Journal of Metallurgy and Materials Science, Vol. 64, No. 1-2, January-June 2022
Printed in India, © NML, ISSN 0972-4257

Recycling of Nd-Fe-B Magnets to Reclaim Nd Salt and Pigment

NITYANAND SINGH[1], REKHA PANDA[1], RUKSHANA PARWEEN[1], OM SHANKAR DINKAR[1], PANKAJ KUMAR CHOUBEY[1], RAJESH KUMAR JYOTHI[2], MANIS KUMAR JHA[1]*

[1]Metal Extraction and Recycling Division, CSIR-National Metallurgical Laboratory, Jamshedpur, India-831007

[2]Resources Utilization Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 34132, South Korea

Abstract : Hard disk of computers is the most essential part, which plays significant role for programming the computers. Hard disk contains permanent Nd-Fe-B magnet as a most powerful magnet, these magnets become waste rapidly by reaching its end-of-life, therefore the metallic content (Nd, Pr, Dy) in it is also act losses which is present in limited stock in nature therefore recycling of these waste is necessary to get the metallic content from it and also preserve the natural resources. This study provide a proper technique and development of hydrometallurgical process to extract REMs from $Nd_2Fe_{14}B$ magnets, which includes general flow chart such as manual dismantling, demagnetization (300 °C, 3h), crushing to get the material in its homogenous form, leaching (2M H_2SO_4, 100 g/L, 25 °C, 1h), solvent extraction of REMs (pH~2, 15 min), air sparging to remove iron from the solution (pH~3.5, 50-60 °C, 1h), etc. about >95% of rare earth metals were recovered by this techniques and remaining metals left in the liquor can be recovered by further hydrometallurgical processes.

Keywords: *REEs, Secondary resources, Recycling, Pretreatment, Hydrometallurgy, Nd-Fe-B magnet*

1. INTRODUCTION :

Nowadays, the electrical and electronic device has become the world's biggest and fastest growing technology. Electronic products are used extensively in maximum aspect of day to day in our life, from portable uses (e.g. toys, mobile phones and i-Pads) to large-scale uses (e.g. televisions, computers and vehicles) [1], and the wastes generated at the same time through it after its end of life are disposed in illegal manner, by which the metallic content in it will be lost and it will harm the environment. Disposal of WEEEs is one of the rapidly increasing environmental problems in global worldwide. It might be due to the increasing consumption of electronic devices which often discarded in the landfill sites after reaching its end-of-life in developing countries to pollute the environment in the form of soil and water [2]. Almost 53.5 Mt of e-wastes were produced in 2019 and it has been reported that it will produce 74.7 million tons of e-waste by 2030 [3]. Among the different electronic scraps, hard disc of personal computer contains rare earth magnet inside it which

***Corresponding Author :**
E-mail: mkjha@nmlindia.org

contains metals such as Nd, Dy, Pr, and Fe. Hence, it has been considered as one of the alternative resources for recovery of rare earth elements.

Various studies have been made to recover the rare earth elements using pyro/- hydrometallurgy and combination of both processes. Choubey et al. reported leaching with 2 M sulfuric acid, solvent extraction with Cyanex 272, precipitation of Nd salt by using NH_4OH at pH 1.75. Further, 96% of Fe was extracted by precipitation technique at pH 3 [4]. In another study, electrochemical leaching of rare-earth elements of spent Nd-Fe-B magnets were carried out by treating it in a mixture of 0.1 M H_2SO_4 and 0.05 M $H_2C_2O_4$ at current density of 20 A/dm^2 [5]. In subsequent study solvent extraction were also carried out to recover rare earth elements from the Nd-Fe-B magnets using cyanex 572. 99.9% Nd was extracted at eq. pH 0.8 to 1.5 with 0.3 M Cyanex 572 [6]. Niam et al. were also shown solvent extraction process to separate rare earth metals from waste permanent magnets solution by using 1 M D2EHPA as extractant by maintaining pH 2 and 2 M nitric acid was used as stripping agent. The parameters achieved at 90 minutes for Nd, Dy, and Pr was 58.62%, 98.46, and 85.59%, as well as for the recovery was occured 63.13%, 15.21%, and 56.29%, respectively [7]. Onal et al. were done nitration of Nd-Fe-B magnet by mixing with nitric acid and calcinations at 200°C for 2 hrs, >95% REEs were recovered by water leaching at room temperature by maintaining 60g/L pulp density [8]. In another study, oxidative roasting was carried out by using organic acid leaching to recover the REEs from Nd-Fe-B magnet which helps to oxidized metallic species of permanent magnet into acid soluble species at 900 °C in 480 min. Further, the oxidized product was treated with a mixture of malic and citric acids at 90 °C to leach more than 90% REEs [9]. Lee et al. proposed physical and chemical treatment of like demagnetization, grinding, screening and leaching with sulphuric acid of Nd-Fe-B magnets further Nd was separated by precipitation method as $Nd(OH)_3$[10]. Rabatho et al. reported recovery of Nd, Dy and Fe by using solution of 1M HNO_3 and 0.3M H_2O_2, it has been shown that 98% of Nd and 81% of Dy were recovered while Fe remain in the residue, further 91.5% of Nd and 81.8% of Dy were separated by precipitation process with organic acid ($H_2C_2O_2$) [11]. Liu et al. 2021 shows in their study roasting with $NaCO_3$ at 800°C and pressure leaching with Hydrochloric acid of roasted magnets, almost 99% REEs were extracted [12]. Loya et al. developed a process ferric sulfate leaching to provide the raw materials a mechano-chemical conversion, ~95% of REEs were leached in water and get precipitated by treating with oxalic acid at pH 1.9 [13].

Due to similarity of REEs it is hard to target to maximize the selectivity and feasibility of all the process used to recover REEs from Nd-Fe-B magnets, they have many demerits such as high cost, high energy consumptions and many more.

In view of above aspect, present study focused on the hydrometallurgical extraction of rare earth elements (Nd, Pr and Dy) from discarded magnet of hard disk. At first, magnet was demagnetized at elevated temperature and then it was further subjected to manual crushing and grinding and then systematic leaching study of Nd-Fe-B magnets were carried out, to optimize the parameters various sets of experiments were practiced such as effect of acid concentration, temperature, time, pulp density, etc. all metals present in the Magnet such as Nd, Dy, Pr, Co, Fe and Ni completely separated out, after the leaching process with sulphuric acid, it has been shown that the REEs, Fe, and Co were completely dissolve in the leachant while Ni remain in the residue. ~95% REMs were recovered from the leach liquor by precipitation using ammonia solution (NH_4OH) at pH ~1.75-2, to optimize the suitable parameters for the precipitation of REMs; effect of pH was also studied. Furthermore, Excess amount of iron present in the liquor was also removed by air sparging, all the sample prepared in this study was diluted in 5% HCl and analyzed in Atomic Adsorption Spectrometer (AAS).

2. MATERIALS AND METHODS

2.1. Raw Material & Chemicals used

Nd-Fe-B magnets separated from waste Hard disk of CPUs were used as starting material for experimental purpose. Initially, Nd-Fe-B magnet was separated by manual dismantling of waste hard disk of CPUs to recover REEs along with iron. Thereafter, Nd-Fe-B magnet subjected to demagnetization by heated at 300 °C for 3 hrs to reduce the magnetic strength of Nd-Fe-B magnet. The demagnetized magnet was further crushed into small sizes (2 x 2 mm) using the mortar pestle to make the leaching step easier. The generalized process for demagnetization and beneficiation of Nd-Fe-B magnet is presented in Figure 1. The metallic composition of Nd-Fe-B magnet has been shown in Table-1.

Table 1. Composition of waste Nd-Fe-B magnets

Rare Earth Metals (REMs)	Wt. %
Nd	25.13
Pr	2.5
Dy	1.25
Fe	55.12

All the chemicals used in this study such as Ammonium solution, Sulphuric acid, Hydrochloric acid, etc. are analytical grade (AR) supplied by Rankem, India. Apart from concentrated chemical, all dilute solutions used in this study were prepared by using distilled water.

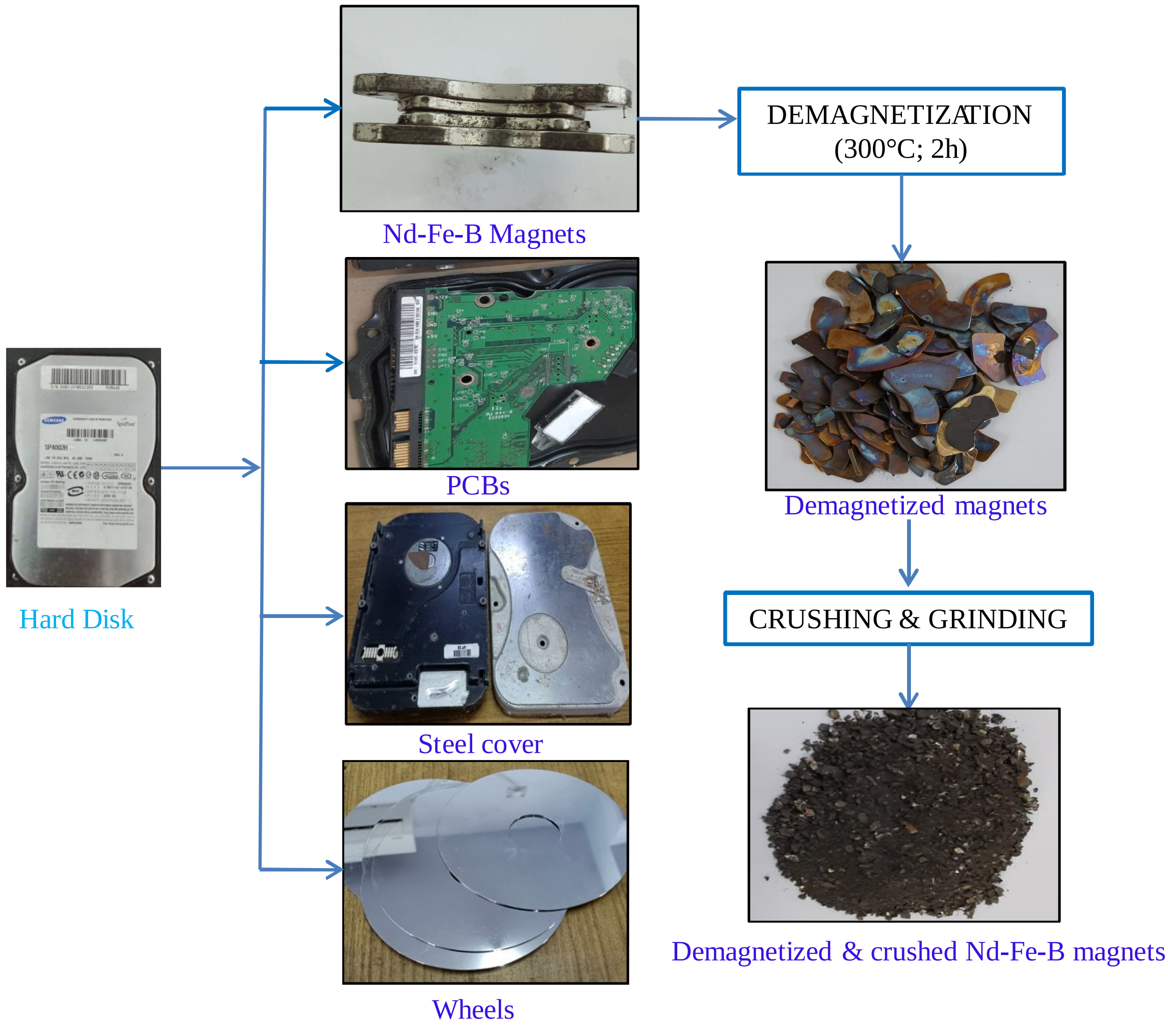

Figure 1. Flow chart showing pretreatment of Hard disk of computer.

2.2. Leaching procedure

Leaching process were carried out to recover rare earth metals from scrap magnets, demagnetised-crushed sample were leached in 100mL solution of 2M sulphuric acid in a glass Pyrex leaching reactor (250mL) fitted with condenser to avoid the loss of liquid in the form of vapour at final temperature and placed in temperature controlled hot plate to maintain the optimized temperature throughout the experiments, a constant stirring was provided to the whole setup by using magnetic stirrer. To optimise the suitable parameters, sampling was done at regular time interval. The residue obtained after the leaching process were collected, washed, dried and then analyzed to optimise the material balance.

2.3. Solvent Extraction Procedure

To demonstrate the separation of REEs from leach liquor of Nd-Fe-B magnets solvent extraction experiments were performed in a beaker using a magnetic stirrer (Borosil, Mumbai, India) at 25°C by maintaining 1:1 ratio of leach liquor and extractant D2EHPA (50 mL/50 mL) were placed in the beaker for proper mixing. NH_4OH was used to maintain the eq. pH in between 1 to 2.5. After getting the equilibrium, the metal-loaded organic extractant and raffinate were separated by the help of a separating funnel. Further, after completion of above process, the concentration of metals present in the raffinate and stripped solution after stripping were analysed to check mass balance.

2.4. Precipitation procedure

Now the REEs free leach liquor was further subjected to air sparging to remove the excess amount of iron present in the liquor, in this process the pH of the solution was maintained at 3.5 and heated at 50-60 °C for 1 hr, after the process the iron precipitate were settled down and the liquor was free from iron, and then filtered the solution, after separation of REEs and Fe, the leach liquor can be subjected to further hydrometallurgical process to recover Ni, Co, and B present in the liquor.

2.5. Analytical procedure

Induced Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES) and Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer model, Analyst 200; USA) was used to analysis the metals present in the leach solution, at first the leach solution was diluted then analyzed. The crushed materials of discarded Nd-Fe-B magnets are first tested in XRD for their phase detection and then SEM-EDS was done with the same sample to know the accurate composition and morphology of metals present in the crushed materials of waste Nd-Fe-B magnets. The whole process used in this study are feasible, eco-friendly and economical, the metals presents in the discarded Nd-Fe-B permanent magnets can be easily recovered by above process used in the study and it will be helpful for the various metal industries and environment.

3. RESULTS AND DISCUSSION

In order to recover the REEs from discarded Nd-Fe-B magnet, a pre-treatment study followed by leaching and precipitation were carried out at different conditions. At first, Nd-Fe-B magnet was demagnetized by heat treatment thereafter crushed effectively to leach the REEs. To optimize the parameters for leaching of REEs, studies were conducted at different conditions such as effect of acid concentration, effect of temperature, effect of time, effect of pulp density, etc., as discussed below

3.1. Effect of acid concentration

Various leaching sets were practiced to investigate the effect of acid concentration with different acid concentration of sulphuric acid such as 0.5M, 1M, 1.5M and 2M, at 25°C for 60 min maintaining pulp density 100 g/L. Analysis shows (figure 2) that increase in concentration of sulphuric acid increasing leaching percentage of rare earth metals. In case of 2.5M sulphuric acid, the dissolution percentage seems almost constant as 2M sulphuric acid therefore, no further experiments were practiced with increase in acid concentration, results indicate that the suitable concentration of sulphuric acid for the leaching of rare earth metals present in the Nd-Fe-B permanent magnets was found 2M.

$$Nd_2Fe_{14}B + H_2SO_4 = (REE)\ SO_4 + FeSO_4 + B_2\ SO_4 \quad (1)$$

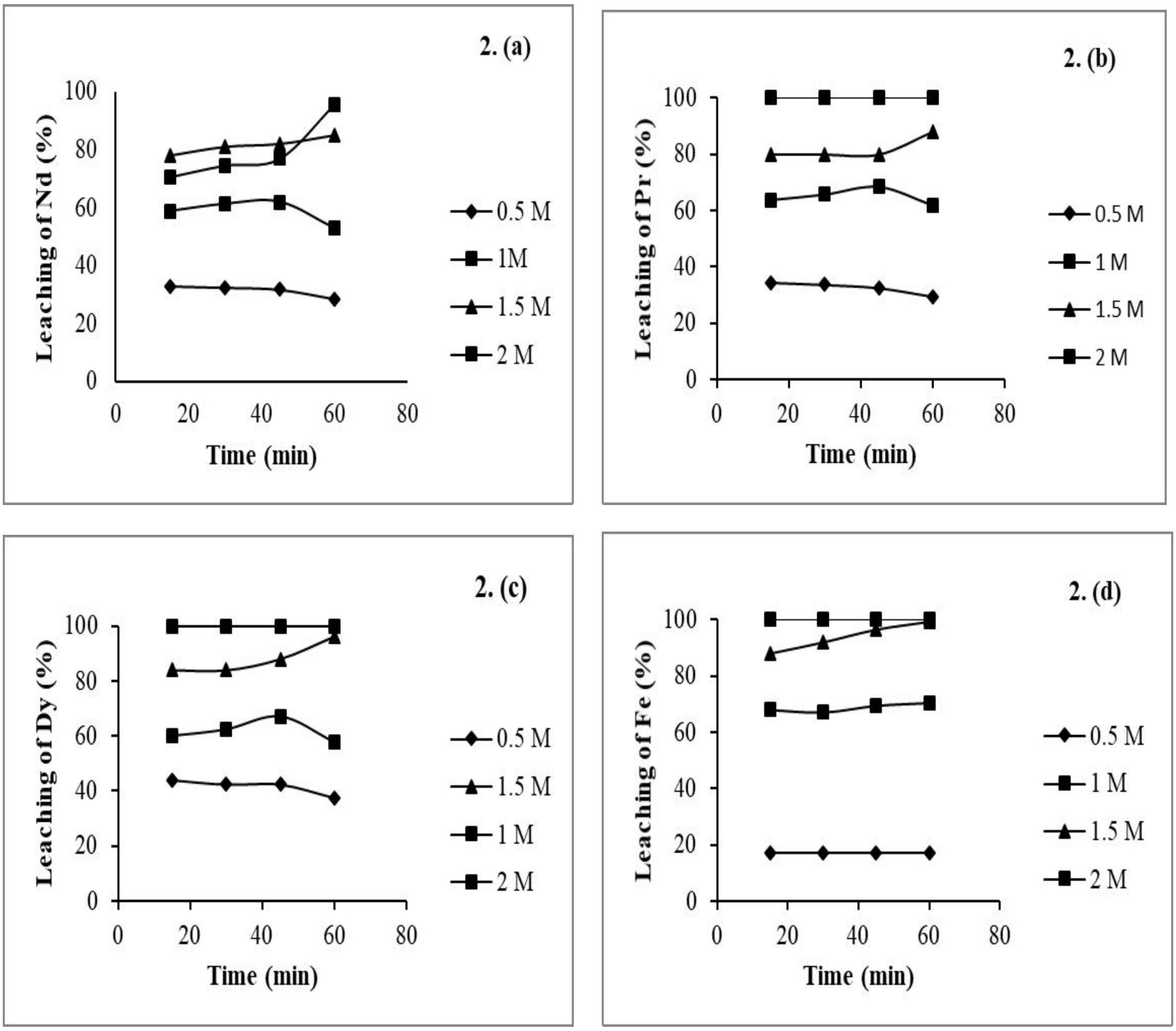

Figure 2. Effect of acid concentration on leaching of metals [2.(a) Nd, 2.(b) Pr, 2.(c) Dy, 2.(d) Fe] from Nd-Fe-B magnets

3.2. Effect of pulp density

For more dissolution of metals, pulp density plays significant role. As pulp density increases, the surface area per unit volume of the solution increases, which help to increase the reaction rate. Pulp density also affects the leaching rate of REMs. For knowing the better optimized condition various sets were practiced with different pulp densities such as 25 g/L, 50 g/L, 75 g/L, 100 g/L, 150 g/L and 200 g/L. Results indicates (figure 3) that the leaching percentage at 100 g/L is maximum and it became constant at 150 g/L and 200 g/L and so on, it is due to the leaching rate is inversely proportional to the pulp density and also due to the sample requires more amount of acid solution as we increases the amount of samples. Therefore 100 g/L pulp density were considered as best optimized condition for the further experiments after practicing various sets of leaching with different pulp density at 25°C for 60 min.

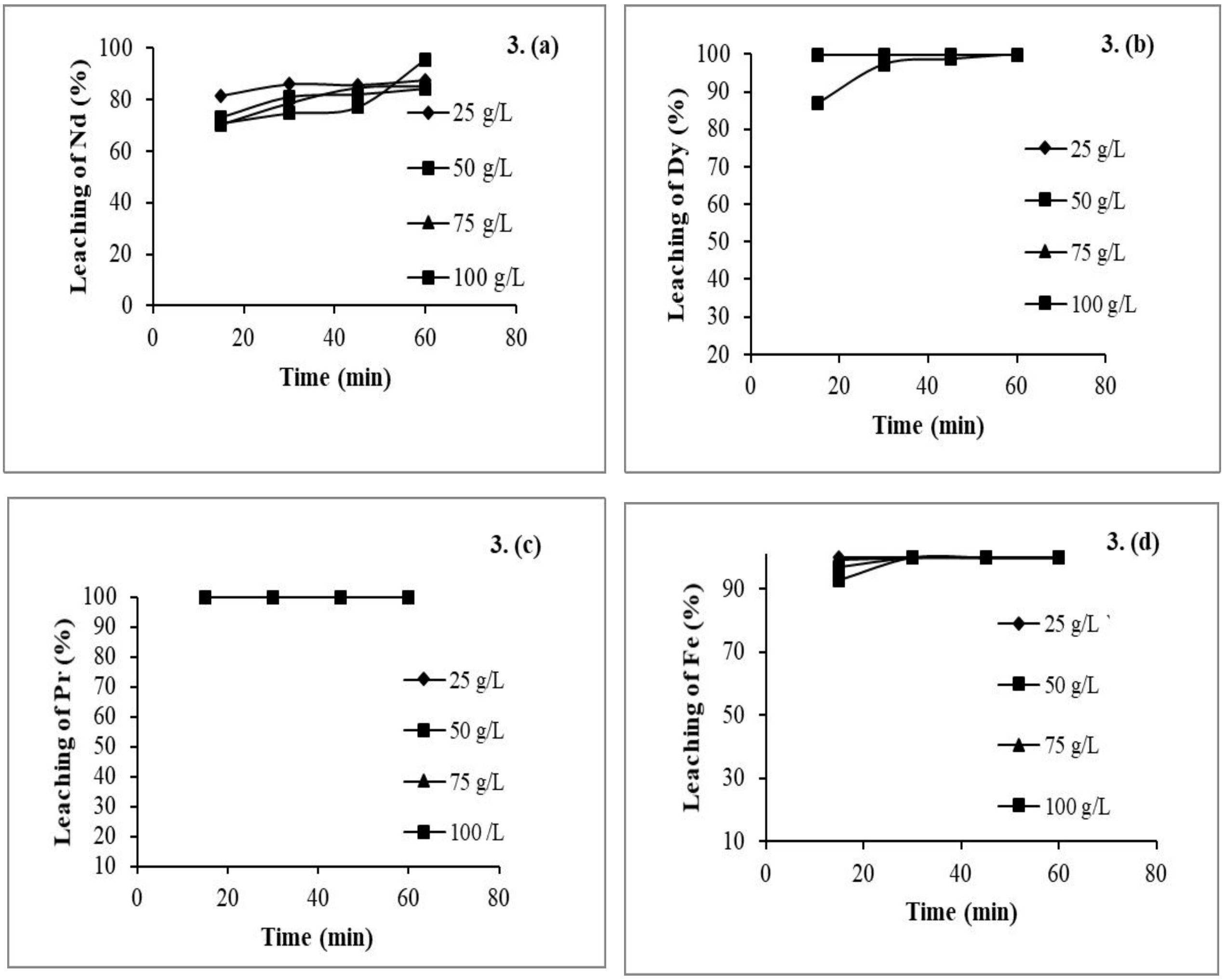

Figure 3. Effect of pulp density on leaching of metals [3.(a) Nd, 3.(b) Dy, 3.(c) Pr, 3.(d) Fe] from Nd-Fe-B magnets.

3.3. Effect of temperature

Temperature of the reaction is one of the most important factor which plays significant role for the recovery of REMs from Crushed Nd-Fe-B magnets. As the temperature of the reaction increases, the rate of reaction increases and vice versa. But, in this study it has been shown that temperature has the negligible effect on the leaching of crushed magnets, the leaching efficiency was high at room temperature and as the temperature was increasing the rate of the reaction is quite constant and recovery percentage seems same as in the case of room temperature. Various sets of experiments were carried out at different temperature to know the effect of temperature such as 25°C, 60°C, 75°C and 90°C with pulp density 100g/L and time 60 min. After analysis, result indicates (Figure 4) that increase in temperature has almost negligible effect on leaching rates of rare earth metal. At 25°C the leaching percentage of REMs was found maximum while at 75°C and 90°C it seems almost constant. Therefore, further experiments were carried out at 25°C as optimized leaching temperature. At this temperature leaching of REMs were found to be 99.9%.

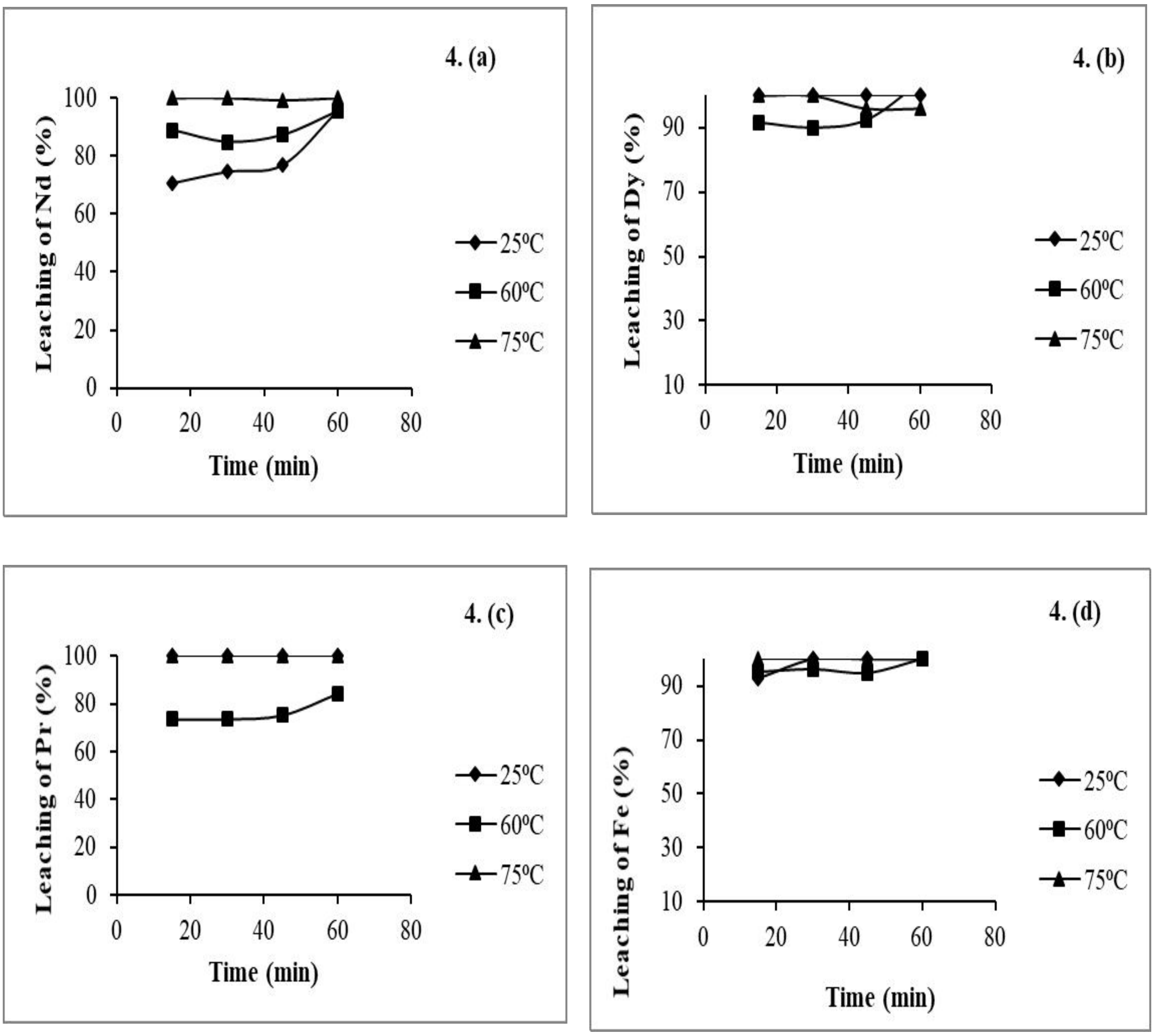

Figure 4. Effect of temperature on leaching of metals [4.(a) Nd, 4.(b) Dy, 4.(c) Pr, 4.(d) Fe] from Nd-Fe-B magnets.

3.4. Removal of iron

Fe present in the solution has been removed from the solution by maintaining the pH of the solution ~3.5 by providing O_2 continuously at 60°C for 1h. To remove excess amount of iron present in the liquor, effect of pH and ammonia dosage also has been investigated after extracting REEs, as various study shown that precipitation of Fe depends upon particular pH therefore ammonia solution was used to precipitate the iron particles of the solution. It has been shown that after extracting the REEs from the liquor at 1.25-2, the pH of the solution was increased up to pH~2.5 the recovery rate of iron was 16.45%. Then further pH of the liquor was increased from 2-4 and then analyzed, it has been shown that at pH~2.5 and 3 the recovery rate of iron was 79.8% but, at pH~3.5 the recovery rate of Fe was increased up to 96.5%. Therefore, 3.5 pH has been considered to the optimized condition. The precipitated Fe particles as $Fe(OH)_3$ was filtered and dried at 110°C for 1h to convert it into red oxide [Eq. (2) & (3)].

$$FeSO_4 + NH_4OH = Fe(OH)_3 + NH_4SO_4 \quad (2)$$

$$Fe(OH)_3 + Heat = Fe_2O_3 + H_2O \quad (3)$$

3.5. Solvent extraction studies for separation of REEs

Table 2. Extraction of REEs from different media using D2EHPA

Media	Reagents	pH	Reference
Sulfate	20% D2EHPA	2	[7]
Membrane	1.5 M D2EHPA (O/A=1:1, 23°C)	--	[14]
Sulfate	1.2 M D2EHPA; 25 ± 1°C; O: A: 1:1.	1.1	[15]
Chloride	0.8 M D2EHPA;1:1; 60 min	1.3	[16]

Various studies have been reported to recover rare earth elements from by solvent extraction technique with extraction D2EHPA (Table 2). In this study, 20% D2EHPA was used to extract rare earth metals from the obtained leach liquor. At first, the extractant was prepared with kerosene as diluents and 3% isodecanal as modifier. Further, the leach liquor and the extractant were mixed together in a ratio of 1:1 for 20 min. The equilibrium pH was maintained by using NH_4OH. It was found that at pH 2, the recovery rate of Nd was 96%. However, on increasing equilibrium pH above 2 the excess of Fe present in the liquor also started to extract. Therefore, pH 2 was considered suitable. The loaded organic was stripped with 2 M nitric acid.

4. CONCLUSIONS

In order to recover of rare earth metals from discarded Nd-Fe-B magnet of hard disk as discussed below.

1. The de-magnetization of Nd-Fe-B magnet was carried out at 300°C for 3 h.
2. The complete leaching of Nd, Pr, Dy and Fe were occurred in 2 M H_2SO_4 25 ^{0}C, 1 h while maintain the pulp density 100 g/L.
3. 96.5% Fe was also recovered by precipitation technique as ferric ion at pH ±3.5 by maintaining the temperature between 50 to 60°C.
4. Further, solvent extraction is carried out to recover ~96% Nd, ~95% Pr and ~81% Dy from the leach liquor of discarded magnet in a pH range of 1.25 to 2 at room temperature in 15 min and the loaded extractant was stripped in dilute nitric acid.

ACKNOWLEDGMENT

The authors are thankful to the Director, CSIR-National Metallurgical Laboratory, Jamshedpur, India for kind permission to publish the paper.

REFERENCES

[1] Luk, P.C.-K.; Abdulrahem, H.A.; Xiz, B. Low-cost high-performance ferrite permanent magnet machines in EV applications: a comprehensive review, transportation. 2020, 6, 100080.

[2] V. Gruber, M. Carsky. New technology for lanthanide recovery from spent Nd-Fe-B magnet. S. Afr. J. of Chem. Eng. 2020, 33, 35–38.

[3] Dhir, A.; Malodia, S.; Awan, U.; Sakashita, M.; Kaur P. Extended valence theory perspective on consumers' e-waste recycling intentions in Japan. J. Clean. Prod. 2021, 312, 127443.

[4] Choubey, P. K.; Singh, N.; Panda, R.; Jyothi, R. K.; Yoo, K.; Park,I.; Jha, M. K. Development of Hydrometallurgical Process for Recovery of Rare Earth Metals (Nd, Pr, and Dy) from Nd-Fe-B Magnets. Metals 2021, 11, 1987

[5] Makarova, I.; Soboleva, E.; Osipenko, M; Kurilo, I.; Laatikainen, M. Electrochemical leaching of rare-earth elements from spent NdFeB magnets. Hydrometallurgy. 2020, 192, 105264.

[6] Pavon, S.; Fortunya, A.; Collb, M.T.; Sastrec, A.M. Neodymium recovery from NdFeB magnet wastes using Primene 81R·Cyanex 572 IL by solvent extraction. J. Environ. Manage. 2018, 222, 359–367.

[7] Niam, A. C.; Wang, Y.; Chen,S.; Chang, G.; You, S. Simultaneous recovery of rare earth elements from waste permanentmagnet (WPMs) leach liquor by solvent extraction and hollow fiber supported liquid membrane. Chem Eng Process. 2020, 148, 107831.

[8] Onal, M. A. R.; Aktan, E.; Borra, C. R.; Blanpain, B.; Gerven, T. V.; Guo,M. Recycling of NdFeB

magnets using nitration, calcination and water leaching for REE recovery. Hydrometallurgy. 2017, 167, 115–123.

[9] Reisdorfer, G.; Bertuol, D.; Tanabe, E. H.; Recovery of neodymium from the magnets of hard disk drives using organic acids. Miner. Eng. 2019, 143, 105938.

[10] Lee, C. H.; Chen, Y. J.; Liao, C. H.; Popuri, R. S.; Tsai, S. L.; Hung, C. E. Selective leaching process for Neodymium recovery from scrap Nd-Fe-B magnet. Metall Mater Trans A Phys Metall Mater Sci. 2013, 44, 5825-5833

[11] Rabatho, J. P.; Tongamp, W.; Takasaki, Y.; Haga, K.; Shibayama, A. Recovery of Nd and Dy from rare earth magnetic waste sludge by hydrometallurgical process. J. Mater. Cycles Waste Manag. 2013, 15, 171-178.

[12] Liu, F.; Porvali, A.; Wang, J.; Wang, H.; Peng, C.; Wilson, B. P.; Lundstrom. M Recovery and separation of rare earths and boron from spent Nd-Fe-B Magnets. Miner. Eng. 2020, 145, 106097.

[13] Loya, S. V.; Onal, M. A. R.; Binnemans, K.; Gervena, T. V. Recovery of valuable metals from NdFeB magnets by mechanochemically assisted ferric sulfate leaching. Hydrometallurgy. 2020, 191, 105154.

[14] S. Wu, L. Wang, Patrick Zhang, Hassan El-Shall, Brij Moudgil, Xiaowei Huang, Longsheng Zhao, Lifeng Zhang, Zongyu Feng Simultaneous recovery of rare earths and uranium from wet process phosphoric acid using solvent extraction with D2EHPA doi:10.1016/j.hydromet.2017.10.025

[15] Marino Gergoric, Christian Ekberg, Britt-Marie Steenari, Teodora Retegan. Separation of Heavy Rare-Earth Elements from Light Rare-Earth Elements Via Solvent Extraction from a Neodymium Magnet Leachate and the Effects of Diluents. J. Sustain. Metall. 2017, 3:601–610.

[16] Verónica C ristina Arellano Ruiz, Rambabu Kuchi, Pankaj Kumar Parhi, Jin-Young Lee, Rajesh Kumar Jyothi. Environmentally friendly comprehensive hydrometallurgical method development for neodymium recovery from mixed rare earth aqueous solutions using organo-phosphorus derivatives. 2020, 10:16911 | https://doi.org/10.1038/s41598-020-74041-9