RECOVERING RARE EARTH OXIDE FROM NdFeB MAGNET OF WASTE HDDs BY LEACHING AND SELECTIVE PRECIPITATION METHODS

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Received: 11 August 2017; Accepted for publication: 9 October 2017

ABSTRACT

Rare earth metal elements have been used widely in many different fields such as in fluorescence, polishing powder, nuclear, laser applications, fiber optics, superconductors, permanent magnets, capacitors and radar technology, etc. In recent years, the development and demand trend led to a large amount of electric and electronic waste (e-waste) generated annually. Faced with issues of shortage on using demand of rare earth metal, many studies have been done in order to recover, recycle and reuse this metal from e-waste. In this research, rare earth elements were recovered from permanent magnet which was dismantled from some kinds of waste hard disk drives HDDs.

Result of reseach showed that magnetic flux density of the NdFeB magnet was eliminated completely at 300 ºC in one hour. The leaching efficiency of magnet powder sample reached 99.4 % after 10 min reaction in H_2SO_4 acid have concentration > 0.3 M under the leaching conditions: stirring speed of 200 rpm, particle size < 0.25 mm, solid/liquid (S/L) ratio 20 g/1l and temperature reaction is 25 ºC. Total rare earth metal elements can be recovered by the using selective crystallization and precipitation method in leaching solution by Na_2SO_4 and oxalic acid up to 98.36 % was with purity up to 94.32 %. $Nd_2(C_2O_4)$ transformed into Nd_2O_3 after being calcinated at 700 °C.

Keywords: E-waste, rare earth magnet, FeNdB, leaching, selective precipitation.

1. INTRODUCTION

Nowadays, e-waste has been a world wide problem, the global e-waste monitor result forecasted there will be 49.8 billion tons of e-waste [1]. In Vietnam, until 2020 the quantities of each type electronic devices are forcasted as 4,852,039 televisions, 1,444,038 computers, 3,533,465 mobile devices, 2,267,318 refrigerators, 873,163 air conditions, 2,625,882 washing machines. This number can be corresponded to 600,000 tons of electronic waste [2, 3]. If there is no proper treating method for e-waste, the human health and living environment will be damage seriously. Furthermore, fast development and overmanufacture leads to the exhaustion of

resources. Therefore, the treatment, recovery and recycling task of rare and precious metals in e-waste should be enforced for clean environment and high economic.

At the present, two main methods, pyrometallurgy and hydrometallurgy methods, to treat and to recover metals from e-waste [4]. Pyrometallurgy method can release toxic gases while final product always in the form of alloys which needed other technologies to separate metals [5]. In this research, hydrometallurgy method was used to recovery rare earth metal from HDDs due to final purified product [6, 7].

2. EXPERIMENT AND METHODS

In this study, the permanent magnet was collected from discarded HDDs on the Vietnam market from several brands as follow Samsung, Seagate, Maxtor, Western Digital and Quantum.

For the purpose of recovering rare earth from this discarded magnet, the research team synthesized the data and produced the following process.

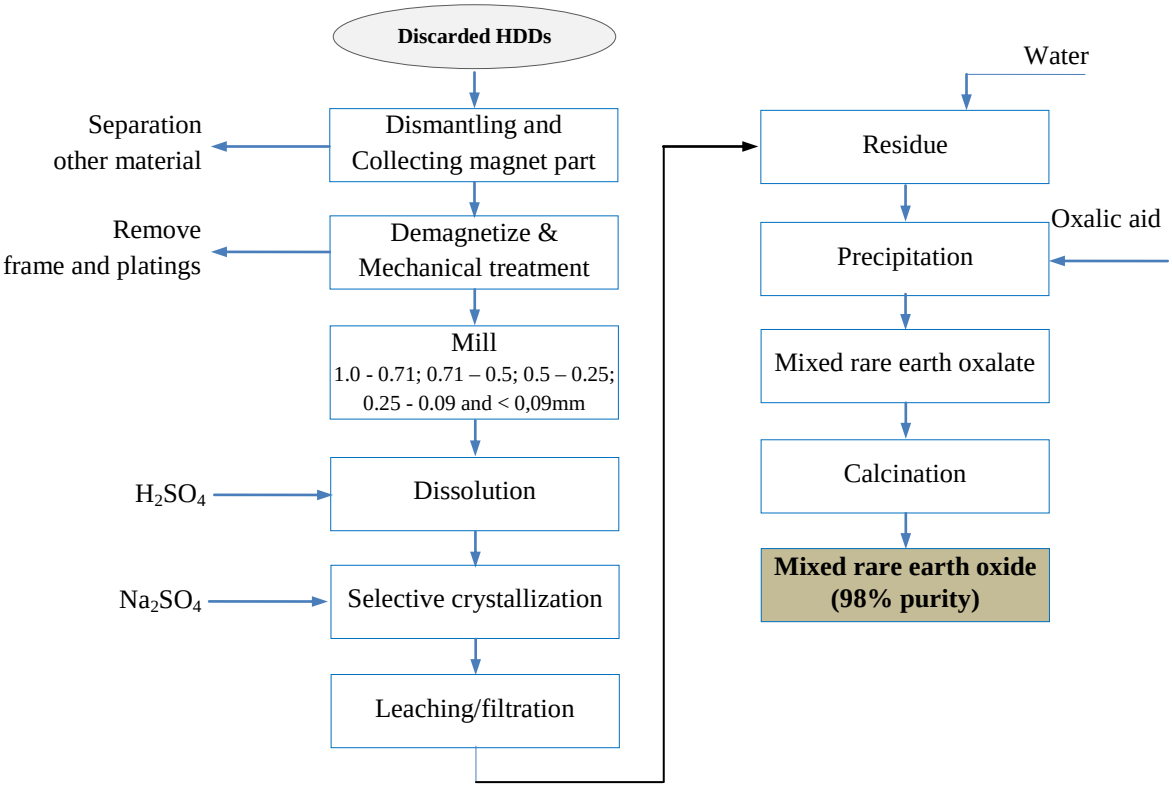

Figure 1. Flow sheet of the recovery process of rare earth.

The flow sheet of experiment consists of five major steps: (1) collecting and pretreatment sample; (2) dissolve magnet powder with acid; (3) crystallized by Na_2SO_4 and filtration; (4) dissolved by water and precipitated by oxalic acid; (5) Calcinated (Fig. 1).

Magnet parts first were heated in an electric furnace up to 300 ºC with different dwelling times and temperatures with the purpose to demagnetize and separate the frame [8, 9]. In the study, we also evaluated the effect of different calcination temperature levels to the effective of demagnetizing process and magnetic flux density of the NdFeB magnet was measured

(equipment Hirst – GM05) before and after the heat treatment for each temperature level and gap of time.

After calcination, the sample was milled to different particle sizes ranged from 1.0 - 0.71; 0.71 - 0.5; 0.5 - 0.25; 0.25 - 0.09 and < 0,09 mm [10] by ball mill and rotary mill machines.

Leaching experiments were carried out in jacketed reactor with H_2SO_4 and HCl having circulator temperature stability equipment and was connected with agitator having centrifugal Teflon impeller. During leaching experiments one of the parameters was changed such as type and concentration of acid, S/L ratio, practice size, reaction time… while other parameters were maintained constant such as stirring speed was 200 rpm, media temperature was 25 ºC or depending each type of test. Selective crystallization experiments were carried out by the addition Na_2SO_4 into leaching solution and filtering precipitation of complex salt after 12 - 24 hours. After that, complex salt rare earth natri sulfate – $ReNaSO_4$ will be washed by water and added oxalic acid to create oxalate rare earth precipitation [11].

Composition and structure of solid sample and in leaching solution were analysed by methods as follows: Inductively Coupled Plasma Mass Spectrometry (ICP-MS Elan 9000 – Perkin Elmer). X-ray diffraction (XRD 8D Advance – Bruker), Energy-dispersive X-ray spectroscopy (EDX FESEM S-4800) and Thermo-gravimetric analysis (TGA NETZSCH – STA 409 PC/PG). Table 1 is analysis result of the composition of collected rare earth magnets.

Table 1. Composition of rare earth magnet by ICP-MS methods.

Element	**Rare earth**				**Metal**					
	Nd	Pr	Dy	Tb	Fe	Na	B	Co	Al	other
Mass *(g)*	20.870	3.556	1.253	0.140	62.168	0.360	0.809	0.690	0.200	9.954

3. RESULTS AND DISCUSSIONS

3.1. Influence of calcination temperature to the demagnetizing

From recovered magnetic parts, with the aim of reducing the influence of the magnetic field that may cause subsequent processes. Based on the theory that the crystal structure of the magnetic material will be destroyed at high temperatures. Magnet parts was calcined at different temperature levels and different period of time.

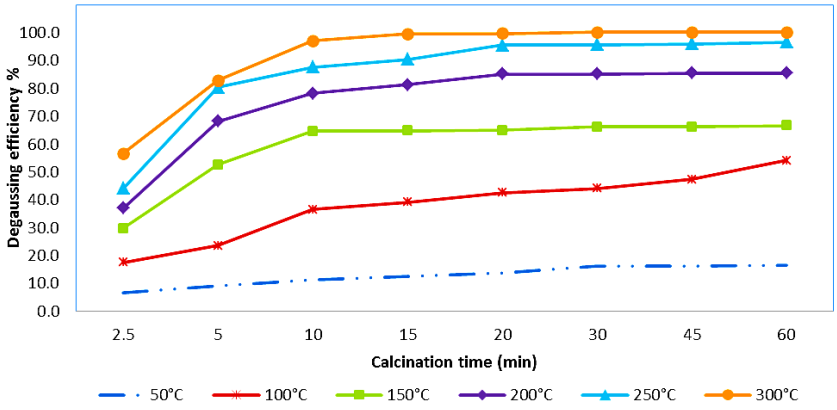

Figure 2. Effect of time and calcination temperature on demagnetizing treatment.

Intially flux density of NdFeB magnet is 110 mT. In Fig 2 the degauss efficiency increases with the increase of calcination temperature and calcination time. The results showed that magnetism of the magnet was eliminated completely after 1 hour of 300 ºC degaussing in an electric furnace.

3.2. Influence factors to leaching process

In this step, HCl and H_2SO_4 were used to evaluate leaching capacity magnet powder sample with aicd concentration is 1M, S/L ratio is 20 g/L, particle sizes < 0.25 mm.

The reactions between acid and metals result in the formation of metal sulphates. M is metal including rare earth element

$$2M + 3H_2SO_4 \rightarrow M_2(SO_4)_3 + 3H_2$$

$$M + 3HCl \rightarrow MCl_3 + 3/2\ H_2$$

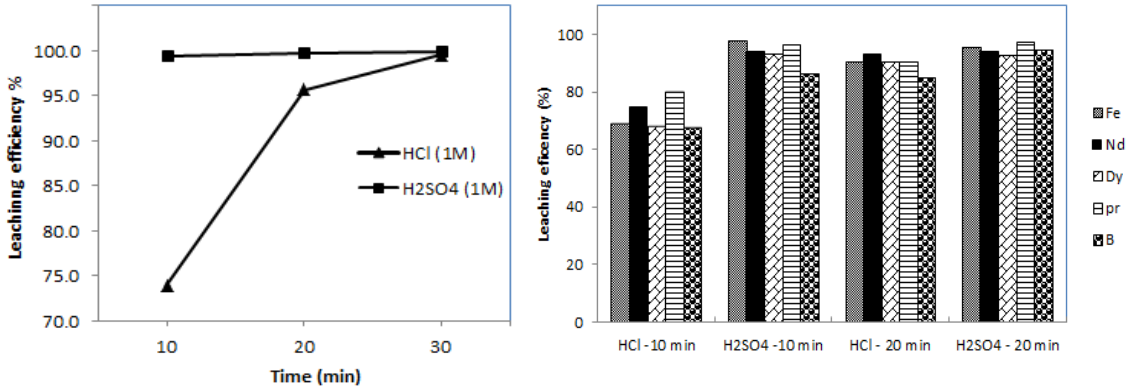

Figure 3. Effect of: (a) acid type on leaching; (b) leaching efficiency of each main element.

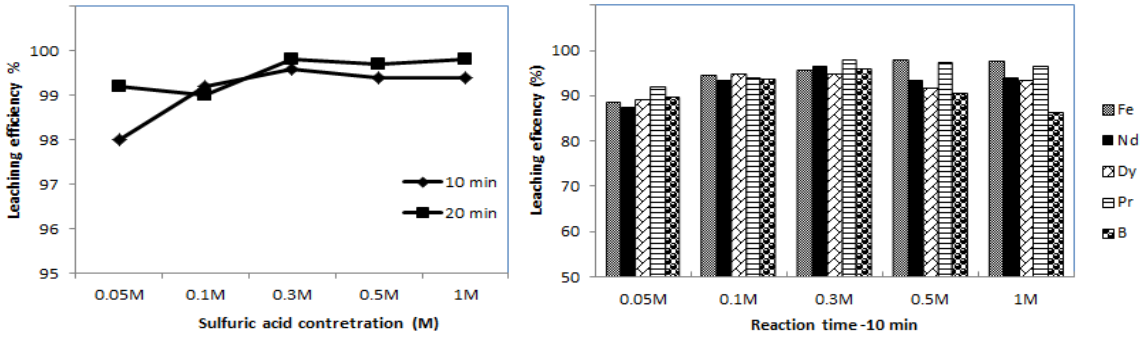

Figure 4. Effect of: (a) H_2SO_4 acid concentrations; (b) leaching efficiency of each main element.

In Fig 3 showed that using H_2SO_4 to leach the sample is more efficient than HCl, after 10 minutes of reaction, the leaching efficiency by H_2SO_4 reached 99.4 % and HCl was 74 %; after 20 minutes leaching efficiency of H_2SO_4 and HCl was 99.5 and 95.59 % respecriverly; after 30 minutes leaching efficiency nearly 100 %. The experiment was conducted on several H_2SO_4 acid concentrations as follows 0.05 M; 0.1M; 0.3 M; 0.5 M và 1 M. Fig 4 showed that by the use H_2SO_4 acid achived high leaching efficiency and with concentration > 0.3 M after 10 minutes of

reaction, leaching efficiency was 99.6 %. Concentration of element in leaching solution depends on the concentration of H_2SO_4.

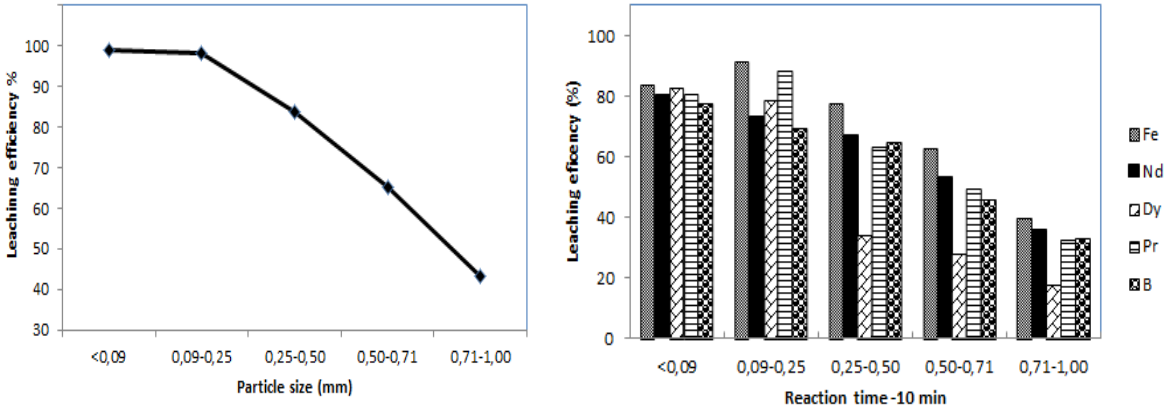

Figure 5. Effect of: (a) Grain size powder magnet; (b) leaching efficiency of each main element.

In Fig. 5 (a) it is shown that with particle size smaller than 0.25 mm, leaching efficiency of powder FeNdB magnet was higher than 98 % and decreased when particle size increasing and performance was only a 43.2 % at size 1.0 - 0.71 mm. These results showed that particle size has a significant effect on the leaching process of powder FeNdB magnet and the best leaching efficiency is with particle < 0.25 mm.

3.3. Recovery of rare earth from leaching solution

Basing above result, main parameter was choosed for next step to recover rare erth from the NdFeB magnet powder with pratical size < 0.25 mm, dissolved by H_2SO_4 acid with concentrations 0.3 M; 0.5 M;1 M; 2 M and 3 M.

Leaching solution having salt of rare earth sulphate and other was added Na_2SO_4 to crystallize selectively only for rare earth with the ratio Re:Na_2SO_4 are 1:1; 1:2; 1:3 based on the rare earth content in the powder NdFeB magnet, the reaction formulation as follows

$$Re_2(SO_4)_3 + Na_2SO_4 \rightarrow 2NaRe(SO_4)_2 \downarrow$$

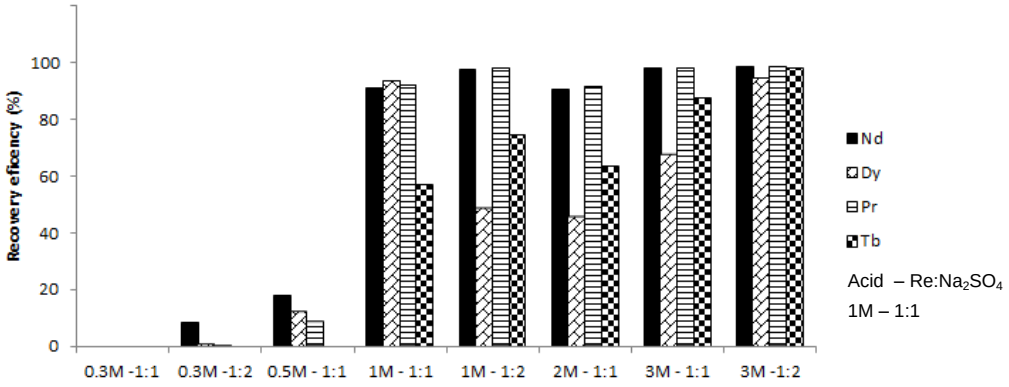

Figure 6. Recovery efficiency of rare earth by selectively crystallize method with Na_2SO_4.

Experimental results show that, samples were dissolved by H_2SO_4 acid 0.3 M and 0.5 M having ratio S:L were 10 g/L and 20 g/L, selectively crystallization process did not happen to creat complex salt $NaRe(SO_4)_2$. This process only appeared easily on the samples were dissolved by acid having concentration > 1M with ratio S:L is 40 g/L. And recovery eficeincy from 88.31 to 98.36 %.

The total of rare earth metal elements recovered by selective crystallize method in leaching solution by Na_2SO_4 is raised by 98.36 % with the ratio between total rare earth and Na_2SO_4 of 1:2. Recovery efficiency of rare earth by selectively crystallize method is shown in Fig.6.

Complex salt aflter filtration will be soluted by distilled water and added Oxalic acid to create rare earth oxalate precipitation.

$$NaNd(SO_4)_2.H_2O + H_2O \rightarrow Nd_2(SO_4)_3 + Na_2SO_4 + H_2O$$

$$Nd_2(SO_4)_3 + 3\ H_2C_2O_4 \rightarrow Nd_2(C_2O_4)_3\downarrow + 3\ H_2SO_4$$

With selective precipitation method by oxalic acid, rare earth elements have purity up to 94.32 %. Table 2 is analyzing result of rare earth oxalate precipitation sample.

Table 2. Composition of rare earth Oxalate precipitation by ICP-MS methods.

Element	Metal				
	Nd	Pr	Dy	Tb	Na
Mass *(mg)*	177.872	33.472	6.08	2.03	13.207

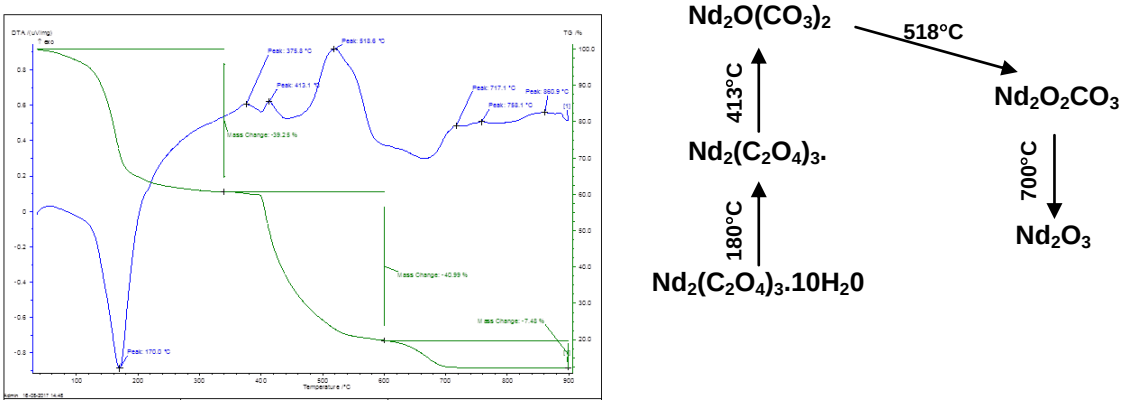

Figure 7. (a) TGA result of Oxalate precipitation (b) Phase transformation.

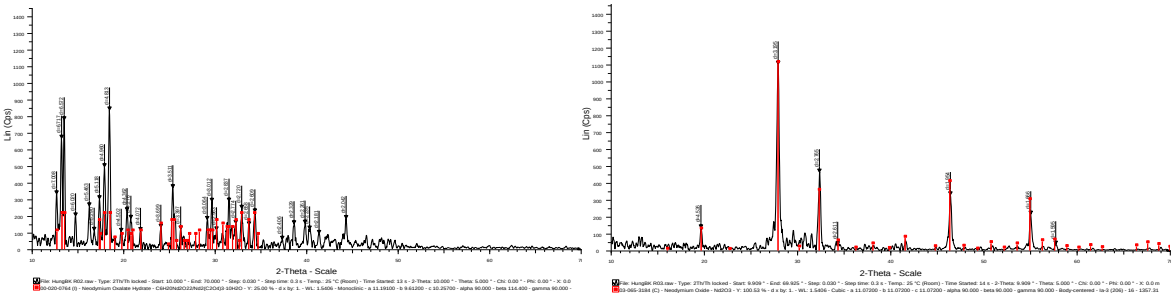

Figure 8. XRD result (a) Oxalate precipitation-$Nd_2(C_2O_4)$; (b) Nd_2O_3 - cancianed oxalate precipitation at 700°C

To select optimal calcination temperature and determine phase transition, the rare earth oxalate precipitation was analysed by thermo-gravimetric analysis method (TGA). TGA result is shown in Fig. 7 a.

Basing on result of TGA and XRD, the phase transition diagram from rare earth oxalate precipitation to rare earth oxide with Neodyum is the main component was shown in Fig. 8. The results show that with calcination temperatures above 700 °C, $Nd_2(C_2O_4)$ transformed into Nd_2O_3.

4. CONCLUSION

The recovery of Neodymium from NdFeB magnet which contains 26 % of total rare earth and 60 % of Fe by crystallization and precipitation method has worked. Magnetic flux density of the NdFeB magnet was eliminated completely at 300 ºC after one hour in electric furnace. By the using selective crystallize and precipitation method by Na_2SO_4 and oxalic acid, all other metals were removed in leaching solution of NdFeB magnet powder. Leaching efficiency up to 99.4 % with acid H_2SO_4 having concentration > 0.3 M under the leaching conditions: stirring speed of 200 rpm, particle size < 0.25 mm, S/L ratio 20 g/L, temperature reaction 25 ºC. When Na_2SO_4 was added into solution containing Nd and other rare earth created rare earth natri sulfate preferentially crystallized with recovery rate up to 98.36 %. After complex salt $NaRe(SO_4)_2$ was dissolved by distilled water, oxalic acid was added solution to create rare earth oxalate. $Nd_2(C_2O_4)$ transformed into Nd_2O_3 after being calcinated electric furnace for an hour at 700 °C. The recovered rare earth had purity up to 94.32 %.

Acknowledgements. This study was supported by Hanoi University of Mining and Geology and Hanoi University of Science and Technology.

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