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Recovery of mixed rare earth oxide and fine powder of metallic iron from spent NdFeB magnet of wind turbines

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Abstract

NdFeB magnet is used in various application such as generators, electric vehicles, hard disc, rare earth roll magnetic separator etc. due to its excellent magnetic properties. Currently, ~26% of rare earths produced worldwide are used for the production of NdFeB magnet, but less than 1% of the rare earths are recycled after completing their life cycle. Due to continuous increase in demand of rare earths and scarcity of their primary resources, end-of-life NdFeB magnet emanated as potential source of rare earths. Therefore, now-a-days research is primarily focused on the utilization of waste NdFeB magnets for recycling and recovery of valuables metals in the usable form. Investigation has been carried out to separate rare earth oxide and metallic Fe directly by magnetic separation after selective oxidation of rare earths in NdFeB magnet. But the magnetic separation is ineffective due to partial oxidation of iron. In the present study, the rare earths are recovered selectively during leaching from the roasted NdFeB magnet powder and the leach residue of iron oxide is utilized to produce fine powder of metallic iron. Mixed oxide of rare earths of 99% purity is obtained from the rare earth rich leach liquor. The reduction of the leach residues has been studied using waste graphite of spent electrodes of arc furnace as reductant, in horizontal tubular furnace at different temperature and for various time period. It is found that 93% of iron oxide reduces to fine powder of metallic iron. The fine powder obtained after reduction, has been characterized by XRD which confirm the conversion of iron oxide to metallic iron phase. Thus, the present investigation highlights the recovery of mixed rare earth oxide and fine powder of metallic iron obtained as valuables from waste NdFeB magnet, which can be utilized directly as raw material for the production of fresh magnet.

Keywords: NdFeB magnet; Leaching; Rare earth oxide; Reduction; Iron powder

1. Introduction

The application of rare earth elements is increasing continuously in modern technologies. It is widely used in permanent magnets, florescent light bulbs, hybrid electric vehicles, NiMH batteries, catalyst etc. According to an analysis, the worldwide demand of REOs estimated to grow each year between 10% and 20% **(Reuters, 2009)**. Rare earth magnets especially NdFeB play crucial role in support of **'Green Energy'** application such as wind turbines and hybrid cars. During usage of magnets at high heating condition, magnets oxidize easily and become scrap after completing their life span. Recovery of REMs from primary resources are associated with many disadvantages such as difficulties in mining, occurrence of REMs with radioactive elements (such as thorium, uranium etc.), the huge environmental impacts related to low rare earth concentrations in natural deposits and the requirement of numerous separation stage for achieving individual REMs of desired purity. Secondary resources such as scraps or end-use products can play significant role in this context for comparatively easier processing and economical recovery of rare earth metals with little environmental impact.

Many processes were explored for the selective recovery of rare earth metals from scrap magnet using different approaches. Studies were carried out using liquid metal extraction using magnesium metal in the temperature range of 675-800℃ (Na et al., 2014; Okabe et al., 2003). Bian et al. (2015) have used FeO-B_2O_3 flux for the separation of oxides of neodymium from Fe-based metals. Different slag systems such as SiO_2-Al_2O_3, Cao-CaF_2 etc. were studied for complete extraction of rare earth into slag phase followed by leaching in H_2SO_4 (Abrahami et

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al., 2015). Process of chemical vapor transport has also been attempted for selective recovery of rare earth metals from scrap magnet powder (Itoh et al., 2009). Investigation has been carried out to separate rare earth oxide and metallic Fe directly by magnetic separation after selective oxidation of rare earths in NdFeB magnet. But the magnetic separation is ineffective due to partial oxidation of iron (Lyman and Palmer, 1993a). During hydrometallurgical process, the scrap magnet was completely dissolved in high sulfuric acid concentration followed by precipitation of neodymium sodium or ammonium sulfate double salt (Lee et al., 2013, 2015; Lyman and Palmer, 1993b). In this process, the yields of neodymium recovery are 70% for ammonium systems. Iron is removed from leach solutions by precipitating as jarosite which is not considered as a usable form of iron (Tanaka et al., 2013). Therefore, the present study deals with the selective recovery of rare earths from NdFeB magnet and obtaining iron in the usable form. Rare earths (Nd, Pr and Dy) are recovered selectively in the leach liquor and iron oxide is obtained in the leach residue. Reduction studies were carried out by varying different parameters in order to convert iron oxide residue into fine powder of metallic iron.

2. Experimental

2.1 Materials and Methodologies

The spent magnet of wind turbines was used for the study. The chemical composition of magnet sample was determined by chemical analysis. All the chemicals were used in the experiments were analytical grade reagents. Prior to leaching study, magnets were crushed and ground after demagnetization. Powder magnet sample were roasted in muffle furnace. The leaching studies were carried out with roasted sample in 3-necked glass reactor placed over a magnetic hotplate with stirrer. Samples were taken out for analysis at different time interval and analyzed in ICP-OES. The leach liquor and leach residue were separated using filtration. The leach liquor was used to precipitate as oxalate by adding stoichiometric amount of oxalic acid. The oxalates were heated to obtain the oxides of metals. The phases present in leach residue were analyzed by XRD. The XRD peaks were obtained with Cu Ka (k = 1.54178 A°) radiation ranging from 2Θ = 20 to 70° at a scanning rate of 2Θ/min. The reduction study of leach residue was carried out in horizontal tubular furnace under argon atmosphere. Spent graphite electrode of electric arc furnace were used as reductant for the reduction experiments. For each reduction experiment, 10 g of leach residue is homogeneously mixed with stoichiometric amount of graphite powder and filled properly in quartz crucible. Then, quartz crucible was placed inside the heating zone of tubular furnace for fixed residence time at fixed reduction temperature. The changes in mass of the sample were noted before and after the reduction experiment. The change in phase of the sample after reduction were analyzed by XRD. Reduction efficiency was calculated by using experimental and theoretical change in mass as mentioned in Eq.1. The

$$\text{Reduction efficiency} = \frac{(\text{loss in mass during experimental investigation})}{\text{theoretical loss in mass}} \qquad (1)$$

3. Results & Discussion

3.1 Leaching of rare earths and precipitation as mixed oxide

The chemical composition of magnet sample was obtained as: 23% Nd, 5.6% Pr, 0.42% Dy, 1% B, 67.3% Fe and others (Al, Co etc). The crushed magnet powder was roasted at 850 °C for 6h for complete oxidation. Series of leaching experiments were carried out in order to study the different leaching parameters such as acid concentration, pulp density, leaching temperature and leaching time. At the optimized leaching condition of 0.5M HCl, 100 g/L pulp density, 95 °C temperature and 5h leaching time, rare earths (Nd, Pr and Dy) were selectively leaches out in leach liquor leaving behind iron in the leach residue. The rare earth leach solution obtained after leaching contained 16.8 g/L Nd, 3.8 g/L Pr and 0.28 g/L Dy. The rare earths were precipitated by adding stoichiometric amount of oxalic acid dropwise to the leach solution at pH 2. The obtained white precipitates of mixed rare earth oxalate was roasted at 800 °C for 2 h. The mixed oxide of rare earths (Nd, Pr and Dy) of 99% purity was formed which was confirmed by XRD analysis.

3.2 Reduction studies of leach residue

The leach residue obtained after leaching at optimized condition was characterized by XRD. The peaks indicated the major presence of iron oxide (Fe_2O_3) as shown in Fig. 1. The chemical analysis of leach residue indicated the presence of ~93% iron oxide along with minor impurities. The reduction studies of obtained leach residue were carried out in order to convert iron oxide to metallic iron having high values and various applications. All reduction experiments were carried out using stoichiometric amount of graphite powder as reductant in horizontal tubular furnace under argon atmosphere. In order to study the effect of temperature, reduction experiments were carried out initially at 900 and 1000 °C for 1 hour residence time. It was found that reduction efficiency increased with increase in temperature. At 1000 °C, the reduction efficiency obtained was 83%. Further, the effect of residence time on reduction were studied by varying the residence time at 0.5, 1 and 2 hours at 1000 °C temperature. It was found that reduction efficiency increased with increase in residence time as shown in Fig. 2. The reduction efficiency increased from 24 to 93% when residence time increased from 0.5 to 2 hour. Thus, the optimum reduction condition obtained was 2 hours residence time and temperature 1000 °C. The product obtained after reduction were analyzed by XRD and SEM as shown in Fig. 3. The peaks of XRD confirmed the conversion of iron oxide to metallic iron phase. The fine powder of metallic iron was also analyzed by particle size analyzer. It indicates that 90% of the particles were of the size range of 112 µm which can be utilized for various industrial purpose and direct applications.

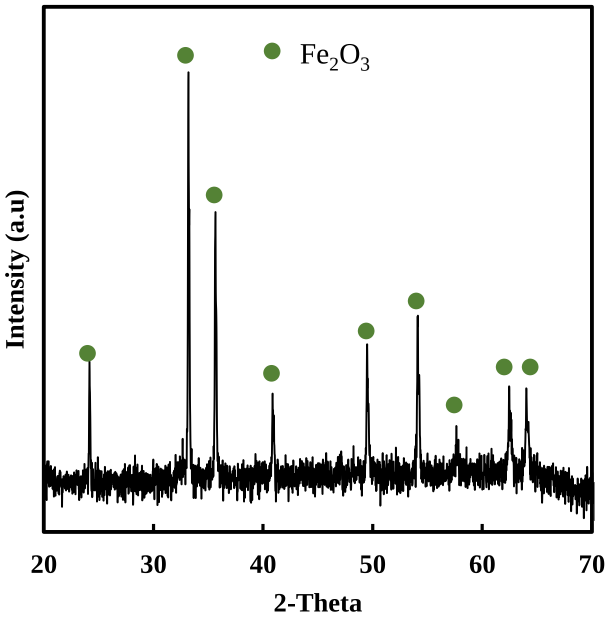

Fig. 1 XRD of leach residue

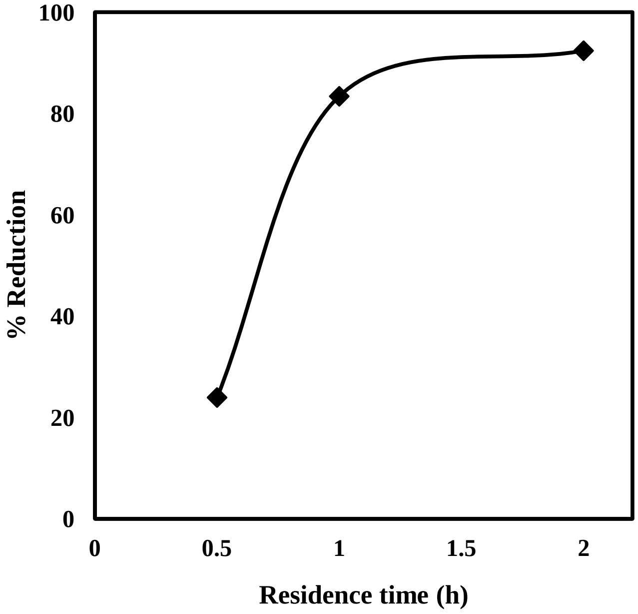

Fig. 2 Effect of residence time on % reduction

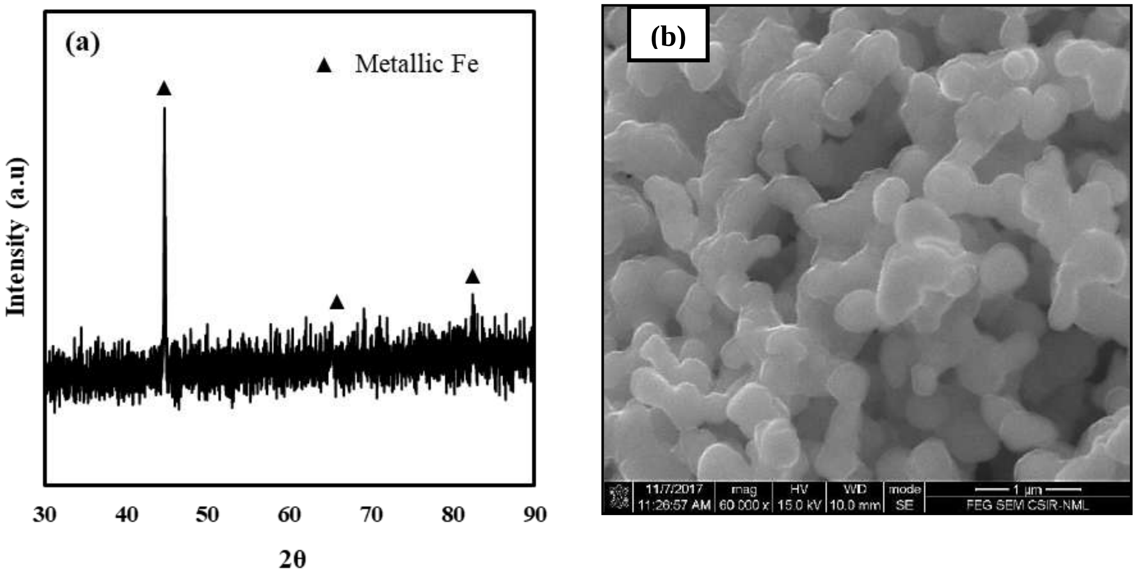

Fig. 3. Characterization of fine powder obtained after reduction (a) XRD (b) SEM image

4. Conclusions

The present investigation focused on the recovery of rare earths and iron as usable form from spent NdFeB magnet of wind turbines. Leaching studies were carried out for selective recovery of rare earths from magnet. The rare earth leach solution of Nd, Pr and Dy were precipitated and mixed rare earth oxides of 99% purity was obtained. The leach residue obtained from leaching at optimum leaching condition comprised of iron oxide (hematite) phase. The reduction studies were carried out for the conversion of iron oxide to metallic iron by varying different parameters such as temperature and residence time. At 1000 °C temperature and 2 h residence time, 93 % reduction efficiency was obtained. The fine powder obtained after reduction were characterized by XRD, SEM and particle size analyzer. The XRD peaks confirmed the presence of metallic iron phase. Thus, the process was developed for the recovery of mixed rare earth oxide and fine powder of metallic iron from spent NdFeB magnet of wind turbines.

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