Neodymium and Iron. Generally solubility salts of majority of the metals in water increases as temperature increases. But this is not the trend exhibited by the salts of REEs. Because as a consequence of the well known 'lanthanide contraction' - size of tripositive ions decreases from La-57 to Lu-71 (Fig.4). As a result solubility of salts of REEs interestingly decreases as temperature increases (Fig.5).



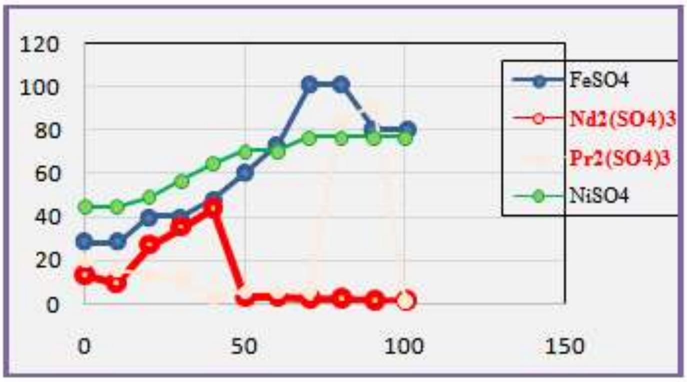


Fig.4 Tripositive ionic radii decreases From La-57 to Lu-71

Fig.5.Solubility of salts in water as function of Temp. (X-axis, Temp. Y- Axis Solubility)

This unique property has been used in the separation of Neodymium Sulphate from Iron Sulphate by 'fractional crystallisation'. Leachate containing Neodymium Sulphate and Iron Sulphate was heated. As the temp. reached to about 90^{0}C, Neodymium Sulphate crystallises out. Solid Neodymium Sulphate was collected by decantation of supernatant solution. This exercise was repeated several times till all the Neodymium Sulphate present associated with Iron sulphate was completely extracted. Solid obtained was further recrystallized to get mainly pink coloured $Nd_2(SO_4)_3.10H_2O$ crystals (Fig.6b)**.**Left over solution containing Iron sulphate free from Neodymium Sulphate was separately collected, evaporated, concentrated, crystallised and recrystallized to get light green coloured $FeSO_4.7H_2O$(Fig.6c)**.** $Nd_2(SO_4)_3.10H_2O$ crystals have been spectroscopically characterised (Fig.13).

Fig. 6(a) Nickel Sulphate, (6b) Neodymium Sulphate and (6c) Ferrous sulphate

III (v): Conversion of Neodymium Sulphate to Neodymium Oxalate

Neodymium Sulphate cannot be directly converted in to Neodymium oxalate. Therefore it was first converted in to Neodymium nitrate and further Neodymium nitrate was converted into Neodymium oxalate using oxalic acid according to the equation.

$$2Nd\,(NO_3)_3 + 3H_2C_2O_4 \longrightarrow Nd_2(C_2O_4)_3\,.10H_2O + 2HNO_3$$

Neodymium oxalate obtained was collected by filtration, washed thoroughly till it was free from oxalate and re crystallised to get solid $Nd_2(C_2\,O_4)_3.10H_2O$ which appears light pink (Fig.7) on exposure to incandescent light and almost colourless in fluorescent light (Fig.8)

Fig.7 $Nd_2(C_2O_4)_3$ exposed to incandescent light

Fig.8 $Nd_2(C_2O_4)_3$ exposed to fluorescent light

Fig.9 REEs oxide

III (vi) Conversion Of Neodymium Oxalate To Neodymium Oxide

Neodymium oxalate obtained on roasting to temp. of 950^{0}C decomposed to produce brown coloured solid mainly containing Neodymium oxide and other REEs (Fig.9).

Resources recovered such as Neodymium magnets, Neodymium Oxalate, and Neodymium oxide have been characterised by EDXRF spectroscopy besides Neodymium Oxalate has been characterised by IR spectroscopy. To ensure complete conversion of Neodymium sulphate to Neodymium oxalate its IR spectrograph also has been recorded and its thermal decomposition was studied by TGA, DTA and DTG.The whole process of recovery of REEs from HDD magnets is presented in the following flow sheet diagram (Fig 10).

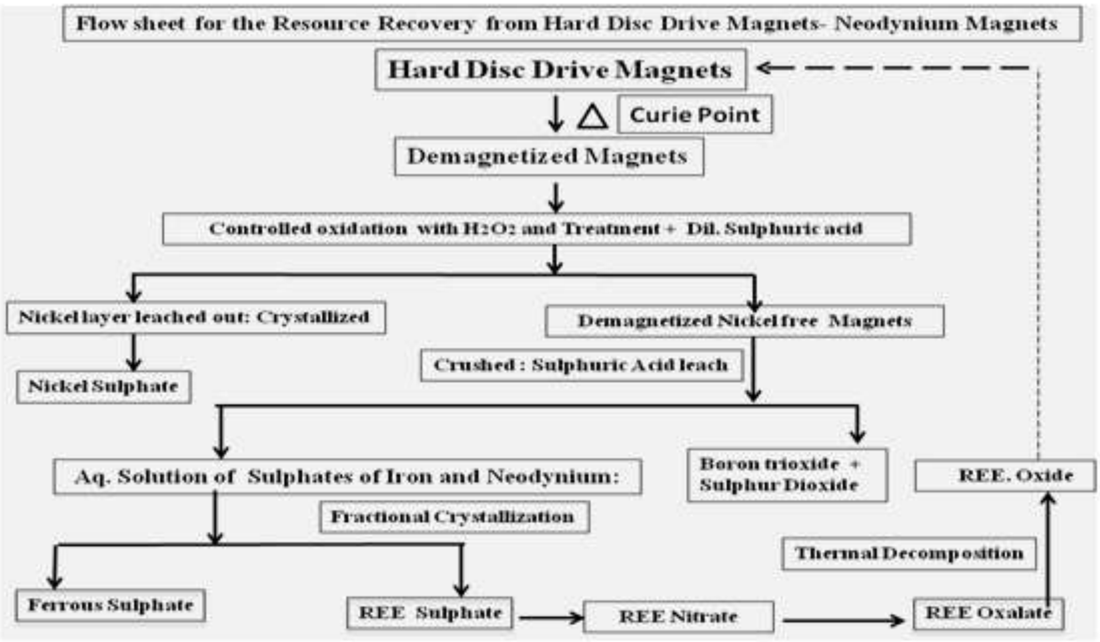


Fig.10 Flow sheet for the recovery of REEs from HDD magnets

IV. RESULTS

Results based on EDXRF spectroscopic studies of Demagnetised magnets, Nd.oxalate, Nd oxide IR of Nd.oxalate, EDXRF and TGA of Nd.oxalte have been presented below

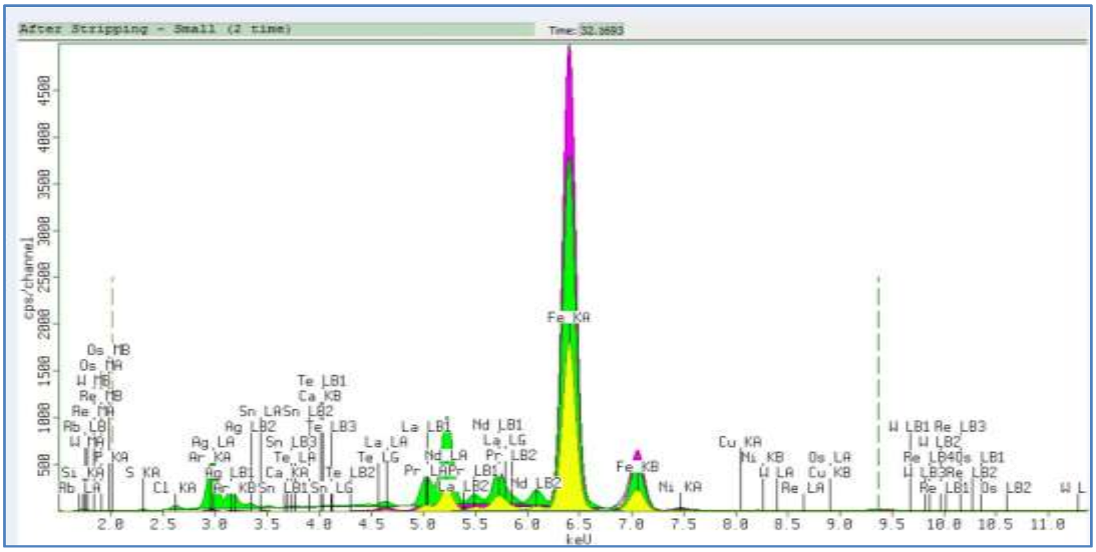


Fig.11 EDXRF of Demagnetised HDD Magnets

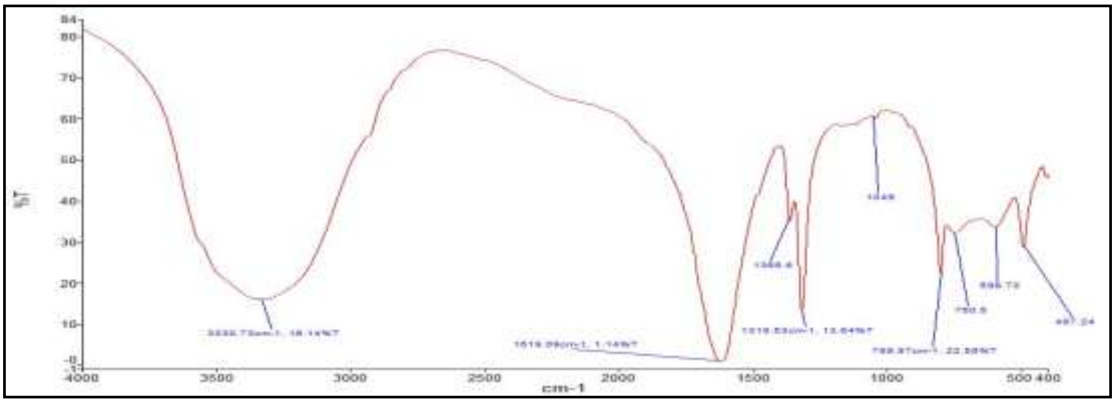


Fig.12 IR spectra of Neodymium oxalate

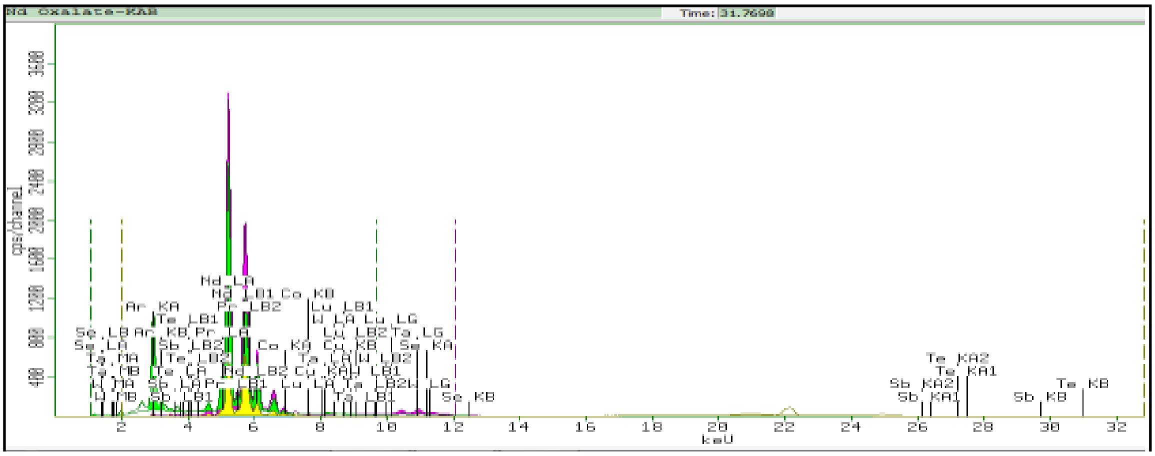


Fig.13 EDXRF of Nd. Oxalate

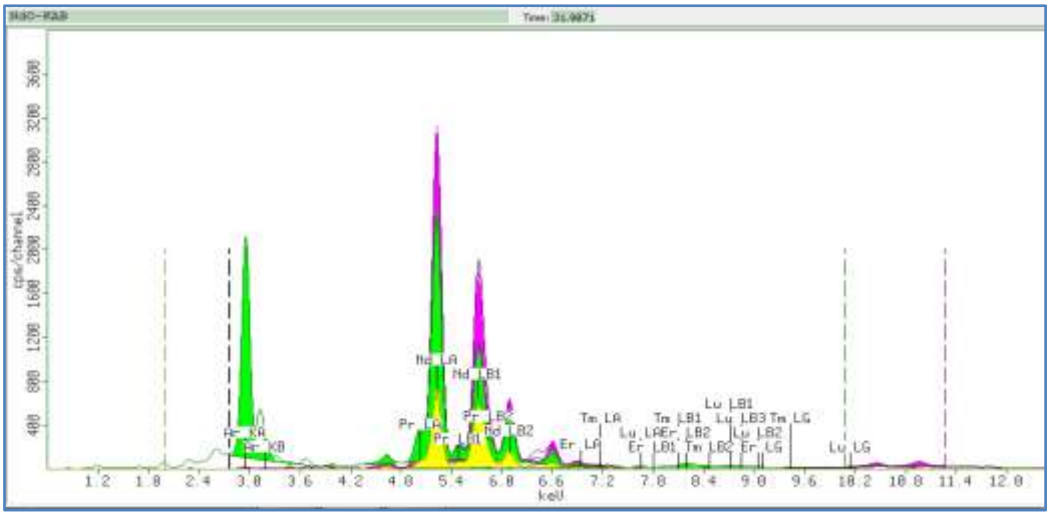


Fig.14 EDXRF of Nd Oxide

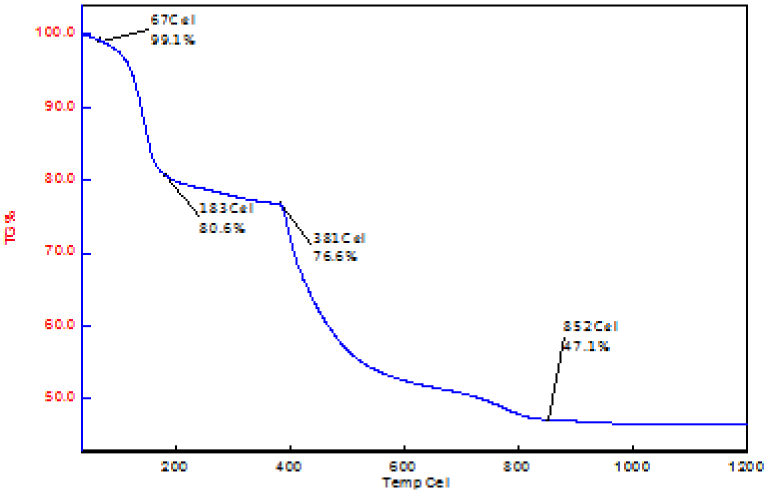


Fig.15. TGA of Neodymium oxalate

Table 1 Analysis Based on EDXRF spectra of HDD Magnets, REE oxalate & REE Oxide

Sl.no	De Magnetised HDD Magnet (A)		REE. Oxalate (B)	REE Oxide (C)	Remarks
1	Al	0.691290%.	-	-	
2	Si	0.79485%	-	-	
3	Cl	0.15153%	-	-	
4	Fe	65.36791	-	-	
5	Ni	0.5845%	-	-	
6	Cu	0.16663	-	-	
7	**Pr**	**6.50317%**	**8.572%**	**5.8782%**	• REEs Recovered from HDD Magnets • Nd enriched from about 25.5% in the magnet to 93.66% (as oxide)
8	**Er**	**ND***	**ND***	**317.7 ppm**	
9	**Nd**	**25.4861%**	**91.08%**	**93.66%**	
10	**Tm**	**ND***	**ND***	**0.2778%**	
11	**Lu**	**ND***	**0.168%**	**0.147%**	

ND* Not detected

V. DISCUSSION

- Fig.11 Suggests the composition of NIBs Nd (26-30 wt%) and Fe (69 wt %) calculated based on molecular mass ($Nd_2Fe_{14}B$ Mol. mass = 1082) and analysed by EDXRF almost agree with each other. Lower Lα. peak at 5.229 keV and highest peak at 6.398 keV for Nd and Fe respectively.
- Fig.4 explains the typical 'lanthanide contraction' i.e. decrease in the radii of tripositive ions of REEs from La 57 to Lu-71.
- Fig.5 explains the solubility of Ferrous Sulphate, Neodymium sulphate and Nickel sulphate as function of temp. It should be noted that the solubility of Neodymium sulphate decreases as temp. increases at O^0 C 13g /100 ml where as 1.2 g /100 ml at 100^0C. Ferrous sulphate and Nickel sulphate show usual trend of increased solubility as the temp. Increases.
- Fig.13 EDXRF analysis of Neodymium oxalate with highest peak at Lα 5.229 keV indicates 91.08% Nd, peak at Lα 5.03keV suggests presence of 8.572% Pr and peak at 5.432 keV presence of 0.168% Lu
- Fig.14 EDXRF analysis of Neodymium oxide with highest peak at Lα 5.229 keV indicates 93.665% Nd, peak at Lα 5.03keV suggests presence of 5.87% Pr and peak at 5.432 keV suggests presence of 0.147 % Lu, peak at 7.179keV confirms the presence of 0.2778% Tm and that at 6.947 keV suggests the presence of 317.69 ppm of Er.
- Table 1 describes major metal composition of Nd magnets (A), REE Oxalates (B) and REE Oxide (C) respectively.
- Table 1(C): EDXRF Spectral analysis of REE oxalate and REE oxide do not show the presence of Fe and Ni suggesting that REEs are completely isolated from other metals like Fe and B originally present in the HDD magnets. This confirms mainly Neodymium content in the magnet enriched from 25.48612 % to 93.665% as Neodymium oxide.
- It is noteworthy that, once Iron and Boron present in the magnet are completely removed, REEs like Er, Tm and Lu open up and quantified also as presented in Table 1(C).
- Fig.12 IR spectroscopic characterisation of Neodymium oxalate- $Nd_2(C_2O_4)_3\,xH_2O$ presents

i) Band width at 3325.cm-1 confirms the presence of –OH group since the compound obtained is hydrated in addition to the presence of –OH as part of carboxylate group.

ii) Band width at about 1361cm^{-1}, 1619 cm^{-1} and 487 cm^{-1} confirm the presence of (CO + CC), (C= O) and (O-C=O) group respectively of oxalate anion and also supporting the conversion of Neodymium sulphate in to its oxalate.

- Fig.15 Based on TGA results, tentative mechanisms of thermal decomposition of NdPr (C_2O_4).10 H_2O have been proposed

i) NdPr(C_2O_4).10 H_2O loses water crystallisation in two stages, first seven molecules of water removed at a temp range of 67-183^{0}C

$$NdPr(C_2O_4).10\ H_2O \longrightarrow NdPr(C_2O_4).3\ H_2O$$

ii) At a temp range of 183^{0}C to 381^{0}C oxalate became anhydrous

$$NdPr(C_2O_4).\ 3\ H_2O \longrightarrow NdPr(C_2O_4).$$

iii) Beyond 380^{0}C decaboxylation takes place in two stages and finally at 900^0 C and beyond $NdPrO_3$ was obtained

$$NdPr(C_2O_4). \longrightarrow NdPrO_3$$

Thermal decomposition studies of the oxalate-hydrates of Praseodymium and neodymium giving stable intermediate products (basic carbonates) before final decomposition to the oxide. The final stage of dehydration of these oxalates is followed by rapid decomposition, indicating that the anhydrous oxalates are unstable; however, anhydrous REE oxalates are fairly stable at about 380°C.

VI. CONCLUSION

- Permanent (HDD) magnets are the sources of REEs that can be recovered by urban mining.
- Recycling of Permanent magnets is an ecological solution to the difficulties of supply in REEs especially for the developing countries.
- With the rapid growth in the use of NIBs magnets, growing environmental need to conserve both energy and raw materials, recycling of magnets shall be an ever important issue.
- Recycling of REEs from secondary materials by urban mining compliments the traditional mining of extraction of REEs from primary ores.
- Recycling is the first step towards environmental protection. Every ton of Permanent magnets recycled by urban mining reduces emission of 11tons of carbon dioxide and saves 46% of energy consumption as compared to what is observed in the extraction of Neodymium by traditional mining.
- Neodymium oxalate, Neodymium oxides obtained as intermediates, have tremendous applications in 'optical glass industry' particularly for the production of cooling glasses
- Combination of Physico-Chemical principles practiced here can be easily scaled up and easily implemented in developing countries.
- Along with strategic elements like Nd, Pr, Ferrous sulphate can also be produced as an important by product.
- The new supply of neodymium magnets lowers the price of neodymium magnets, stabilizes the often-fluctuating neodymium market monopolized by and gives an environmentally sound option to recycle Neodymium magnets that are initially processed in a very toxic extraction process.
- While developed countries are competing for REEs resources, it becomes inevitable much more essential for the developed countries to recover strategic metals like REEs
- Demand for strategic REEs unbelievably increases in the 21st century and combination of hydrometallurgical, pyrometallurgical and/or electrometallurgical technologies will be the future.
- Recycling of REE magnets in developing countries would be an inevitable challenge but not impossible.

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