

A Major Project Thesis
on
**RECOVERY OF RARE EARTH METALS FROM LAPTOP PERMANENT
MAGNETS**

Submitted in partial fulfilment of the requirements for the award of degree of

BACHELOR OF TECHNOLOGY

in

METALLURGICAL ENGINEERING

by

VARDHINI SIVANGI (17011A0646)

VIJVAL VEMULA (17011A0651)

Under the esteemed guidance of

EXTERNAL GUIDE:

Dr. U. RAMBABU, M.Phil, Ph.D,
Principal Scientist & Head of RoHS
Department, C-MET, Phase III
Hcl-Post, Cherlapally
Hyderabad – 500 057

INTERNAL GUIDE:

Dr. B. RAMESH CHANDRA
Associate Professor
Metallurgical Engineering
JNTUHCEH
Kukatpally, Hyd – 500 085



DEPARTMENT OF METALLURGICAL ENGINEERING
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY HYDERABAD
COLLEGE OF ENGINEERING
(AUTONOMOUS)
HYDERABAD-500 085
TELANGANA STATE

2021

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY HYDERABAD

COLLEGE OF ENGINEERING HYDERABAD – 500 085

(AUTONOMOUS)

DEPARTMENT OF METALLURGICAL ENGINEERING



CERTIFICATE

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17011A0646

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SIGNATURE OF THE HEAD OF THE DEPARTMENT

Dr. K. SRINIVASA VADAYAR,

Head of the department & Associate Professor,

Department of Metallurgical Engineering,

JNTUH College of Engineering, Hyderabad.

CENTRE FOR MATERIALS FOR ELECTRONICS TECHNOLOGY (CMET)
IDA, PHASE III, HCL-POST, CHERLAPALLY, HYDERABAD – 500 057
DEPARTMENT OF RESTRICTION OF HAZARDOUS SUBSTANCES (RoHS)



CERTIFICATE

This is to certify that **VARDHINI SIVANGI (17011A0646)** and **VIJVAL VEMULA (17011A0651)** of 4th year B.Tech. from Department of Metallurgical Engineering, JNTUH College of Engineering, Hyderabad, carried out their project “**RECOVERY OF RARE EARTH METALS FROM LAPTOP PERMANENT MAGNETS**” at Centre for Materials for Electronics Technology (CMET), Hyderabad, as a part of the curriculum from 27th of March 2021 to the 22nd of April 2021.

Dr. U. RAMBABU, M.Phil, Ph.D,
Principal Scientist and Head of RoHS Department,
Centre for Materials for Electronics Technology (CMET),
Hyderabad.

CENTRE FOR MATERIALS FOR ELECTRONICS TECHNOLOGY (CMET)
IDA, PHASE III, HCL-POST, CHERLAPALLY, HYDERABAD – 500 057
DEPARTMENT OF RESTRICTION OF HAZARDOUS SUBSTANCES (RoHS)



CERTIFICATE

This is to certify that **VARDHINI SIVANGI (17011A0646)** of 4th year B.Tech. from Department of Metallurgical Engineering, JNTUH College of Engineering, Hyderabad, carried out her project **“RECOVERY OF RARE EARTH METALS FROM LAPTOP PERMANENT MAGNETS”** at Centre for Materials for Electronics Technology (CMET), Hyderabad, as a part of the curriculum from 27th of March 2021 to the 22nd of April 2021.

Dr. U. RAMBABU, M.Phil, Ph.D,
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Centre for Materials for Electronics Technology (CMET),
Hyderabad.

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DEPARTMENT OF RESTRICTION OF HAZARDOUS SUBSTANCES (RoHS)



CERTIFICATE

This is to certify that **VIJVAL VEMULA (17011A0651)** of 4th year B.Tech. from Department of Metallurgical Engineering, JNTUH College of Engineering, Hyderabad, carried out his project **“RECOVERY OF RARE EARTH METALS FROM LAPTOP PERMANENT MAGNETS”** at Centre for Materials for Electronics Technology (CMET), Hyderabad, as a part of the curriculum from 27th of March 2021 to the 22nd of April 2021.

Dr. U. RAMBABU, M.Phil, Ph.D,
Principal Scientist and Head of RoHS Department,
Centre for Materials for Electronics Technology (CMET),
Hyderabad.

DECLARATION

We hereby declare that the Major project entitled “**RECOVERY OF RARE EARTH METALS FROM LAPTOP PERMANENT MAGNETS**” is carried out by us at Centre For Materials For Electronics Technology (CMET), Hyderabad during the academic year 2020-2021 in partial fulfilment of the requirement for the award of Bachelor of Technology in Metallurgical Engineering from Jawaharlal Nehru Technological University Hyderabad as an undergraduate undersupervision of **Dr. U. RAMBABU, Principal Scientist & Head of RoHS Department, C-MET, Hyderabad**. We have not submitted the same to any other university or organization for the award of any other degree.

Date:

Place:

VARDHINI SIVANGI (17011A646)

VIJVAL VEMULA (17011A0651)

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VARDHINI SIVANGI (17011A0646)
VIJVAL VEMULA (17011A651)

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ABSTRACT

NdFeB permanent magnets have different life cycles, depending on the applications: from as short as 2–3 years in consumer electronics to 20–30 years in wind turbines. The size of the magnets ranges from less than 1 g in small consumer electronics to about 1 kg in electric vehicles (EVs) and hybrid and electric vehicles (HEVs), and can be as large as 1000–2000 kg in the generators of modern wind turbines. NdFeB permanent magnets contain about 31–32 wt% of rare-earth elements (REEs). Recycling of REEs contained in this type of magnets from the End-of-Life (EOL) products will play an important and complementary role in the total supply of REEs in the future. However, collection and recovery of the magnets from small consumer electronics imposes great social and technological challenges. This paper gives an overview of the sources of NdFeB permanent magnets related to their applications, followed by a summary of the various available technologies to recover the REEs from these magnets, including physical processing and separation, direct alloy production, and metallurgical extraction and recovery. At present, no commercial operation has been identified for recycling the EOL NdFeB permanent magnets and the recovery of the associated REE content. Most of the processing methods are still at various research and development stages. It is estimated that in the coming 10–15 years, the recycled REEs from EOL permanent magnets will play a significant role in the total REE supply in the magnet sector, provided that efficient technologies will be developed and implemented in practice.

Keywords: NdFeB Permanent magnets, Rare-Earth Elements (REEs), Electronics, Electrical Vehicles, Hybrid Electrical Vehicles

1. INTRODUCTION

1.1 RARE EARTH ELEMENTS:

The rare-earth elements, also called the rare-earth metals or rare-earth oxides, or the lanthanides are a set of 17 nearly indistinguishable lustrous silvery-white soft heavy metals. Scandium and yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties, but have different electronic and magnetic properties.

The 1985 International Union of Pure and Applied Chemistry "Red Book" recommends that *lanthanoid* is used rather than *lanthanide*. The ending "-ide" normally indicates a negative ion. However, owing to wide current usage, "lanthanide" is still allowed and is roughly analogous to rare earth elements.

In pure form, these metals tarnish slowly in air at room temperature, and react slowly with cold water to form hydroxides, liberating hydrogen. They react with steam to form oxides, and at elevated temperature (400 °C) ignite spontaneously and burn with a fierce colorful pyrotechnic flame.

These elements and their compounds have no known biological function. The water-soluble compounds are mildly to moderately toxic, but the insoluble ones are not.

The rare earths have diverse applications in electrical and electronic components, lasers, glass, magnetic materials, and industrial processes, but since they do not occur as base metals or in lump or visible quantities like iron or aluminum, their names and properties are unfamiliar in everyday life. One of the most familiar may be unusually powerful neodymium magnets sold as novelties.

Despite their name, rare-earth elements are relatively plentiful in Earth's crust, with cerium being the 25th most abundant element at 68 parts per million, more abundant than copper. All isotopes of promethium are radioactive, and it does not occur naturally in the earth's crust; however, a trace amount is generated by decay of uranium 238. They are often found in minerals with thorium, and less commonly uranium. Because of their geochemical properties, rare-earth elements are typically dispersed and not often found concentrated in rare-earth minerals. Consequently, economically exploitable ore deposits are sparse (i.e. "rare"). The first rare-earth mineral discovered (1787) was gadolinite, a black mineral composed of cerium, yttrium, iron, silicon, and other elements. This mineral was extracted from a mine in the village of Ytterby in Sweden; four of the rare-earth elements bear names derived from this single location.

Fig. 1.1 Position of REE in the Periodic Table

The first rare earth element discovered was the black mineral "ytterbite" (renamed to gadolinite in

ceria and yttria (the similarity of the rare-earth metals' chemical properties made their separation difficult).

In 1839 Carl Gustav Mosander, an assistant of Berzelius, separated ceria by heating the nitrate and dissolving the product in nitric acid. He called the oxide of the soluble salt *lanthana*. It took him three more years to separate the lanthana further into *didymia* and pure lanthana. Didymia, although not further separable by Mosander's techniques, was in fact still a mixture of oxides.

In 1842 Mosander also separated the yttria into three oxides: pure yttria, terbia and erbia (all the names are derived from the town name "Ytterby"). The earth giving pink salts he called *terbium*; the one that yielded yellow peroxide he called *erbium*.

So in 1842 the number of known rare-earth elements had reached six: yttrium, cerium, lanthanum, didymium, erbium and terbium.

Nils Johan Berlin and Marc Delafontaine tried also to separate the crude yttria and found the same substances that Mosander obtained, but Berlin named (1860) the substance giving pink salts *erbium*, and Delafontaine named the substance with the yellow peroxide *terbium*. This confusion led to several false claims of new elements, such as the *mosandrium* of J. Lawrence Smith, or the *philippium* and *decipium* of Delafontaine. Due to the difficulty in separating the metals (and determining the separation is complete), the total number of false discoveries was dozens, with some putting the total number of discoveries at over a hundred.



Fig: 1.2 Rare Earth Ore



Fig: 1.3 Refined rare-earth oxides are heavy gritty powders usually brown or black, but can be lighter colors as shown here.

1.1.1.1 Spectroscopic identification:

There were no further discoveries for 30 years, and the element didymium was listed in the periodic table of elements with a molecular mass of 138. In 1879 Delafontaine used the new physical process of optical flame spectroscopy and found several new spectral lines in didymia.

Also in 1879, the new element *samarium* was isolated by Paul Émile Lecoq de Boisbaudran from the mineral samarskite.

The samaria earth was further separated by Lecoq de Boisbaudran in 1886, and a similar result was obtained by Jean Charles Galissard de Marignac by direct isolation from samarskite. They named the element *gadolinium* after Johan Gadolin, and its oxide was named "gadolinia".

Further spectroscopic analysis between 1886 and 1901 of samaria, yttria, and samarskite by William Crookes, Lecoq de Boisbaudran and Eugène-Anatole Demarçay yielded several new spectroscopic lines that indicated the existence of an unknown element. The fractional crystallization of the oxides then yielded *europium* in 1901.

In 1839 the third source for rare earths became available. This is a mineral similar to gadolinite, *uranotantalum* (now called "samarskite"). This mineral from Miass in the southern Ural Mountains was documented by Gustav Rose. The Russian chemist R. Harmann proposed that a new element he called "ilmenium" should be present in this mineral, but later, Christian Wilhelm Blomstrand, Galissard de Marignac, and Heinrich Rose found only tantalum and niobium (columbium) in it.

The exact number of rare-earth elements that existed was highly unclear, and a maximum number of 25 was estimated. The use of X-ray spectra (obtained by X-ray crystallography) by Henry Gwyn Jeffreys Moseley made it possible to assign atomic numbers to the elements. Moseley found that the exact number of lanthanides had to be 15, and that element 61 had yet to be discovered.

Using these facts about atomic numbers from X-ray crystallography, Moseley also showed that hafnium (element 72) would not be a rare-earth element. Moseley was killed in World War I in 1915, years before hafnium was discovered. Hence, the claim of Georges Urbain that he had discovered element 72 was untrue. Hafnium is an element that lies in the periodic table immediately below zirconium, and hafnium and zirconium are very similar in their chemical and physical properties.

During the 1940s, Frank Spedding and others in the United States (during the Manhattan Project) developed chemical ion-exchange procedures for separating and purifying the rare-earth elements. This method was first applied to the actinides for separating plutonium-239 and neptunium from uranium, thorium, actinium, and the other actinides in the materials produced in nuclear reactors. Plutonium-239 was very desirable because it is a fissile material.

The principal sources of rare-earth elements are the minerals bastnäsite, monazite, and loparite and the lateritic ion-adsorption clays. Despite their high relative abundance, rare-earth minerals are more difficult to mine and extract than equivalent sources of transition metals (due in part to their similar chemical properties), making the rare-earth elements relatively expensive. Their industrial use was very limited until efficient separation techniques were developed, such as ion exchange, fractional crystallization and liquid–liquid extraction during the late 1950s and early 1960s.

Some ilmenite concentrates contain small amounts of scandium and other rare-earth elements, which could be analysed by XRF.

1.1.1.2 Early classification

Before the time that ion-exchange methods and elution were available, the separation of the rare earths was primarily achieved by repeated precipitation or crystallization. In those days, the first separation was into two main groups, the cerium earths (scandium, lanthanum, cerium, praseodymium, neodymium, and samarium) and the yttrium earths (yttrium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium). Europium, gadolinium, and terbium were either considered as a separate group of rare-earth elements (the terbium group), or europium was included in the cerium group, and gadolinium and terbium were included in the yttrium group. The reason for this division arose from the difference in solubility of rare-earth double sulfates with sodium and potassium. The sodium double sulfates of the cerium group are poorly soluble, those of the terbium group slightly, and those of the yttrium group are very soluble. Sometimes, the yttrium group was further split into the erbium group (dysprosium, holmium, erbium, and thulium) and the ytterbium group (ytterbium and lutetium), but today the main grouping is between the cerium and the yttrium groups. Today, the rare-earth elements are classified as light or heavy rare-earth elements, rather than in cerium and yttrium groups.

1.1.1.3 Light versus heavy classification

The classification of rare-earth elements is inconsistent between authors. The most common distinction between rare-earth elements is made by atomic numbers; those with low atomic numbers are referred to as light rare-earth elements (LREE), those with high atomic numbers are the heavy rare-earth elements (HREE), and those that fall in between are typically referred to as the middle rare-earth elements (MREE). Commonly, rare-earth elements with atomic numbers 57 to 61 (lanthanum to promethium) are classified as light and those with atomic numbers greater than 62 are classified as heavy-rare earth elements.^[23] Increasing atomic numbers between light

copper). The exception is the highly unstable and radioactive promethium "rare earth" is quite scarce. The longest-lived isotope of promethium has a half-life of 17.7 years, so the element exists in nature in only negligible amounts (approximately 572 g in the entire Earth's crust). Promethium is one of the two elements that do not have stable (non-radioactive) isotopes and are followed by (i.e. with higher atomic number) stable elements (the other being technetium).

The rare-earth elements are often found together. During the sequential accretion of the Earth, the dense rare-earth elements were incorporated into the deeper portions of the planet. Early differentiation of molten material largely incorporated the rare-earths into mantle rocks. The high field strength and large ionic radii of rare-earths make them incompatible with the crystal lattices of most rock-forming minerals, so REE will undergo strong partitioning into a melt phase if one is present. REE are chemically very similar and have always been difficult to separate, but a gradual decrease in ionic radius from LREE to HREE, called lanthanide contraction, can produce a broad separation between light and heavy REE. The larger ionic radii of LREE make them generally more incompatible than HREE in rock-forming minerals, and will partition more strongly into a melt phase, while HREE may prefer to remain in the crystalline residue, particularly if it contains HREE-compatible minerals like garnet. The result is that all magma formed from partial melting will always have greater concentrations of LREE than HREE, and individual minerals may be dominated by either HREE or LREE, depending on which range of ionic radii best fits the crystal lattice.

Among the anhydrous rare-earth phosphates, it is the tetragonal mineral xenotime that incorporates yttrium and the HREE, whereas the monoclinic monazite phase incorporates cerium and the LREE preferentially. The smaller size of the HREE allows greater solid solubility in the rock-forming minerals that make up Earth's mantle, and thus yttrium and the HREE show less enrichment in Earth's crust relative to chondritic abundance than does cerium and the LREE. This has economic consequences: large ore bodies of LREE are known around the world and are being exploited. Ore bodies for HREE are more rare, smaller, and less concentrated. Most of the current supply of HREE originates in the "ion-absorption clay" ores of Southern China. Some versions provide concentrates containing about 65% yttrium oxide, with the HREE being present in ratios reflecting the Oddo–Harkins rule: even-numbered REE at abundances of about 5% each, and odd-numbered REE at abundances of about 1% each. Similar compositions are found in xenotime or gadolinite.

Well-known minerals containing yttrium, and other HREE, include gadolinite, xenotime, samarskite, euxenite, fergusonite, yttrotantalite, yttrotungstite, yttrifluorite (a variety of fluorite), thalenite, yttrialite. Small amounts occur in zircon, which derives its typical yellow fluorescence from some of the accompanying HREE. The zirconium mineral eudialyte, such as is found in southern Greenland, contains small but potentially useful amounts of yttrium. Of the above yttrium minerals, most played a part in providing research quantities of lanthanides during the discovery days. Xenotime is occasionally recovered as a byproduct of heavy-sand processing, but is not as abundant as the similarly recovered monazite (which typically contains a few percent of yttrium). Uranium ores from Ontario have occasionally yielded yttrium as a byproduct.

Enriched deposits of rare-earth elements at the surface of the Earth, carbonatites and pegmatites, are related to alkaline plutonism, an uncommon kind of magmatism that occurs in tectonic settings where there is rifting or that are near subduction zones. In a rift setting, the alkaline magma is produced by very small degrees of partial melting (<1%) of garnet peridotite in the upper mantle (200 to 600 km depth). This melt becomes enriched in incompatible elements, like the rare-earth elements, by leaching them out of the crystalline residue. The resultant magma rises as a diapir, or diatreme, along pre-existing fractures, and can be emplaced deep in the crust, or erupted at the surface. Typical REE enriched deposits types forming in rift settings are carbonatites, and A- and M-Type granitoids. Near subduction zones, partial melting of the subducting plate within the asthenosphere (80 to 200 km depth) produces a volatile-rich magma (high concentrations of CO₂ and water), with high concentrations of alkaline elements, and high element mobility that the rare-earths are strongly partitioned into. This melt may also rise along pre-existing fractures, and be emplaced in the crust above the subducting slab or erupted at the surface. REE enriched deposits forming from these melts are typically S-Type granitoids.

Rare-earth elements can also be enriched in deposits by secondary alteration either by interactions with hydrothermal fluids or meteoric water or by erosion and transport of resistant REE-bearing minerals. Argillization of primary minerals enriches insoluble elements by leaching out silica and other soluble elements, recrystallizing feldspar into clay minerals such as kaolinite, halloysite and montmorillonite. In tropical regions where precipitation is high, weathering forms a thick argillized regolith, this process is called supergene enrichment and produces laterite deposits; heavy rare-earth elements are incorporated into the residual clay by absorption. This kind of deposit is only mined for REE in Southern China, where the majority of global heavy rare-earth element production occurs. REE-laterites do form elsewhere, including over the carbonatite at

Mount Weld in Australia. REE may also be extracted from placer deposits if the sedimentary parent lithology contained REE-bearing, heavy resistant minerals.

In 2011, Yasuhiro Kato, a geologist at the University of Tokyo who led a study of Pacific Ocean seabed mud, published results indicating the mud could hold rich concentrations of rare-earth minerals. The deposits, studied at 78 sites, came from hot plumes from hydrothermal vents pull[ing] these materials out of seawater and depositing them on the seafloor, bit by bit, over tens of millions of years. One square patch of metal-rich mud 2.3 kilometers wide might contain enough rare earths to meet most of the global demand for a year, Japanese geologists report in *Nature Geoscience*.

1.1.3.1 Geochemistry applications:

The application of rare-earth elements to geology is important to understanding the petrological processes of igneous, sedimentary and metamorphic rock formation. In geochemistry, rare-earth elements can be used to infer the petrological mechanisms that have affected a rock due to the subtle atomic size differences between the elements, which causes preferential fractionation of some rare earths relative to others depending on the processes at work.

In geochemistry, rare-earth elements are typically presented in normalized "spider" diagrams, in which concentration of rare-earth elements are normalized to a reference standard and are then expressed as the logarithm to the base 10 of the value. Commonly, the rare-earth elements are normalized to chondritic meteorites, as these are believed to be the closest representation of unfractionated solar system material. However, other normalizing standards can be applied depending on the purpose of the study. Normalization to a standard reference value, especially of a material believed to be unfractionated, allows the observed abundances to be compared to initial abundances of the element. Normalization also removes the pronounced 'zig-zag' pattern caused by the differences in abundance between even and odd atomic numbers. The trends that are observed in "spider" diagrams are typically referred to as "patterns", which may be diagnostic of petrological processes that have affected the material of interest.

The rare-earth elements patterns observed in igneous rocks are primarily a function of the chemistry of the source where the rock came from, as well as the fractionation history the rock has undergone. Fractionation is in turn a function of the partition coefficients of each element. Partition coefficients are responsible for the fractionation of a trace elements (including rare-earth elements) into the liquid phase (the melt/magma) into the solid phase (the mineral). If an element preferentially remains in the solid phase it is termed 'compatible', and it preferentially partitions

into the melt phase it is described as 'incompatible'. Each element has a different partition coefficient, and therefore fractionates into solid and liquid phases distinctly. These concepts are also applicable to metamorphic and sedimentary petrology.

In igneous rocks, particularly in felsic melts, the following observations apply: anomalies in europium are dominated by the crystallization of feldspars. Hornblende, controls the enrichment of MREE compared to LREE and HREE. Depletion of LREE relative to HREE may be due to the crystallization of olivine, orthopyroxene, and clinopyroxene. On the other hand, depletion of HREE relative to LREE may be due to the presence of garnet, as garnet preferentially incorporates HREE into its crystal structure. The presence of zircon may also cause a similar effect.

In sedimentary rocks, rare-earth elements in clastic sediments are a representation provenance. The rare-earth element concentrations are not typically affected by sea and river waters, as rare-earth elements are insoluble and thus have very low concentrations in these fluids. As a result, when a sediment is transported, rare-earth element concentrations are unaffected by the fluid and instead the rock retains the rare-earth element concentration from its source.

Sea and river waters typically have low rare-earth element concentrations. However, aqueous geochemistry is still very important. In oceans, rare-earth elements reflect input from rivers, hydrothermal vents, and aeolian sources; this is important in the investigation of ocean mixing and circulation.

Rare-earth elements are also useful for dating rocks, as some radioactive isotopes display long half-lives. Of particular interest are the La-Ce, Sm-Nd and Lu-Hf systems.

1.1.4 GLOBAL RARE-EARTH PRODUCTION:

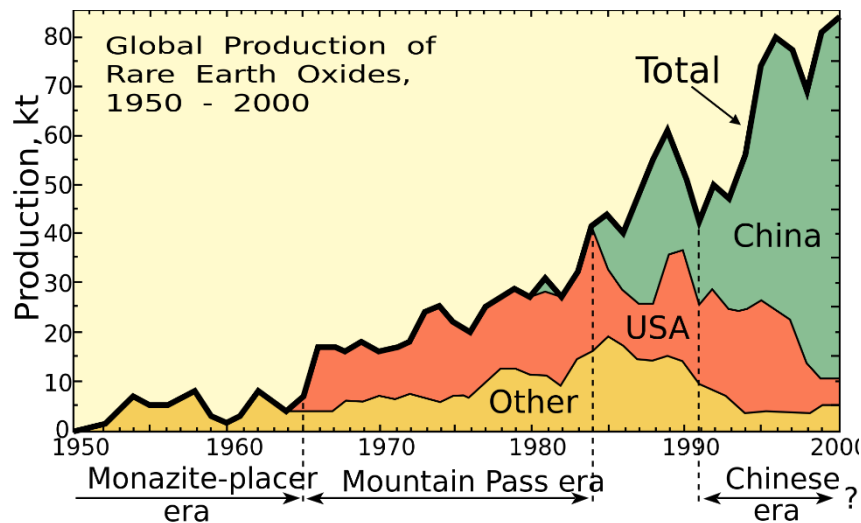


Fig: 1.5 Global Production 1950-2000

Until 1948, most of the world's rare earths were sourced from placer sand deposits in India and Brazil. Through the 1950s, South Africa was the world's rare-earth source, from a monazite-rich reef at the Steenkampskraal mine in Western Cape province. Through the 1960s until the 1980s, the Mountain Pass rare earth mine in California made the United States the leading producer. Today, the Indian and South African deposits still produce some rare-earth concentrates, but they are dwarfed by the scale of Chinese production. In 2017, China produced 81% of the world's rare-earth supply, mostly in Inner Mongolia, although it had only 36.7% of reserves. Australia was the second and only other major producer with 15% of world production. All of the world's heavy rare earths (such as dysprosium) come from Chinese rare-earth sources such as the polymetallic Bayan Obo deposit. The Browns Range mine, located 160 km south east of Halls Creek in northern Western Australia, is currently under development and is positioned to become the first significant dysprosium producer outside of China.

Increased demand has strained supply, and there is growing concern that the world may soon face a shortage of the rare earths. In several years from 2009 worldwide demand for rare-earth elements is expected to exceed supply by 40,000 tonnes annually unless major new sources are developed. In 2013, it was stated that the demand for REEs would increase due to the dependence of the EU on these elements, the fact that rare earth elements cannot be substituted by other elements and that REEs have a low recycling rate. Furthermore, due to the increased demand and low supply, future prices are expected to increase and there is a chance that countries other than China will open REE mines. REE is increasing in demand due to the fact that they are essential for new and innovative technology that is being created. These new products that need REEs to be

produced are high technology equipment such as smart phones, digital cameras, computer parts, semiconductors, etc. In addition, these elements are more prevalent in the following industries: renewable energy technology, military equipment, glass making, and metallurgy.

1.1.4.1 China:

These concerns have intensified due to the actions of China, the predominant supplier. Specifically, China has announced regulations on exports and a crackdown on smuggling. On September 1, 2009, China announced plans to reduce its export quota to 35,000 tons per year in 2010–2015 to conserve scarce resources and protect the environment. On October 19, 2010, *China Daily*, citing an unnamed Ministry of Commerce official, reported that China will further reduce quotas for rare-earth exports by 30 percent at most next year to protect the precious metals from over-exploitation. The government in Beijing further increased its control by forcing smaller, independent miners to merge into state-owned corporations or face closure. At the end of 2010, China announced that the first round of export quotas in 2011 for rare earths would be 14,446 tons, which was a 35% decrease from the previous first round of quotas in 2010. China announced further export quotas on 14 July 2011 for the second half of the year with total allocation at 30,184 tons with total production capped at 93,800 tonnes. In September 2011, China announced the halt in production of three of its eight major rare-earth mines, responsible for almost 40% of China's total rare-earth production. In March 2012, the US, EU, and Japan confronted China at WTO about these export and production restrictions. China responded with claims that the restrictions had environmental protection in mind. In August 2012, China announced a further 20% reduction in production. The United States, Japan, and the European Union filed a joint lawsuit with the World Trade Organization in 2012 against China, arguing that China should not be able to deny such important exports.

In response to the opening of new mines in other countries (Lynas in Australia and Molycorp in the United States), prices of rare earths dropped. The price of dysprosium oxide was 994 USD/kg in 2011, but dropped to US\$265/kg by 2014.

1.1.4.2 Outside China:

As a result of the increased demand and tightening restrictions on exports of the metals from China, some countries are stockpiling rare-earth resources.^[55] Searches for alternative sources in Australia, Brazil, Canada, South Africa, Tanzania, Greenland, and the United States are ongoing. Mines in these countries were closed when China undercut world prices in the 1990s, and it will take a few years to restart production as there are many barriers to entry. One example

is the Mountain Pass mine in California, which announced its resumption of operations on a start-up basis on August 27, 2012. Other significant sites under development outside China include Steenkampskraal in South Africa, the world's highest grade rare earths and thorium mine, which is gearing to go back into production. Over 80% of the infrastructure is already complete. Other mines include the Nolans Project in Central Australia, the Bokan Mountain project in Alaska, the remote Hoidas Lake project in northern Canada, and the Mount Weld project in Australia. The Hoidas Lake project has the potential to supply about 10% of the \$1 billion of REE consumption that occurs in North America every year. Vietnam signed an agreement in October 2010 to supply Japan with rare earths from its northwestern Lai Châu Province.

In central Spain, Ciudad Real Province, the proposed rare-earth mining project 'Matamulas' may provide, according to its developers, up to 2,100 Tn/year (33% of the annual UE demand). However, this project has been suspended by regional authorities due to social and environmental concerns. Adding to potential mine sites, ASX listed Peak Resources announced in February 2012, that their Tanzanian-based Ngualla project contained not only the 6th largest deposit by tonnage outside of China, but also the highest grade of rare-earth elements of the 6. North Korea has been reported to have exported rare-earth ore to China, about US\$1.88 million worth during May and June 2014.

1.1.4.3 Malaysian refining plans:

In early 2011, Australian mining company, Lynas, was reported to be "hurrying to finish" a US\$230 million rare-earth refinery on the eastern coast of Peninsular Malaysia's industrial port of Kuantan. The plant would refine ore — lanthanides concentrate from the Mount Weld mine in Australia. The ore would be trucked to Fremantle and transported by container ship to Kuantan. Within two years, Lynas was said to expect the refinery to be able to meet nearly a third of the world's demand for rare-earth materials, not counting China. The Kuantan development brought renewed attention to the Malaysian town of Bukit Merah in Perak, where a rare-earth mine operated by a Mitsubishi Chemical subsidiary, Asian Rare Earth, closed in 1994 and left continuing environmental and health concerns. In mid-2011, after protests, Malaysian government restrictions on the Lynas plant were announced. At that time, citing subscription-only Dow Jones Newswire reports, a Barrons report said the Lynas investment was \$730 million, and the projected share of the global market it would fill put at "about a sixth." An independent review initiated by the Malaysian Government, and conducted by the International Atomic Energy

Agency (IAEA) in 2011 to address concerns of radioactive hazards, found no non-compliance with international radiation safety standards.

However, the Malaysian authorities confirmed that as of October 2011, Lynas was not given any permit to import any rare-earth ore into Malaysia. On February 2, 2012, the Malaysian AELB (Atomic Energy Licensing Board) recommended that Lynas be issued a temporary operating license subject for completion of a number of conditions. On 2 September 2014, Lynas was issued a 2-year full operating stage license by the AELB.

1.1.4.4 Other sources:

Significant quantities of rare-earth oxides are found in tailings accumulated from 50 years of uranium ore, shale and loparite mining at Sillamäe, Estonia. Due to the rising prices of rare earths, extraction of these oxides has become economically viable. The country currently exports around 3,000 tonnes per year, representing around 2% of world production. Similar resources are suspected in the western United States, where gold rush-era mines are believed to have discarded large amounts of rare earths, because they had no value at the time.

In May 2012, researchers from two universities in Japan announced that they had discovered rare earths in Ehime Prefecture, Japan.

In January 2013 a Japanese deep-sea research vessel obtained seven deep-sea mud core samples from the Pacific Ocean seafloor at 5,600 to 5,800 meters depth, approximately 250 kilometres (160 mi) south of the island of Minami-Tori-Shima. The research team found a mud layer 2 to 4 meters beneath the seabed with concentrations of up to 0.66% rare-earth oxides. A potential deposit might compare in grade with the ion-absorption-type deposits in southern China that provide the bulk of Chinese REO mine production, which grade in the range of 0.05% to 0.5% REO.

1.1.1.5 Recycling:

Another recently developed source of rare earths is electronic waste and other wastes that have significant rare-earth components. New advances in recycling technology have made extraction of rare earths from these materials more feasible, and recycling plants are currently operating in Japan, where there is an estimated 300,000 tons of rare earths stored in unused electronics. In France, the Rhodia group is setting up two factories, in La Rochelle and Saint-Fons, that will produce 200 tons of rare earths a year from used fluorescent lamps, magnets and batteries. Coal and coal by-products are a potential source of critical elements including rare earth elements (REE) with estimated amounts in the range of 50 million metric tons.

1.1.5 APPLICATIONS OF REE:

The uses, applications, and demand for rare-earth elements has expanded over the years. Globally, most REEs are used for catalysts and magnets. In USA, more than half of REEs are used for catalysts, and ceramics, glass and polishing are also main uses. Other important uses of rare-earth elements are applicable to the production of high-performance magnets, alloys, glasses, and electronics. Ce and La are important as catalysts, and are used for petroleum refining and as diesel additives. Nd is important in magnet production in traditional and low-carbon technologies. Rare-earth elements in this category are used in the electric motors of hybrid and electric vehicles, generators in wind turbines, hard disc drives, portable electronics, microphones, speakers.

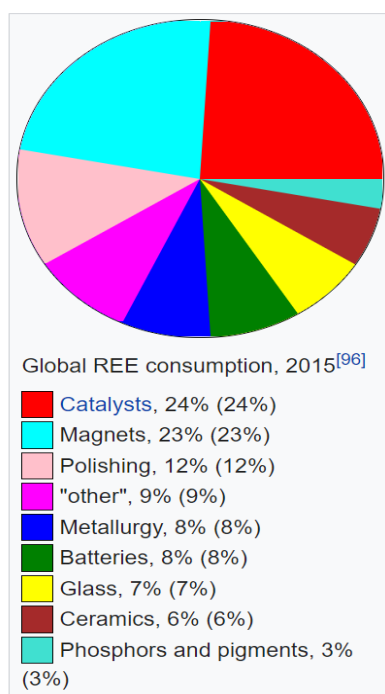


Fig: 1.6 Global consumption of REE

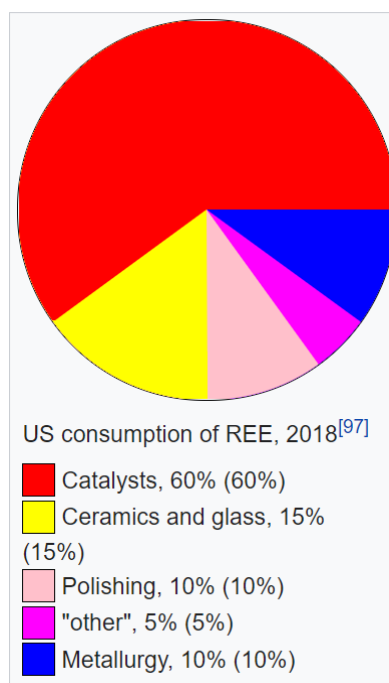


Fig: 1.7 REE consumption in US

Ce, La and Nd are important in alloy making, and in the production of fuel cells and nickel-metal hydride batteries. Ce, Ga and Nd are important in electronics and are used in the production of LCD and plasma screens, fibre optics, lasers, as well as in medical imaging. Additional uses for rare-earth elements are as tracers in medical applications, fertilizers, and in water treatment.

REEs have been used in agriculture to increase plant growth, productivity, and stress resistance seemingly without negative effects for human and animal consumption. REEs are used in agriculture through REE-enriched fertilizers which is a widely used practice in China. In addition, REEs are feed additives for livestock which has resulted in increased production such as larger animals and a higher production of eggs and dairy products. However, this practice has resulted in

REE bio-accumulation within livestock and has impacted vegetation and algae growth in these agricultural areas. Additionally, while no ill effects have been observed at current low concentrations the effects over the long term and with accumulation over time are unknown prompting some calls for more research into their possible effects. Given the limited supply, industries directly compete with each other for resources, e.g., the electronics sector is in direct competition with renewable energy use in windfarms, solar panels and batteries.

1.1.6 ENVIRONMENTAL CONSIDERATIONS:

REEs are naturally found in very low concentration in the environment. Mines are often in countries where environmental and social standards are very low, causing human rights violations, deforestation and contamination of land and water.

Near mining and industrial sites, the concentrations can rise to many times the normal background levels. Once in the environment REEs can leach into the soil where their transport is determined by numerous factors such as erosion, weathering, pH, precipitation, ground water, etc. Acting much like metals, they can speciate depending on the soil condition being either motile or adsorbed to soil particles. Depending on their bio-availability REEs can be absorbed into plants and later consumed by humans and animals. The mining of REEs, use of REE-enriched fertilizers, and the production of phosphorus fertilizers all contribute to REE contamination. Furthermore, strong acids are used during the extraction process of REEs, which can then leach out in to the environment and be transported through water bodies and result in the acidification of aquatic environments. Another additive of REE mining that contributes to REE environmental contamination is cerium oxide (CeO_2) which is produced during the combustion of diesel and is released as an exhaust particulate matter and contributes heavily to soil and water contamination.



Fig: 1.8 False-color satellite image of the Bayan Obo Mining District 2006

Mining, refining, and recycling of rare earths have serious environmental consequences if not properly managed. Low-level radioactive tailings resulting from the occurrence of thorium and uranium in rare-earth element ores present a potential hazard and improper handling of these substances can result in extensive environmental damage. In May 2010, China announced a major, five-month crackdown on illegal mining in order to protect the environment and its resources. This campaign is expected to be concentrated in the South, where mines – commonly small, rural, and illegal operations – are particularly prone to releasing toxic waste into the general water supply. However, even the major operation in Baotou, in Inner Mongolia, where much of the world's rare-earth supply is refined, has caused major environmental damage. China's Ministry of Industry and Information Technology estimated that clean-up costs in Jiangxi province at \$5.5 billion.

It is however possible to filter out and recover any rare earth elements that flow out with the wastewater from mining facilities. However, such filtering and recovery equipment may not always be present on the outlets carrying the wastewater.

1.1.7 IMPACT OF REE CONTAMINATION:

1.1.7.1 On Vegetation:

The mining of REEs has caused the contamination of soil and water around production areas, which has impacted vegetation in these areas by decreasing chlorophyll production which affects photosynthesis and inhibits the growth of the plants. However, the impact of REE contamination on vegetation is dependent on the plants present in the contaminated environment: some plants retain and absorb REEs and some don't. Also, the ability for the vegetation to intake the REE is dependent on the type of REE present in the soil, hence there are a multitude of factors that influence this process. Agricultural plants are the main type of vegetation affected by REE contamination in the environment, the two plants with a higher chance of absorbing and storing REEs being apples and beets. Furthermore, there is a possibility that REEs can leach out into aquatic environments and be absorbed by aquatic vegetation, which can then bio-accumulate and potentially enter the human food-chain if livestock or humans choose to eat the vegetation. An example of this situation was the case of the water hyacinth (*Eichhornia crassipes*) in China, where the water was contaminated due to a REE-enriched fertilizer being used in a nearby agricultural area. The aquatic environment became contaminated with cerium and resulted in the water hyacinth becoming three times more concentrated in cerium than its surrounding water.

1.1.7.2 On human health:

REEs are a large group with many different properties and levels in the environment. Because of this, and limited research, it has been difficult to determine safe levels of exposure for humans. A number of studies have focused on risk assessment based on routes of exposure and divergence from background levels related to nearby agriculture, mining, and industry. It has been demonstrated that numerous REEs have toxic properties and are present in the environment or in work places. Exposure to these can lead to a wide range of negative health outcomes such as cancer, respiratory issues, dental loss, and even death. However REEs are numerous and present in many different forms and at different levels of toxicity, making it difficult to give blanket warnings on cancer risk and toxicity as some of these are harmless while others pose a risk.

The rare earth mining and smelting process can release airborne fluoride which will associate with total suspended particles (TSP) to form aerosols that can enter human respiratory systems and cause damage and respiratory diseases. Research from Baotou, China shows that the fluoride concentration in air near REE mines is higher than the limit value from WHO, which can affect the surrounding environment and become a risk to those that live or work nearby.

1.1.7.3 On animal health:

Experiments exposing rats to various cerium compounds have found accumulation primarily in the lungs and liver. This resulted in various negative health outcomes associated with those organs. REEs have been added to feed in livestock to increase their body mass and increase milk production. They are most commonly used to increase the body mass of pigs, and it was discovered that REEs increase the digestibility and nutrient use of pigs' digestive systems. Studies point to a dose response when considering toxicity versus positive effects. While small doses from the environment or with proper administration seem to have no ill effects, larger doses have been shown to have negative effects specifically in the organs where they accumulate. The process of mining REEs in China has resulted in soil and water contamination in certain areas, which when transported into aquatic bodies could potentially bio-accumulate within aquatic biota. Furthermore, in some cases animals that live in the REE-contaminated areas have been diagnosed with organ or system problems. REEs have been used in freshwater fish farming because it protects the fish from possible diseases. One main reason why they have been avidly used in animal livestock feeding is that they have had better results than inorganic livestock feed enhancers.

1.2 RARE-EARTH MAGNETS:

Rare-earth magnets are strong permanent magnets made from alloys of rare-earth elements. Developed in the 1970s and 1980s, rare-earth magnets are the strongest type of permanent magnets made, producing significantly stronger magnetic fields than other types such as ferrite or alnico magnets. The magnetic field typically produced by rare-earth magnets can exceed 1.4 teslas, whereas ferrite or ceramic magnets typically exhibit fields of 0.5 to 1 tesla.

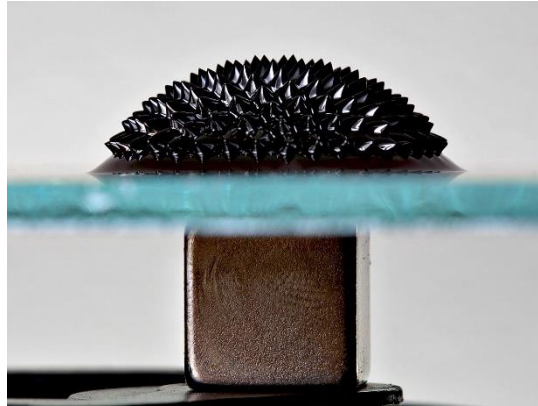


Fig: 1.9 Ferrofluid on glass, with rare-earth magnet underneath

There are two types: neodymium (NdFeB) magnets and samarium–cobalt magnets. Rare-earth magnets are extremely brittle and also vulnerable to corrosion, so they are usually plated or coated (usually with Nickel) to protect them from breaking, chipping, or crumbling into powder.

The development of rare-earth magnets began around 1966, when K. J. Strnat and G. Hoffer of the US Air Force Materials Laboratory discovered that an alloy of yttrium and cobalt, YCo_5 , had by far the largest magnetic anisotropy constant of any material then known.

The term "rare earth" can be misleading, as some of these metals can be as abundant in the Earth's crust as tin or lead, but rare earth ores do not exist in seams (like coal or copper), so in any given cubic kilometre of crust they are "rare". The major source is currently China. Some countries classify rare earth metals as strategically important, and recent Chinese export restrictions on these materials have led some to initiate research programs to develop strong magnets that do not require rare earth metals.

1.2.1 STRENGTH:

The rare-earth (lanthanide) elements are metals that are ferromagnetic, meaning that like iron they can be magnetized to become permanent magnets, but their Curie temperatures (the temperature above which their ferromagnetism disappears) are below room temperature, so in pure form their

magnetism only appears at low temperatures. However, they form compounds with the transition metals such as iron, nickel, and cobalt, and some of these compounds have Curie temperatures well above room temperature. Rare-earth magnets are made from these compounds.

The greater strength of rare-earth magnets is mostly due to two factors:

- First, their crystalline structures have very high magnetic anisotropy. This means that a crystal of the material preferentially magnetizes along a specific crystal axis but is very difficult to magnetize in other directions. Like other magnets, rare-earth magnets are composed of microcrystalline grains, which are aligned in a powerful magnetic field during manufacture, so their magnetic axes all point in the same direction. The resistance of the crystal lattice to turning its direction of magnetization gives these compounds a very high magnetic coercivity (resistance to being demagnetized), so that the strong demagnetizing field within the finished magnet does not reduce the material's magnetization.
- Second, atoms of rare-earth elements can have high magnetic moments. Their orbital electron structures contain many unpaired electrons; in other elements, almost all of the electrons exist in pairs with opposite spins, so their magnetic fields cancel out, but in rare-earths there is much less magnetic cancellation. This is a consequence of incomplete filling of the f-shell, which can contain up to 7 unpaired electrons. In a magnet it is the unpaired electrons, aligned so they spin in the same direction, which generate the magnetic field. This gives the materials high remanence (saturation magnetization J_s). The maximal energy density $B \cdot H_{\max}$ is proportional to J_s^2 , so these materials have the potential for storing large amounts of magnetic energy. The magnetic energy product $B \cdot H_{\max}$ of neodymium magnets is about 18 times greater than ordinary magnets by volume. This allows rare-earth magnets to be smaller than other magnets with the same field strength.

1.2.2 MAGNETIC PROPERTIES:

Some important properties used to compare permanent magnets are: remanence (B_r), which measures the strength of the magnetic field; coercivity (H_{ci}), the material's resistance to becoming demagnetized; energy product ($B \cdot H_{\max}$), the density of magnetic energy; and Curie temperature (T_C), the temperature at which the material loses its magnetism. Rare-earth magnets have higher remanence, much higher coercivity and energy product, but (for neodymium) lower Curie temperature than other types. The table below compares the magnetic performance of the two types of rare-earth magnets, neodymium ($\text{Nd}_2\text{Fe}_{14}\text{B}$) and samarium-cobalt (SmCo_5), with other types of permanent magnets.

Magnet	Preparation	B_r (T)	H_{ci} (kA/m)	$B \cdot H_{max}$ (kJ/m³)	T_C (°C)
Nd ₂ Fe ₁₄ B	sintered	1.0–1.4	750–2000	200–440	310–400
Nd ₂ Fe ₁₄ B	bonded	0.6–0.7	600–1200	60–100	310–400
SmCo ₅	sintered	0.8–1.1	600–2000	120–200	720
Sm(Co,Fe,Cu,Zr)	sintered	0.9–1.15	450–1300	150–240	800
Alnico	sintered	0.6–1.4	275	10–88	700–860
Sr-ferrite	sintered	0.2–0.4	100–300	10–40	450
Iron (Fe) bar magnet	annealed	-----	800	-----	770

Table: 1.1 Magnetic Properties of different rare-earth magnets

1.2.3 TYPES:

1.2.3.1 Samarium-cobalt:

Samarium–cobalt magnets (chemical formula: SmCo₅), the first family of rare-earth magnets invented, are less used than neodymium magnets because of their higher cost and lower magnetic field strength. However, samarium–cobalt has a higher Curie temperature, creating a niche for these magnets in applications where high field strength is needed at high operating temperatures. They are highly resistant to oxidation, but sintered samarium–cobalt magnets are brittle and prone to chipping and cracking and may fracture when subjected to thermal shock.

1.2.3.2 Neodymium:

Neodymium magnets, invented in the 1980s, are the strongest and most affordable type of rare-earth magnet. They are made of an alloy of neodymium, iron, and boron (Nd₂Fe₁₄B), sometimes abbreviated as NIB. Neodymium magnets are used in numerous applications requiring strong, compact permanent magnets, such as electric motors for cordless tools, hard disk drives, magnetic holdowns, and jewelry clasps. They have the highest magnetic field strength and have a higher coercivity (which makes them magnetically stable), but they have a lower Curie temperature and are more vulnerable to oxidation than samarium–cobalt magnets.



Fig: 1.10 Neodymium (NdFeB) magnet with nickel plating mostly removed

Corrosion can cause unprotected magnets to spall off a surface layer or to crumble into a powder. Use of protective surface treatments such as gold, nickel, zinc, and tin plating and epoxy-resin coating can provide corrosion protection; the majority of neodymium magnets use nickel plating to provide a robust protection.

Originally, the high cost of these magnets limited their use to applications requiring compactness together with high field strength. Both the raw materials and the patent licenses were expensive. However, since the 1990s, NIB magnets have become steadily less expensive, and their lower cost has inspired new uses such as magnetic construction toys.

1.2.4 HAZARDS:

The greater force exerted by rare-earth magnets creates hazards that are not seen with other types of magnet. Magnets larger than a few centimeters are strong enough to cause injuries to body parts pinched between two magnets or a magnet and a metal surface, even causing broken bones. Magnets allowed to get too near each other can strike each other with enough force to chip and shatter the brittle material, and the flying chips can cause injuries. Starting in 2005, powerful magnets breaking off toys or from magnetic construction sets started causing injuries and deaths. Young children who have swallowed several magnets have had a fold of the digestive tract pinched between the magnets, causing injury and in one case intestinal perforations, sepsis, and death.

A voluntary standard for toys, permanently fusing strong magnets to prevent swallowing, and capping unconnected magnet strength, was adopted in 2007. In 2009, a sudden growth in sales of magnetic desk toys for adults caused a surge in injuries, with emergency room visits estimated at

3,617 in 2012. In response, the U.S. Consumer Product Safety Commission passed a rule in 2012 restricting rare-earth magnet size in consumer products, but it was vacated by a US federal court decision in November 2016, in a case brought by the one remaining manufacturer. After the rule was nullified, the number of ingestion incidents in the country rose sharply, and is estimated to exceed 1,500 in 2019.

1.2.5 APPLICATIONS OF RARE-EARTH MAGNETS:

Since their prices became competitive in the 1990s, neodymium magnets have been replacing alnico and ferrite magnets in the many applications in modern technology requiring powerful magnets. Their greater strength allows smaller and lighter magnets to be used for a given application.

1.2.5.1 Common applications:

Common applications of rare-earth magnets include:

- computer hard disk drives
- wind turbine generators
- speakers / headphones
- bicycle dynamos
- MRI scanners
- fishing reel brakes
- permanent magnet motors in cordless tools
- high-performance AC servo motors
- traction motors and integrated starter-generators in hybrid and electric vehicles
- mechanically powered flashlights, employing rare earth magnets for generating electricity in a shaking motion or rotating (hand-crank-powered) motion
- industrial uses such as maintaining product purity, equipment protection, and quality control
- capture of fine metallic particles in lubricating oils (crankcases of internal combustion engines, also gearboxes and differentials), so as to keep said particles out of circulation, thereby rendering them unable to cause abrasive wear of moving machine parts.

1.2.5.2 Other applications:

Other applications of rare-earth magnets include:

- Linear motors (used in maglev trains, etc.)
- Stop motion animation: as tie-downs when the use of traditional screw and nut tie-downs is impractical.
- Diamagnetic levitation experimentation, the study of magnetic field dynamics and superconductor levitation.
- Electrodynamic bearings
- Launched roller coaster technology found on roller coaster and other thrill rides.
- LED Throwies, small LEDs attached to a button cell battery and a small rare earth magnet, used as a form of non-destructive graffiti and temporary public art.
- Neodymium magnet toys
- Electric guitar pickups
- Miniature figures, for which rare-earth magnets have gained popularity in the miniatures gaming community for their small size and relative strength assisting in basing and swapping weapons between models.

1.2.6 RECYCLING EFFORTS:

The European Union's ETN-Demeter project (European Training Network for the Design and Recycling of Rare-Earth Permanent Magnet Motors and Generators in Hybrid and Full Electric Vehicles) is examining sustainable design of electric motors used in vehicles. They are, for example, designing electric motors in which the magnets can be easily removed for recycling the rare earth metals.

The European Union's European Research Council also awarded to Principal Investigator, Prof. Thomas Zemb, and co-Principal Investigator, Dr. Jean-Christophe P. Gabriel, an Advanced Research Grant for the project "Rare Earth Element reCYCling with Low harmful Emissions : REE-CYCLE", which aimed at finding new processes for the recycling of rare earth.

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2. ELEMENTAL ANALYSIS

Elemental Analysis is a process where a sample of some material (e.g., soil, waste, minerals, chemical compounds) is analyzed for its elemental and sometimes isotopic composition. Elemental analysis can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present). Elemental analysis falls within the ambit of analytical chemistry, the set of instruments involved in deciphering the chemical nature of our world. In our project, we have used two methods for elemental analysis: EDXRF and ICP-OES analysis, which are discussed below in detail.

2.1 ENERGY-DISPERSIVE X-RAY FLUORESCENCE (EDXRF):

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry is a nondestructive, rapid, multielement, highly accurate, and environment friendly analysis compared with other elemental detection methods. Thus, EDXRF spectrometry is applicable for production quality control, ecological environment monitoring, geological surveying, food inspection, and heritage analysis, among others. A hardware platform for the EDXRF spectrometer is designed in this study based on the theoretical analysis of energy-dispersive X-ray. The platform includes a power supply subsystem, an optical subsystem, a control subsystem, and a personal computer. A fluorescence spectrum analytical method is then developed to obtain the category and content of elements in a sample. This method includes qualitative and quantitative analyses. Finally, a series of experiments is performed. Results show that the precision of the proposed measurement method is below 8%, whereas its repeatability is below 2%.

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry exhibits several advantages over other methods that measure elemental content. This technique can measure numerous sample forms and can satisfy different measurement requirements. Moreover, EDXRF spectrometry can detect a wide range of elements, even several elements simultaneously. This technique is nondestructive, fast, highly accurate, and environment friendly. EDXRF spectrometry can be used on different types of sample, such as bulk, liquid, powder, and gas. It can also detect particles in the air.

2.1.1 EDXRF PRINCIPLE:

Direct excitation is a process by which atoms in a specimen are excited by primary photons from external sources, such as an X-ray tube, radioactive source, and synchrotron beam, to produce primary fluorescence. An alternative process is indirect excitation, in which the observed fluorescence is produced as a secondary process by photons or particles (electrons) originating from direct excitation or other secondary processes within the specimen. X-ray is an electromagnetic radiation generated by high-energy particles bombarding atoms. This radiation has wave-particle duality. X-ray fluorescence (XRF) spectrometry uses primary X-ray photons or other microscopic particles to excite the atoms in the test material to produce secondary XRF for material composition analysis and chemical state research.

2.1.2 XRF SPECTROMETER HARDWARE:

2.1.2.1 Structure of EDXRF Spectrometer:

The EDXRF spectrometer is designed according to Moseley's law. The system is illustrated in Figure 2.1. The spectrometer consists of a power supply, a light path subsystem, a control circuit, and a personal computer (PC). High-voltage power is supplied to the X-ray tube to emit a primary X-ray, which irradiates the sample. The sample is then stimulated to emit XRF, which is received by an XRF detector. The detector classifies the received photons according to energy and counts the number of photons that correspond to different energy levels. The detector then sends the results to the PC, which completes the qualitative and quantitative analyses.

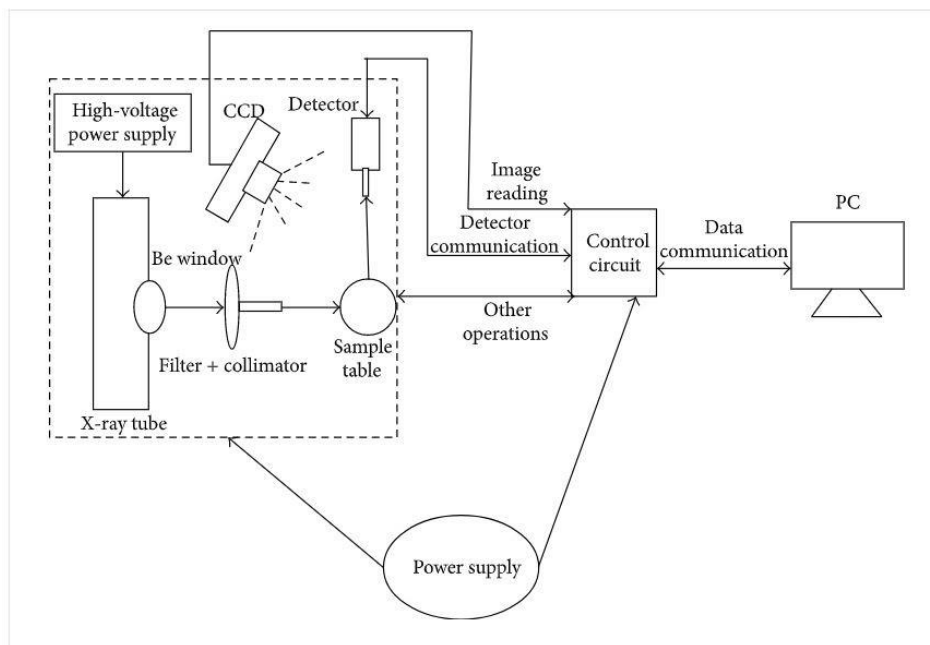


Fig: 2.1 Structural diagram of EDXRF spectrometer

2.1.2.2 Light Path Subsystem:

The light path subsystem is responsible for emitting, receiving, and counting the XRF photons. Its operation is as follows. A high-voltage power supply provides high-voltage energy to the X-ray tube, which is stimulated to emit primary X-ray. The primary X-ray passes through the Be window, filter, and collimator, finally irradiating the sample. The sample is stimulated to emit XRF that can be recognized by the detector. The received XRF is transformed into a low-voltage pulse by the preamplifier. The pulse amplitude that is strictly proportional to the energy of the received XRF is further amplified by the main amplifier. The analog-to-digital converter then transforms the amplified voltage into a digital signal. The digital signal is further shaped, sorted, and transformed

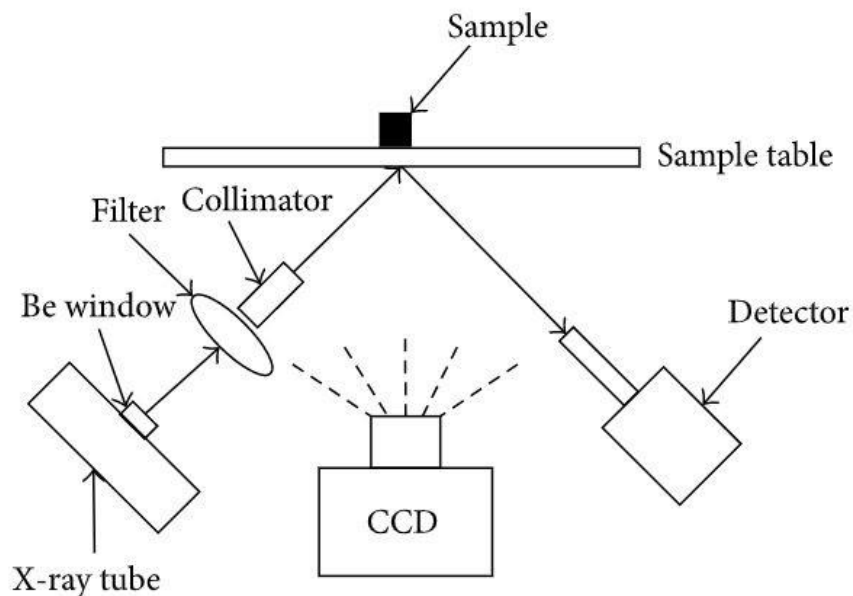


Fig: 2.2 Structural diagram of light path subsystem

into a pulse counter with amplitude information. This information is stored in a multichannel analyzer according to its amplitude and finally formatted to an XRF spectral line. The detector transmits spectral information to the PC through a USB hub in the control circuit for qualitative and quantitative analyses.

The light path subsystem, which includes the X-ray tube, filter, collimator, detector, and a charge-coupled device (CCD) camera, is shown in Figure 2.2.

2.1.3 XRF SPECTRAL SOFTWARE:

Qualitative analysis is performed to identify the elements in the sample. By contrast, quantitative analysis is used not only to identify the elements but also to determine elemental content. According to Moseley's law, the XRF photons of a certain element possess a fixed energy; that is, the XRF photons of elements are unique. The abscissa of a channel address reflects the photon energy in the spectral line. The peak position of the abscissa corresponds to the energy of the characteristic XRF of a certain element. Channel address range of a detector in this system is designed from 0 to 2048. Each XRF photon energy ranges from 103 eV to 104 eV. Therefore, the enlargement factor of the energy/channel address is designed as 20 eV/channel. For example, the photon energy of $K\alpha$ for Ag is approximately 22.162 keV. The channel address should be near 1108 according to the energy calibration of 20 eV/channel. The $K\alpha$ ray of Ag frequently appears in the channel address of 1106.

2.1.3.1 Qualitative Analysis:

Qualitative analysis is the basis of quantitative analysis. Existing element types can be determined using the former analysis. Qualitative analysis is generally divided into three steps.

(1) *Peak Location*. The uncertainty of a large peak is approximately ± 10 keV, whereas that of a small peak is up to ± 50 eV. Small peaks can be neglected when they overlap with a large peak, particularly when its energy level is below 12 keV. Spectral overlap and interference frequently occur in the K line (where the atomic number is between 22 and 35) and the L line (where the atomic number is between 56 and 96). All aforementioned factors hamper an accurate qualitative analysis.

(2) *Peak Recognition*. The uncertainty of the peak position generally increases the difficulty of peak recognition. More than one peak corresponds to the energy peak in the spectrum in several cases. Accumulated, escape, and scattering peaks can also interfere with recognition.

(3) *Element Determination*. Except for light elements, such as Na, Mg, Al, Si, P, and S, identifying an element typically requires more than two characteristic spectral peaks. When the voltage of the X-ray tube is over 30 keV for atomic numbers 19Z to 42Z, the spectral peaks $K\alpha$ and $K\beta$ appear simultaneously. Furthermore, relative intensities in different spectral peaks should also be considered.

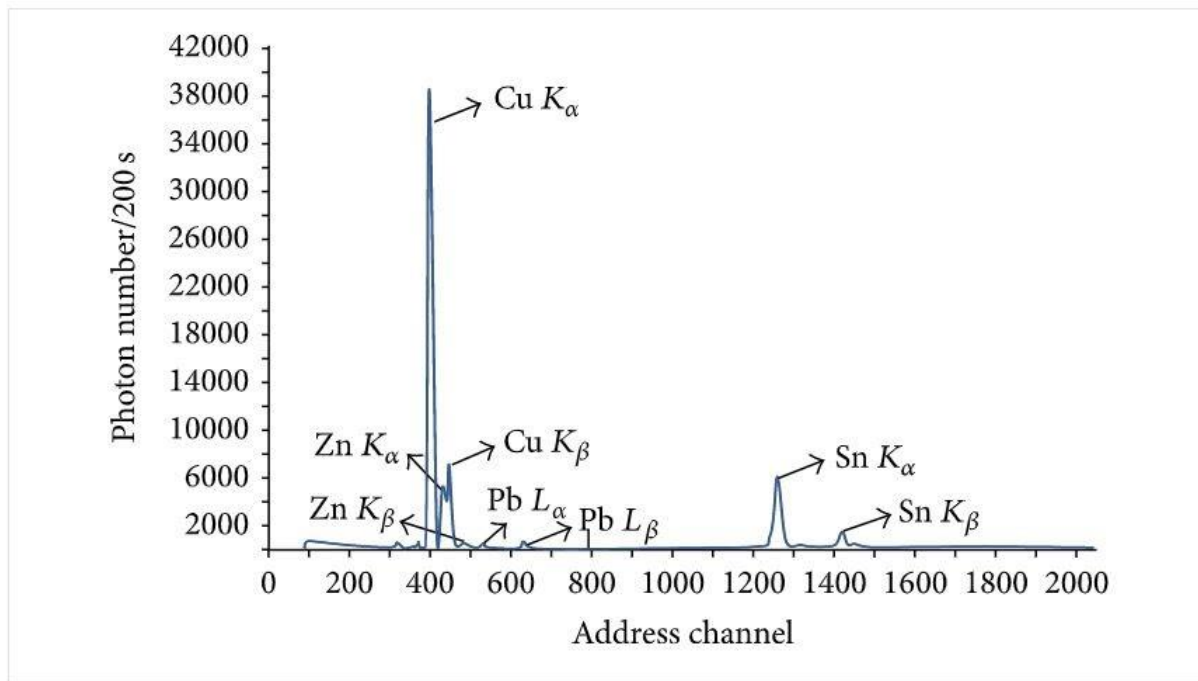


Fig: 2.3 Spectral line of Cu

The characteristic peak area of the relative element in the qualitative analysis is calculated. This area corresponds to the photon number of the relative energy. The intensity of the characteristic peak can then be achieved. However, interference peaks should be considered in calculating the peak area.

The peak in the peak location, which is an interference peak to the main peak, is called a pseudopeak. Such peak includes accumulated, escape, and scattering peaks. The accumulated peak is also called the sum peak, which is a phenomenon of peak hyperplasia resulting from the accumulation of signal pulses while counting at a high rate. In a sum peak, the peak position does not correspond to the characteristic energy but to the sum of two independent peaks.

When the energy of an X-ray photon is higher than the detection limit, some energy of the characteristic X-ray can escape because of its high transparency. The escaped energy forms an escape peak in the low-energy position. The energy difference between the main and escape peaks is equal to that of the energy of the characteristic X-ray photons, which is recognized by the detector. The Si-PIN detector shows that the escape peak energy is 1.74 keV lower than the main peak, which is the Si K_α energy. The height of the escape peak is approximately 1/1000 to 2/100 of the main peak. However, the escape peak does not appear when the atomic number is over 30.

2.1.4 EXPERIMENTS:

The EDXRF spectrometer is shown in Figure 2.4. The sample table in Figure 2.4(b) holds the sample. Figure 2.4(c) shows the control circuit that controls the instrument and communicates with the PC.



Fig: 2.4 Instrument Appearance



2.4(a) Light Path System



2.4(b) Sample Table



2.4(c) Control Circuit

The EDXRF spectrometer follows a set of operating steps, namely, preheating, initialization, mode selection, measurement starting, qualitative analysis, and quantitative analysis.

The EDXRF spectrometer should be preheated for approximately 40 min before the experiment. Preheating is performed to increase tube pressure and tube flow gradually to protect the light pipe and stabilize the instrument more.

Initialization is necessary to calibrate channel magnification. A standard Ag sample is stimulated, and magnification is adjusted during initialization. This step does not terminate until the main characteristic XRF stimulated from Ag is located near the address of 1106. This step can ensure that system hardware remains in the best situation.

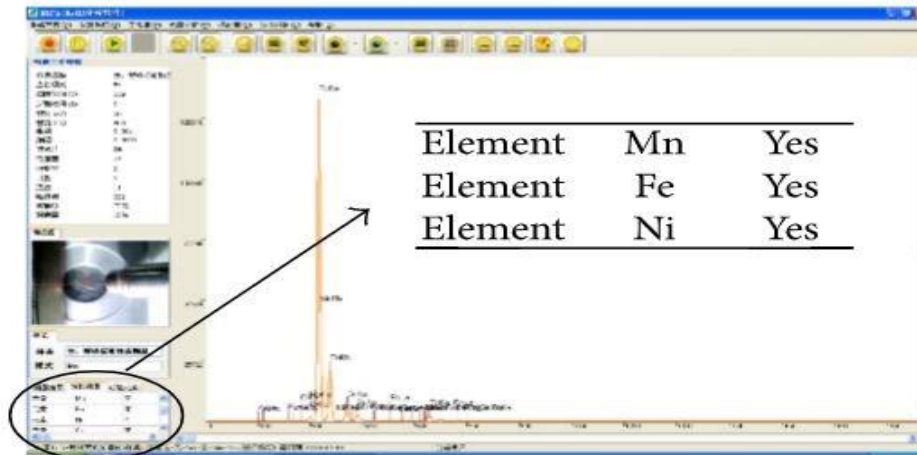


Fig: 2.5 Typical results of EDXRF qualitative analysis

2.2 INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES):

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is an analytical technique that is used to identify the atomic composition of a particular sample. The technique makes use of the unique photophysical signals of each element to successfully detect the type and relative amount of each element within the complexity of a compound. ICP-OES has utility in the analysis of complex samples and has been used in applications such as analyzing trace elements in the human brain, determining the chemical composition of electronic cigarettes, and assessing the purity of pharmaceutical compounds.



Fig: 2.6 ICP-OES Instrument appearance

2.2.1 WORKING:

To perform ICP-OES, one needs the following key components:

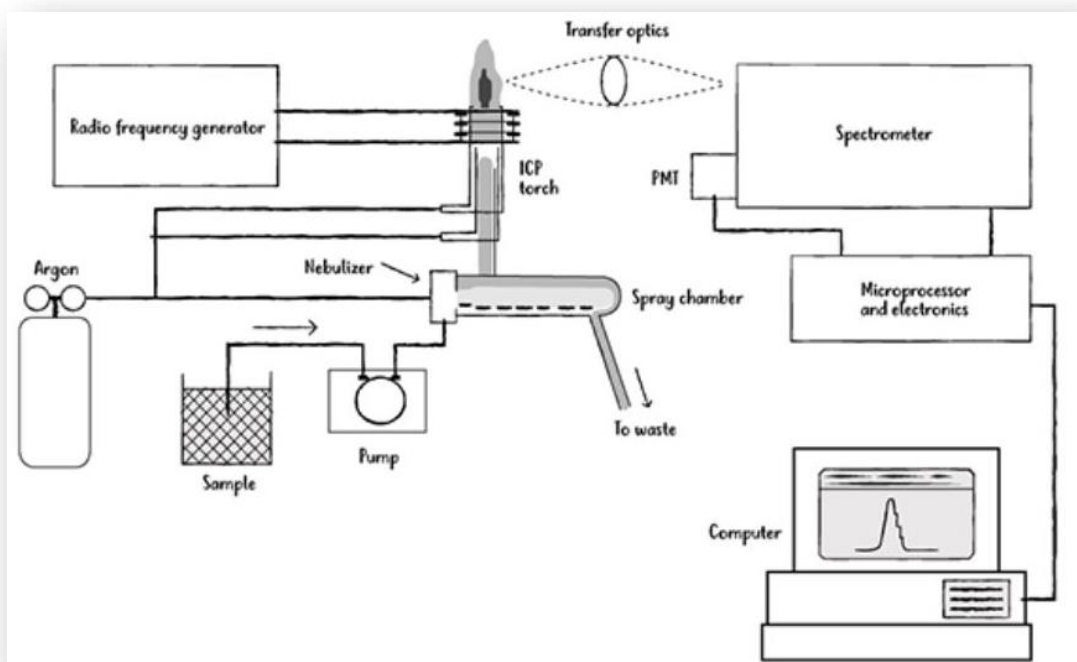


Fig: 2.7 ICP-OES Setup

- (a) High energy plasma: This plasma is most commonly composed of argon, although nitrogen gas and mixed gas compositions have also been reported. It is generated through the use of a high-power radio frequency signal or through microwave irradiation, which causes the gas to ionize to form electrons and other charged species within the plasma matrix.
- (b) A sample aerosolizer: Interactions between the plasma matrix and the sample are critical for successful analysis, and obtaining those interactions requires the sample to be aerosolized. Aerosolizing of the sample generally occurs through the use of a nebulizer, and also needs a mechanism for sample transport from the injection port to the point of aerosolization. Following successful aerosolization, interactions between the high energy plasma and the sample result in degradation of the sample to its individual elements, each of which has a characteristic optical signal that can be detected spectroscopically.
- (c) A wavelength separation mechanism: Although each individual element absorbs and emits light at a characteristic wavelength, signals from multiple elements often overlap, leading to significant challenges in interpreting the results obtained. To address this issue, the wavelengths corresponding to each element are separated, generally via an optical grating device, so that each element can be individually detected. The configuration of the system into either an axial

configuration (where the plasma is viewed head-on) or radial configuration (where the plasma is viewed from the side) has additional effects on the ability to observe the target signals: although generally radial configurations show improved detection capabilities, advances in axial configuration's detection capabilities have recently been reported.

d) A detector and signal processor: This detector, after correlating the wavelengths of light to the identity of the elements, is used to determine the final sample composition. It generally uses either a photomultiplier tube-type mechanism or a charge coupled device (CCD). Moreover, the detector is calibrated with known quantities of the elements targeted for analysis, so that it can effectively match the signals obtained from the sample to its pre-calibrated signals to allow for effective quantitation. Finally, there is a need to remove potentially interfering signals that can compromise detection of the target analyte, although recent studies have used these non-analyte signals to understand the broader matrix effects and overall system composition.

Analyzing a sample by ICP-OES first requires one to determine if and how it can be effectively aerosolized. While this is a relatively straightforward process for liquid samples (which can be accomplished with a nebulizer, *vide supra*), solid samples require additional effort, such as the use of electrothermal vaporization, electrothermal evaporation, laser ablation, or spark ablation. Finally, gas sensing via ICP-OES tends to be a straightforward process, as no aerosolization is needed. Rather, such systems require a mechanism for gas capture and for introduction of the gaseous sample into the detection system.

In addition to figuring out how to successfully introduce a sample into the system, one has a number of choices regarding system configuration, many of which are outlined above. Selecting the gas composition for the plasma can have measurable effects on the ability to ionize the gas effectively and determine atomic composition of the sample, as can the viewpoint (radial, axial, or dual) of the sensor relative to the generated plasma. Many of these choices, however, are made by manufacturers of ICP-OES instruments, and therefore are not necessarily within the purview of the individual ICP-OES user to decide.

2.2.2 ANALYZING ICP-OES DATA:

General guidelines for analysis of ICP-OES data are to look at the intensity of light emitted at particular wavelengths and compare that to calibration data to determine the concentration of atoms that are emitted at that particular wavelength. Most instruments currently in use allow for the selection of multiple wavelengths, and the user should select wavelengths that correspond to the emission signals from the atoms of interest. After correct wavelength selection, identifying the

elements within the sample is generally an automated process, and in recent years has become more sophisticated to facilitate multivariate analysis and highly sensitive identification.

Other concerns in analyzing ICP-OES data relate to potential interferents and their ability to compromise the system performance. To eliminate undesired interferences prior to analysis, users are advised to use an internal standard to correct for sample-to-sample variability and differences in sample processing conditions. Commonly used internal standards are scandium and yttrium, chosen because their wavelengths generally do not overlap with those of other atoms in the sample. After the successful implementation of the internal standards, calibration data allows for a direct comparison of the light intensity obtained from the sample to light intensities of known sample compositions, providing the types of elements found in the sample and their relative ratios within that sample as the key readout data from ICP-OES.

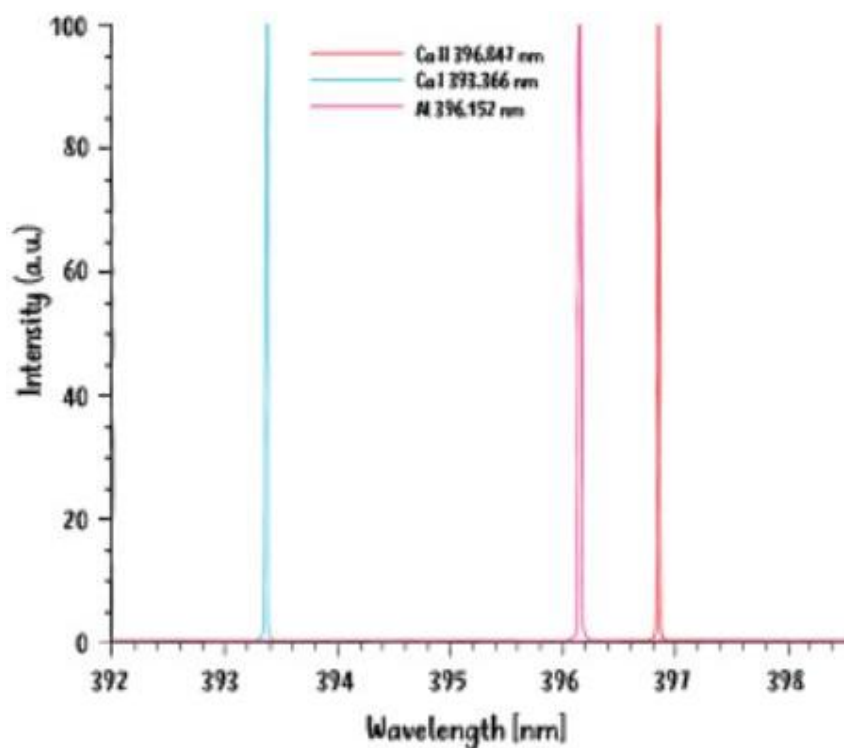


Fig: 2.8 Line spectra produced by ICP-OES

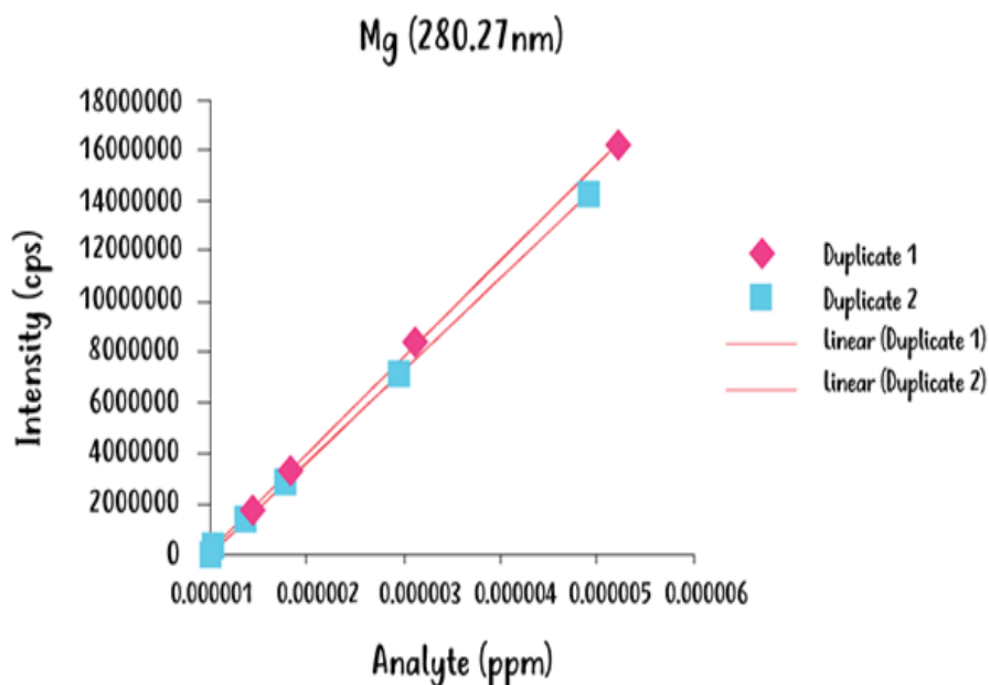


Fig: 2.9 Calibration curve

2.2.3 STRENGTHS OF ICP-OES:

Key strengths of ICP-OES include the ability to identify the types and ratios of elements in complex samples. For example, ICP-OES has been used effectively to analyze the composition of crude oil, contaminated soil, and heavy metal mixtures, all of which would have been challenging to analyze by other methods. Moreover, the ability to detect multiple elements simultaneously by ICP-OES presents another significant advantage, with researchers reporting situations where ICP-OES has detected up to 19 elements in one analytical procedure. Advances in the ability to aerosolize a broader variety of samples has improved the general applicability of ICP-OES, as have advantages in spectral deconvolution and calibration procedures to facilitate effective detection. Even in the case of radioactive samples, ICP-OES can still be used to determine the elemental composition of the sample, with separate measurements used to determine the degree of radioactivity. Finally, the ease of ICP-OES has allowed it to also be used in chemistry education contexts, with both analytical reagent grade and spectral pure grade solvents, and with relatively high throughput for sample preparation and analysis, highlighting the straightforward usability of the system.

2.2.4 LIMITATIONS OF ICP-OES:

Notable limitations of ICP-OES include the fact that samples must be aerosolized. Even though aerosolization procedures have undergone significant advances (*vide supra*), this means that solid and liquid samples cannot be analyzed while they are still in their solid and liquid forms. Moreover, ICP-OES is a destructive analytical procedure, meaning that the sample cannot be recovered after analysis. As a result, highly precious or rare samples cannot be analyzed via this method. Moreover, method development using ICP-OES can be a time-consuming process, as it necessarily involves multiple steps: (a) doing crude analysis to obtain a basic idea of the elements present in the sample; (b) wavelength selection based on that initial knowledge; (c) optimization of separation so that signals from the various wavelengths have limited overlap; (d) comparison with a internal standard to validate the method and system performance; and (e) analysis for spectral interferences and ways to eliminate those from the read-out without eliminating target signals. Finally, ICP-OES requires costly instrumentation for plasma generation, sample aerosolizing, and signal analysis, albeit at a relatively lower cost than other comparable methods such as ICP-MS, which means that access to this technique is necessarily limited.

2.2.5 COMMON PROBLEMS WITH ICP-OES:

Common problems with ICP-OES include poor precision, sample drift, non-ideal detection limits, and inaccurate identification. Each of these problems will be discussed in turn.

Poor Precision is defined as a lack of reproducibility in results obtained for the same sample. Such challenges are likely to be due to issues in the sample introduction system, including mechanisms in which the sample is aerosolized, introduced into the system, and/or transported from the introduction site to the plasma matrix.

Sample drift refers to a situation in which the signal is not stable and changes in position over time. Such issues are usually due to instrument problems, including buildup of the parts of the sample that were not effectively aerosolized in the instrument tubing that slows flow rates, or degradation in the tubing due to highly acidic samples that cause system leakages.

Non-ideal detection limits means that in many cases, the detection limits obtained through the use of ICP-OES are higher than desired for the target application. While detection limits for ICP-OES can theoretically be as low as single digit parts-per-billion (ppb), they are more often reported in the parts-per-million (ppm) range. Optimization of detection limits focuses on ensuring that sample preparation procedures limit dilution and/or sample degradation, as well as optimizing the view of the plasma-generated signal (axial, radial, or dual) to achieve the optimal signal capture.

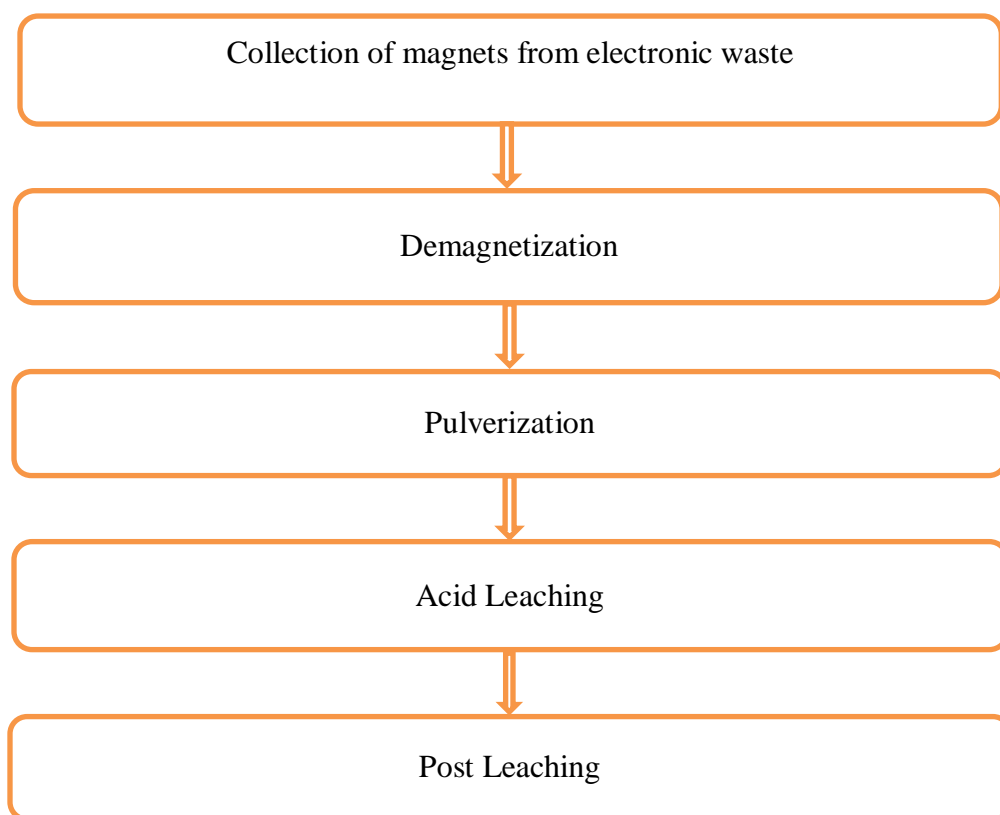
Inaccurate identification refers to situations in which the ICP-OES signal identifies a signal as corresponding to one element when it in fact belongs to a different element. Such situations, while rare, can be minimized by selecting wavelengths for the desired elements that have limited overlap from competing elements. These situations have also been assisted by the recent application of multivariate spectral analysis to ICP-OES signal read-outs, which allows for the use of statistical analysis to deconvolute overlapping signals and facilitate accurate identification.

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3. EXPERIMENTATION

This process of obtaining Rare earth Elements from the recycled permanent NdFeB magnets consists of five major steps. First step being the collection of magnets from the electronic waste (Laptops). Later, these magnets are Demagnetized. These Demagnetized magnets are then pulverized. The pulverized magnetic powder is then leached.

Flow chart of the process



3.1 COLLECTION OF MAGNETS (NdFeB):

Neodymium is one of the most abundant elements in WEEE. As shown in Figure 3.1, it is present in high quantity in different electronic devices. (Loudspeakers, HDD, LCDs, Tablets computers,



Device	Neodymium per device [mg]	
PC	5.030	
Hard disk drive (HDD)	2.441 (1.104-9.076)	
CD-ROM	771 (319 -3.236)	
Loudspeaker	310	
Laptop ¹	4.447	
Hard disk drive	1121 (851-1391)	
CD-ROM	621 (447-794)	
Loudspeaker	626 (550 – 703)	
Tablet Computer	347	
Mobilephone ¹	46.4 (14.3 – 115)	
Smartphone ²	120	
Earphones	260 (38,9-955)	
LCD-television	3650 (0.8– 7. 4)	

Fig: 3.1 Neodymium in electronic devices

etc....). As shown by Figure 3.1, the magnets can be found in different electronic devices with different concentrations of Neodymium (Nd). For example: computer contains in average 5.03 mg Nd: 2.4 mg in HDD, 771 mg in CD-ROM and 310 mg in Loudspeakers; Laptop (4.45 mg Nd): 1121 mg in HDD, 621 mg in CD-ROM and 626 mg in Loudspeakers; Tablet computer (347 mg Nd); Mobile-phone (46.4 mg Nd); Smartphone (120 mg Nd); Earphones (260 mg Nd) and LCD (3650 mg Nd). The laptops are dismantled and the magnets are collected.

3.2 DEMAGNETIZATION:

A permanent magnet can lose some or all of its magnetic field under certain circumstances. When a permanent magnet is magnetized, its magnetic domains are aligned. Certain conditions can cause the domains to lose this alignment; thereby aligning randomly. This will cause the magnet to either have lost some or all of its magnetic field.

- Demagnetization randomizes the orientation of magnetic dipoles.
- Demagnetization processes include heating past the Curie point, applying a strong magnetic field, applying alternating current, or hammering the metal.
- Demagnetization occurs naturally over time. The speed of the process depends on the material, the temperature, and other factors.
- While demagnetization may occur by accident, it is often performed intentionally when metal parts become magnetized or in order to destroy magnetic-encoded data.

3.2.1 THERMAL DEMAGNETIZATION:

The primary method for deliberately de-magnetizing magnets is by heating them. Every magnetic material has a characteristic temperature known as the Curie Temperature. At this temperature the thermal agitations apply more force than the resistance of the magnetic domains to movement and the domains of the magnet randomize. After the material reaches the Curie temperature throughout its bulk, it will show virtually no net magnetization, and can be treated as virgin material.

In the case of samarium-cobalt permanent magnets, there is an additional factor to consider. The Curie temperature of most samarium-cobalt magnets is on the order of 700-800°C (1300-1500°F). At these temperatures, the material itself will tend to break down magnetically. After this process, the material's performance will be significantly degraded.



Fig:3.2 Demagnetized magnets

3.3 PULVERIZATION:

Pulverization (comminution, crushing, grinding) is the process of applying an external force to a (solid) material of a certain size to destroy it and reduce it into pieces that are smaller than the original size. Pulverization has long been done for many materials, including ore, glass, ceramics, grains, paints, and medicines. Crushers are used for this purpose.

A crusher is a machine designed to reduce large rocks into smaller rocks, gravel, sand or rock dust. Crushers may be used to reduce the size, or change the form, of waste materials so they can be more easily disposed of or recycled, or to reduce the size of a solid mix of raw materials (as in rock ore), so that pieces of different composition can be differentiated. Crushing is the process of transferring a force amplified by mechanical advantage through a material made of molecules that bond together more strongly, and resist deformation more, than those in the material being crushed do. Crushing devices hold material between two parallel or tangent solid surfaces, and apply sufficient force to bring the surfaces together to generate enough energy within the material being crushed so that its molecules separate from (fracturing), or change alignment in relation to (deformation), each other. The earliest crushers were hand-held stones, where the weight of the stone provided a boost to muscle power, used against a stone anvil. Querns and mortars are types of these crushing devices.

The following table describes the commonly used crushers:

Type	Hardness	Abrasion limit	Moisture content	Reduction ratio	Main use
Jaw crushers	Soft to very hard	No limit	Dry to slightly wet, not sticky	3/1 to 5/1	Heavy mining, quarried materials, sand & gravel, recycling
Gyratory crushers	Soft to very hard	Abrasive	Dry to slightly wet, not sticky	4/1 to 7/1	Heavy mining, quarried materials
Cone crushers	Medium hard to very hard	Abrasive	Dry or wet, not sticky	3/1 to 5/1	Quarried materials, sand & gravel
Compound crusher	Medium hard to very hard	Abrasive	Dry or wet, not sticky	3/1 to 5/1	Mine, building materials
Horizontal shaft impactors	Soft to medium hard	Slightly abrasive	Dry or wet, not sticky	10/1 to 25/1	Quarried materials, sand & gravel, recycling
Vertical shaft impactors (shoe and anvil)	Medium hard to very hard	Slightly abrasive	Dry or wet, not sticky	6/1 to 8/1	Sand & gravel, recycling
Vertical shaft impactors (autogenous)	Soft to very hard	No limit	Dry or wet, not sticky	2/1 to 5/1	Quarried materials, sand & gravel
Mineral sizers	Hard to soft	Abrasive	Dry or wet and sticky	2/1 to 5/1	Heavy mining
Crusher buckets	Soft to very hard	No limit	Dry or wet and sticky	3/1 to 5/1	Heavy mining, quarried materials, sand & gravel, recycling

Table: 3.1 Common Crushers used for pulverization

3.3.1 ROLL CRUSHER:

Roll Crushers are compression type of crushers and were once widely used in mining. They have, within the last 10 or so years, fallen into dis-favor among mining and processing companies. The probable reason is because the large mines require very large crushed product output with minimal cost, makes the roll crusher uncompetitive. The roll crushers are not as productive as cone crushers, with respect to volume, and they do have a little higher maintenance associated with them. Roll crushers do, however, give a very close product size distribution, and if the ore is not too abrasive, they do not have high maintenance costs.



Fig: 3.3 Roll Crusher

3.3.2 WORKING PRINCIPLE:

Through the feed opening, the raw materials fall to between the two rollers, after crushed, the final products drop naturally. When there are unbreakable materials or the material is too hard, the roller will concede automatically under the effects of spring and hydraulic pressure, which will widen the clearance between the rollers and make the hard or unbreakable so as to avoid damaging the machine. The clearance between the two rollers can be adjusted to change the sizes of final products. Roll crushers are sometimes used as moveable crushers attached to a crane, commonly named Bucket Crushers.

3.3.3 FEATURES:

- Up to a minimum particle size of 2mm
- Maximum reduction ratio of 4:1
- Produces very little dust or fines
- Stable operation



Fig: 3.4 NdFeB magnets powder

3.4 ACID LEACHING:

Hydrometallurgical methods, such as leaching, and precipitation, are attractive and efficient methods for recovery of REEs out of NdFeB magnets. The elements contained in the magnets are normally dissolved/leached into an aqueous solution. Various leaching processes for recovery of REEs out of NdFeB magnets have been developed. In 2016, developed a selective leaching process for REEs by leaching Fe in the solid residue. The NdFeB magnet powder sample was turned into a sulfate mixture by mixing with concentrated H₂SO₄ (12–16 mol/L) in crucibles. After drying and high-temperature treatment, the powder was leached in demineralized water for 15 min to 24 h, which led to >95% recovery of REEs while Fe remained in the solid residue in the form of a sulfate. In 2014, studied the leaching of NdFeB magnet scrap using H₂SO₄ at different temperatures and concentrations. The optimal leaching conditions were determined to be 70 °C and 3 mol/L H₂SO₄ with a leaching time of 4 h. In 2013, carried out an investigation on leaching of NdFeB magnets using H₂SO₄, HCl, HNO₃, and NaOH. Out of the four leaching agents, HCl and H₂SO₄ showed the best leaching performance.

Despite possessing excellent properties for leaching REEs out of NdFeB magnets, strong mineral acids such as HCl, HNO₃ and H₂SO₄ pose the risk of adverse impact on the environment because of issues with regeneration of the used acids, while handling can also pose a great challenge in some situations. In cases where highly concentrated acids are released to the environment, they could acidify the soil and would require further soil treatment to neutralize the acidified soil. Moreover, when using strong mineral acids, evolution of poisonous gasses is often a problem. Using organic acids or significantly more diluted mineral acids could have advantages in this regard because of easier handling, less poisonous gas evolution due to lower acidities, and much easier degradability.

3.4.1 PROCESS:

- The powder (Fig 3.4) is analyzed using EDXRF (Table: 4.1)
- The powdered (NdFeB) is weighed and 0.1g of it is taken.
- It is then dissolved in prepared Aqua regia (HCl: HNO₃ = 9 ml:3ml) (Fig: 3.5).



Fig: 3.5 Aqua regia

- The sample is sent to ICP-OES analysis (Fig: 3.6).
- **Solution for Acid Leaching:**
 - Prepare 2500 ml of approx. 3M H_2SO_4 .
 - 409 ml of concentrated H_2SO_4 in 2500ml distilled water.
- 250g of the powder is weighed and taken.
- Make the required setup for Acid leaching process (Fig: 3.7).



Fig: 3.6 Sample in Centrifugal Tube.



Fig: 3.7 Set Up for Acid Leaching

- Discharge the first 2000ml of 16.26% v/v H_2SO_4 sol into acid leaching vessel.
- Stir for about 5 min and then start adding this 250g of powder slowly into the solution. (Only spoon by spoon). Keep stirring continuously
- After all the powder is added, add the other 500ml of 16.26% v/v H_2SO_4 sol to the beaker.
- Now heat the vessel till it attains 80°C ($160\text{-}200^\circ$ on the device).
- After attaining 80°C , heat it for 2hrs with continuous stirring with maintaining that temperature.
- After 2hrs, let it cool down completely and transfer the leach liquor to 5000ml beaker and evaporate to 1500ml by maintaining 100°C (300°C) (Fig: 3.8)

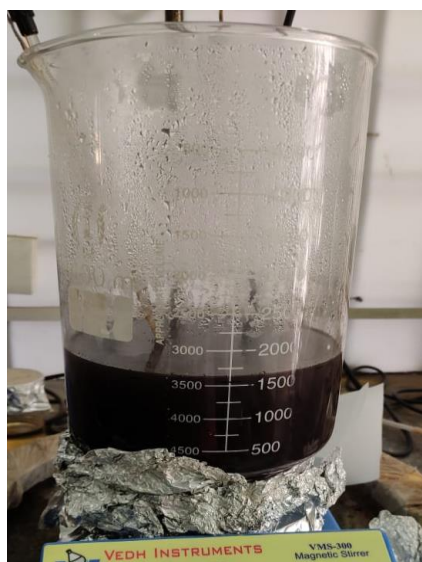


Fig: 3.8 Evaporation

- Now filter the content and wash the residue with 1-2L of boiling distilled water to remove all Fe present.



Fig: 3.9 Residue

- Dry the residue to remove moisture at 110°C for 1hr (if moisture is not eliminated, increase the heating time)(Fig: 3.10).



Fig: 3.10 Hot Oven



Fig: 3.11 Ground powder

- After drying the powder, grind it using agate mortar (Fig: 3.11).
- Weigh 0.1g of it and dissolve it in aqua Regia, make up to 25ml and send it to ICP-OES analysis (Table: 4.4)
- Leach liquor volume is measured and 1ml of it is taken, made it 25ml and sent to ICP-OES analysis (Table: 4.5).
- The Fe obtained is shown in Fig: 3.12



Fig: 3.12 Fe obtained.

3.5 POST LEACHING:

- After leaching the Nd-oxalate obtained is further processed.
- 3 gm of the powder (Fig: 3.11) is taken .
- It is dissolved in 45 ml of HnO₃ (Fig: 3.13) .



Fig: 3.13 Solution of HNO₃.

- It is heated (Fig: 3.14).



Fig: 3.14 Heating HNO₃ solution.

- It is then made to 100 ml.
- The contents are then filtered.
- 3 gm of Oxalic acid is taken (Fig: 3.15).



Fig: 3.15 Oxalic Acid.

- Dissolved in 50 ml D.M and added to the solution.
- Keep Stirring using magnetic stirrer.
- Place pH reader in that solution (Fig: 3.16) .



Fig: 3.16 pH reader

- Keep adding oxalic acid solution until the solution attains a pH of 0.00 (Fig: 3.17).

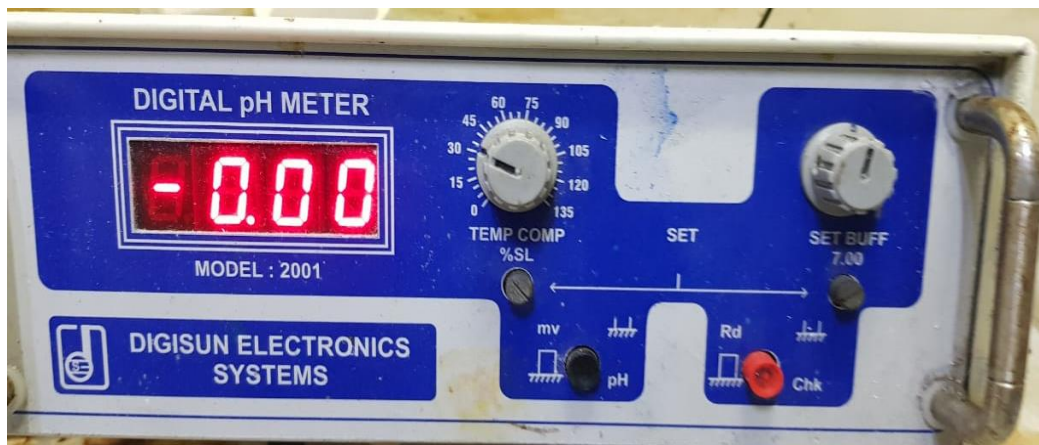


Fig: 3.17 pH Meter

- After attaining a pH of zero filter the contents.
- Wash the residue with Hot Demineralized water (DM) (Fig: 3.18)



Fig: 3.18 Washed Residue

- Heat in the Hot Oven for 1 hr at 110 degrees Celsius (Fig: 3.19).



Fig: 3.19 Dried Powder

- Take 0.1 gm of the Powder dissolve in aqua regia and sent to ICP-OES analysis (Table: 4.6).
- Then 2.97 gm of the powder is taken and added to the crucible (Fig: 3.20).



Fig: 3.20 Crucible



Fig: 3.21 Crucible with powder

- The crucible is then placed in the Muffle Furnace for about 1 Hr. at 800 degrees Celsius.
- Wash it with hot distilled water.
- Place it in the Hot Oven for 1 hr (Fig: 3.22).



Fig: 3.22 Nd₂O₃ powder

- It is then sent to ICP-OES analysis (Table: 4.7).

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4. RESULTS AND DISCUSSION

4.1 EDXRF ANALYSIS REPORT OF PULVURIZED NdFeB MAGNETS:

As we know that we have used Neodymium (NdFeB) magnets for our project. These magnets are pulverized using roll crusher and sent for EDXRF analysis. In general, these magnets contain about 30% rare-earth metal (Nd in our case), and the same has been proven from the EDXRF analysis of pulverized NdFeB magnets. The report is shown below in Table 4.1.

Element	Percent	Element	Percent	Element	Percent	Element	Percent
Fe	22.90%	Cu	0.10%	Ga	0.02%	Pr	0.00%
Dy	7.20%	Nd	32.50%	La	0.10%	Tb	25.00%
Al	4.00%	Er	3.50%	Mo	0.50%	Ti	0.06%
Co	1.80%	Eu	1.00	Ni	1.30	----	----

Table: 4.1 EDXRF analysis report of NdFeB Magnetic Powder

A total of 19 elements are depicted above and it can be clearly deduced from the above report that this magnetic powder has Neodymium as major constituent with about 32.50% by wt. Other significant constituents include Iron (22.90% by wt) and Terbium (25% by wt). These are depicted in red in the report above.

Shown below is the EDXRF spectrum of the same sample

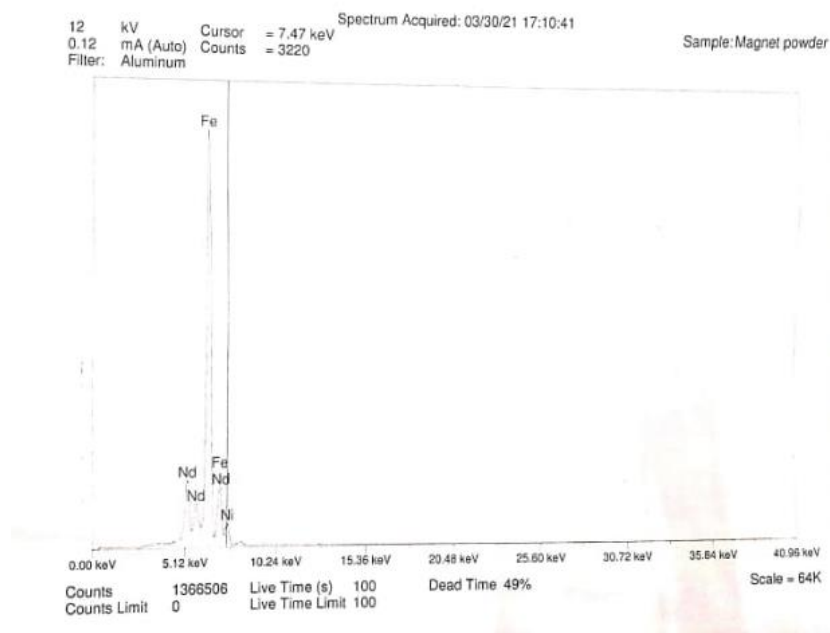


Fig: 4.1 EDXRF Spectrum of NdFeB Magnetic Powder

4.2 RESULTS OF LEACHING:

We have obtained 3 materials from leaching process: Iron Crystals (Fig: 4.2), NdSO_4 powder (Fig: 4.3) and leach liquor.



Fig: 4.2 Fe Crystals obtained from leaching



Fig: 4.3 NdSO_4 powder obtained from leaching

The weight and volumes of the materials obtained are shown below:

Material	Weight(g)
Fe Crystals	131.23
Residue(NdSO ₄)	115.7

Table: 4.2 Weights of materials obtained from leaching

Solution	Volume(ml)
Leach Liquor	965

Table: 4.3 Volume of leach liquor obtained from leaching

The NdSO₄ powder and the leach liquor are sent for ICP-OES analysis and the reports are shown in Table 4.4 and Table 4.5 respectively.

Element	Percent	Element	Percent	Element	Percent	Element	Percent	Element	Percent
Al	0.374%	Dy	0.3172%	Ga	-0.314%	Mo	0.0183%	S	8.892%
B	0.0048%	Er	0.0013%	La	0.0122%	Nd	21.68%	Tb	0.045%
Co	0.0153%	Eu	0.0365%	Li	0.05%	Ni	2.434%	Ti	0.0009%
Cu	0.195%	Fe	0.6472%	Mn	0.0036%	Pr	4.115%	----	----

Table: 4.4 ICP-OES analysis report of NdSO₄ powder

Element	Percent	Element	Percent	Element	Percent	Element	Percent	Element	Percent
Al	0.0022%	Dy	0.0046%	Ga	0.0005%	Mo	~0.00%	S	0.3469%
B	0.0078%	Er	~0.00%	La	~0.00%	Nd	0.018%	Tb	0.0004%
Co	0.0050%	Eu	~0.005%	Li	~0.00%	Ni	0.0016%	Ti	~0.00%
Cu	~0.00%	Fe	0.185%	Mn	0.0002%	Pr	0.0033%	----	----

Table: 4.5 ICP-OES analysis report of leach liquor

NdSO₄ being sulphate it has Neodymium and Sulphur as major constituents. Since all the Iron in leach liquor has been precipitated as crystals, the liquor is left with negligible amounts of Iron.

Material Balance:

Initially, 250g of magnetic powder is taken for leaching and a total of 246.93g of material is obtained. This 246.93g includes Fe crystals and NdSO₄ powder.

4.3 RESULTS OF POST-LEACHING PROCESS:

In the post-leaching process, Nd Oxalate (NdC_2O_4 : Fig 4.4) and Nd-Oxide (Nd_2O_3 : Fig 4.5) powders are obtained. They are sent for ICP-OES analysis and the reports are as follows:

Element	Percent	Element	Percent	Element	Percent	Element	Percent	Element	Percent
Al	0.30%	Dy	0.3472%	Ga	0.007%	Mo	0.0189%	S	0.1062%
B	0.0016%	Er	NA	La	0.0117%	Nd	22.02%	Tb	0.479%
Co	0.0131%	Eu	0.0364%	Li	0.0045%	Ni	0.0142%	Ti	----
Cu	0.0298%	Fe	0.056%	Mn	0.0065%	Pr	4.24%	----	----

Table: 4.6 ICP-OES analysis report of Nd Oxalate

Element	Percent	Element	Percent	Element	Percent	Element	Percent	Element	Percent
Al	0.532%	Dy	0.780%	Ga	0.0150%	Mo	0.0386%	S	0.269%
B	0.0028%	Er	ND	La	0.0258%	Nd	47.79%	Tb	0.105%
Co	0.0053%	Eu	0.0815%	Li	0.0028%	Ni	0.0223%	Ti	----
Cu	0.0661%	Fe	0.0280%	Mn	0.0020%	Pr	9.368%	----	----

Table: 4.7 ICP-OES analysis report of Nd_2O_3

Inference: The initial magnetic powder had about 32% Neodymium by wt. That is in 250g of Magnetic powder we have about 80g of Neodymium. But in Nd_2O_3 , we have about 47.79% Nd by wt, revealing that for same 250g of Nd_2O_3 , we may have about 120g of Nd. There is an increase of 15.79% Nd. This shows that this process is economically feasible.



Fig: 4.4 Nd-Oxalate powder



Fig: 4.5 Nd_2O_3 powder



Fig: 4.6 ICP-OES Samples of Nd-Oxalate and Nd_2O_3

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5. CONCLUSION

Recycling and recovery of REEs (Nd, Pr, Dy, Tb) from Laptop permanent magnets are challenging due to their relatively small sizes used in consumer electrical and electronics, as well as in the conventional automotive industry. Shredding without pre-dismantling of Laptops will pose great difficulties for up-concentration of the permanent magnets. There are many different types of metallurgical recovery methods identified from the literature; however, most of them have been studied for relatively clean and highly concentrated new or manufacturing magnet scrap and waste. At the same time, recovery of the major metals and materials in the dilute magnet waste stream (e.g., shredder products) is an important factor for the total success of the permanent magnet and REE recycling. It is believed that no single metallurgical process can be successful for the efficient recovery of the REEs from NdFeB permanent magnets, and a combination of hydrometallurgical, pyrometallurgical, and/or electrochemical technologies will be the future solution.

It is expected that through the globally increasing efforts (Europe, Japan, USA, China) for the research and development, establishment of technologically and economically feasible REE magnet recycling industry could be realized in the near future, if the NdFeB permanent magnet market continue to develop. Various WEEE streams and products containing permanent magnets were studied in order to identify those that contain Nd-Fe-B magnets. Nd-Fe-B magnets were found in loudspeakers integrated into flat screen devices, where the components have to be small, and therefore the magnets have to be magnetically strong. It was observed that all the loudspeakers in the laptops studied and most of the loudspeakers in the flat TV sets and PC screens contained Nd-Fe-B magnets, whereas normal external loudspeakers contain mainly ferrites. Since LCDs and laptops are being dis-mantled already in the recycling process, it would be an easy task to extract the speakers from them.

LEDs and plasma TVs, which are not dismantled, would require extra labor if the magnets were to be extracted. Hard disk drives have been suggested by several projects or researchers to be the perfect candidate for Nd-Fe-B recycling. It has also been suggested, that in order to recycle the Nd-Fe-B magnets, the magnet has to be removed before the shredding step, where a lot of it would be lost otherwise. If such a solution is implemented, where all the magnets are collected together, a rough estimation based on the flows at this recycling plant suggests that the amount of Nd-Fe-B could be almost doubled if also including loudspeakers from laptops and flat screens.

It should also be noted that although the overall amount of the Nd-Fe-B magnet is still relatively small for this one recycling plant, there are multiple collection sites for WEEE across Europe. For an effective recycling process to be set up in Europe for Nd-Fe-B magnets then multiple streams of feedstock would have to be used for a range of devices and from a range of different companies. A detailed feasibility study is needed to determine a minimum economic scale, based on the findings of the plant data from this study.

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