

Influence of sulphuric acid concentration and solid/liquid ratio on leaching efficiency of rare earth elements from NdFeB postconsumer magnets

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ABSTRACT

The recovery of rare earth elements (REE) was boosted by the 2010 crisis, when the supply of these metals fell sharply in relation to demand and prices were elevated. However, less than 1 % of these metals are recovered worldwide, mainly due to the problems with inefficient scrap collection and economically unprofitable processes. Significant quantities of REE are found in neodymium-iron-boron (NdFeB) permanent magnets present in computer hard disk drives. Therefore, this work aims to evaluate the effect of sulphuric acid concentration and solid/liquid ratio on the recovery of REE through a hydrometallurgical route. For this purpose, acid concentration and solid/liquid assumed each four level values. It was observed that neodymium (Nd) and praseodymium (Pr) reached values close to 100 % of leaching efficiency, however dysprosium (Dy) and Terbium (Tb) only about 45 %, due to differences in solubility. Also, it was noticed that low concentrations of sulfuric acid do not satisfactorily dissolve high solid/liquid ratios, meaning that an optimal arrangement was at intermediate levels of both factors. In addition, the analysis of residual material showed that the main chemical species after leaching batches are nickel and iron, however the REE leaching selectivity towards iron was low, since high content of iron was also leached.

KEYWORDS

Rare earth elements, recycling, hydrometallurgy, NdFeB magnet.

INTRODUCTION

Further increase in demand for rare earth elements (REE) are expected in the near future, as the world is being guided to the use of environmentally friendly technologies, especially regarding the use of highly efficient magnets. The neodymium-iron-boron (NdFeB) permanent magnets are manufactured with the REE neodymium, dysprosium or praseodymium, which show stronger magnetic properties than others, reaching magnetic energy density of about 400 kJ/m³ [1]. This specific property has lead the use of NdFeB magnets in hybrid cars, wind turbines, and hard disk drives, which in 2008 accounted for 25 % of NdFeB magnets production [2].

Between 1990 and 2005, massive overproduction of REE in China led to a price drop for these commodities. As a result, much of the production was stopped in other countries. Consequently, today around more than 80 % of REE are produced in China [3]. Therefore, recycling has become a way to overcome this situation. However, the recycling global rate of REE nowadays does not exceed 1 % due to lack of government incentives, technical knowledge and economic viability [4]. Meanwhile, it is estimated that the recovery of metals by recycling is almost ten times more energy efficient than extraction from ores [5].

In Brazil, only in 2017, according to data from ABINEE (Brazilian Association of the Electrical and Electronics Industry), more than 5 million units of computers were sold [6]. Meanwhile, it is estimated that the useful lifetime continues to decrease, mainly due to the technological innovations. Henceforth, the hydrometallurgical recycling of REE from NdFeB magnets of Hard Disk Drives (HDD) was studied in this work. The focus here was to evaluate the effect on leaching efficiency of REE when using sulphuric acid in different concentrations as well as different solid/liquid ratios.

METHODOLOGY

Initially, twenty desktop HDD between the years of 2001 and 2012 were collected from final consumers and manually dismantled, leading to an amount of 193.95 g of NdFeB magnets. After a 60 minutes thermal demagnetization in muffle furnace (Sanchis) in which the Curie temperature, around 312 °C, was overcome, the sample was comminuted in a knife mill (SM 200, Retsch), leading to particle size < 250 µm. The homogeneous particle amount was then chemically characterized with nitric acid in microwave (Multiwave, Anton Paar) under 20 bar, 175 °C for 20 minutes, solid/liquid proportion of 1/50 and analysed by Inductive Coupled Plasma Optic

Emission Spectrometry ICP OES (Agilent Technologies 5110). The homogeneous sample showed content of 25.5 wt% Nd, 2.8 wt% Pr, 2.4 wt% Dy, 59.5 wt% Fe, among other elements, such as nickel, boron and cobalt.

The leaching experiments were performed in a glass beaker with agitation delivered by a two-propeller electric motor. Temperature and time were set constant throughout batches assuming values of 25 °C and 15 minutes respectively, since it has already been proved that REE solubility is higher when temperature is low [7]. The other two parameters, sulphuric acid concentration and solid/liquid ratio, assumed each one of the four levels according to the following Table 1, summing up to sixteen duplicated experiments. By the end of each batch, the leachate was filtered using Milli-Q® water. The residue was dried overnight, had the weight verified and was analysed by X-Ray Diffraction (Siemens/Bruker D5000). The percentages amount of residual material were calculated according to the Eq. 1, as well as the leaching efficiencies in percentage according to Eq. 2.

$$R = \frac{m_r}{m_o} \times 100 \quad \text{Eq. 1}$$

In which m_r is the amount of residue after the leaching batch and m_o is the initial amount of material, both in mg.

$$E_i = \frac{cL_i}{cM_i} \times 100 \quad \text{Eq. 2}$$

In which E_i is the leaching percentage efficiency of i element, cL_i is the concentration of element i in mg.L^{-1} after leaching batch and cM_i is the concentration of element i in mg.L^{-1} of the initial chemically characterization.

Table 1 – Values assumed by the parameters acid concentration and solid/liquid ratio in leaching experiments

Acid concentration (mol.L^{-1})	0.5	0.75	1.0	1.5
Solid/Liquid Ratio (g.mL^{-1})	1/10	1/20	1/30	1/40

RESULTS AND DISCUSSION

Residual material

The overall average was 38.8 % of residual material, represented by dashed line. At a temperature of 25 °C and only 15 min of leaching, while the combination 1/10 and 0.5 mol.L^{-1} (experiment 13) had more than 80 % of residual material, the combinations 1/20 with 1 mol.L^{-1} (Experiment 11) and 1/30 with 1 mol.L^{-1} (experiment 7) showed around 20 % of residual material. Therefore, two opposite combinations, i.e. a large amount of magnet as feed added and a low acid concentration are not sufficient for efficient dissolution of the elements.

It was observed that at the concentration of 1 mol.L^{-1} the magnet powder was dissolved in greater quantity, as well as in the solid/liquid ratio 1/30. The use of solid/liquid ratio 1/10 showed higher residual material, which obtained only a satisfactory amount of dissolved magnet at highest concentration, as well as the solid/liquid ratio 1/20 and 0.5 mol.L^{-1} .

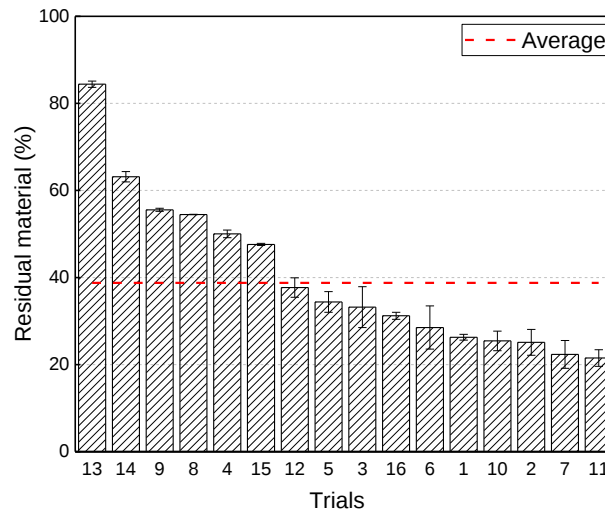


Fig. 1 - Decreasing residual material in percentage of each batch trial. The bars represent the standard deviation and the dashed line is the average of all trials.

According to the X-ray diffractogram (XRD) analysis in Fig. 2, it shows that the residue after leaching was mainly composed of nickel, sulphur and iron phases, what is expected since nickel, which is in the anticorrosion cover layer of magnets, is not influenced by sulphuric acid. This explains the high levels of residue after the leaching batches, meaning that besides the non-leachable REE and other metals, there is the formation of new species, like $\text{FeS}_{2(s)}$.

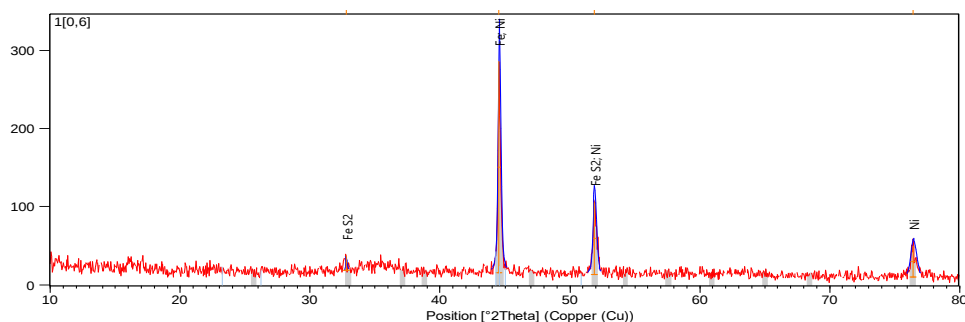


Fig 2. X-ray diffraction of residual material after leaching batch

Leaching efficiency

It is expected that REE and iron react with sulphuric acid resulting in dissociated ionic forms of REE^{3+} and Fe^{2+} , as well as the chemical molecules $\text{REE}_2(\text{SO}_4)_3$ and FeSO_4 in solution, among other species, meaning that no precipitations should occur. Although it contains more proton moles than dilute acid in the same volume, the concentrated sulfuric acid is a little less reactive for REE. Probably this fact is associated to the formation of a protective oxide/sulphate interface between the metal and the acid that slows or inhibits the reaction depending on the stability of the layer [8].

According to Fig. 3, Nd and Pr show higher leaching efficiency than Dy and Tb, due to the fact that Dy and Tb show lower solubilities at room temperature when in the form of sulphates in comparison with Nd and Pr. The compounds $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, respectively show solubilities values of 4.1 and 2.9 g.100 g⁻¹ of water, in contrast with $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ that show solubilities of 7.1 and 12.6 g.100 g⁻¹ of water, respectively [8].

It was observed an increasing in leaching efficiency when the solid/liquid ratio decreases, as well as when the acid concentration increases. However, the effect of the acid concentration was not dominant between solid/liquid ratios 1/20 and 1/40, where the leaching efficiencies are similar among acid concentrations 0.75 and 1.5 mol.L⁻¹. A solid/liquid ratio 1/10 reveals a poor leaching efficiency with exception of higher acid concentration, but doubling the solution amount to 1/20 and reducing the acid concentration to 0.75 mol.L⁻¹, it was possible to obtain almost 100 % of efficiency, which is an optimal arrangement in economic and environmental terms.

The solid/liquid ratio 1:10 was only effective when the acid concentration was higher than 1.5 mol.L⁻¹, which demands high costs for acid anticorrosion equipment. The smaller solid/liquid ratios had satisfactorily high leaching efficiencies when the acid was used at its lowest concentrations, but at this situation the recovery rate would be reduced. In addition, the selectivity of REE towards iron was low, since mostly all the iron was dissolved with sulphuric acid in each batch, meaning that further processes needs to be applied to obtain REE isolated.

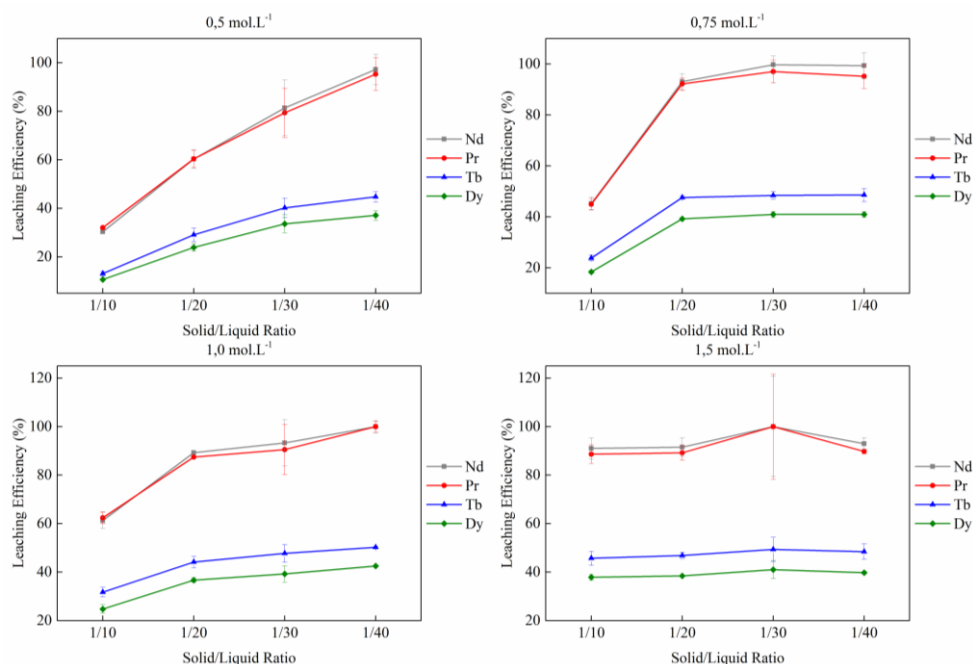


Fig 3. Leaching efficiency vs. sulphuric acid concentration and solid/liquid ratios. Temperature and time were held constant at 25 °C and 15 minutes. The bars represent the error

CONCLUSION

The results showed that the best arrangement considering lower acid concentration and higher solid/liquid ratio are the intermediate. Despite there was a quantity of residual material in all the experiments due to the different metals that compose the NdFeB alloy, since some, like nickel, are less susceptible for reacting with sulfuric acid, Neodymium and Praseodymium were successfully leached. The higher solid/liquid ratios leached only satisfactorily the REE at high concentrations, which is not feasible in industrial terms. However, a slightly lower ratio, 1/20 for example, was effective at lower concentrations, such as 0.75 mol L⁻¹. The XRD analysis did not showed Dysprosium or Terbium although both REE did not reach high leaching efficiencies. This is probably due to their lower content that stayed undissolved and was not detectable by the analysis, since iron was the dominant element. Further work can optimize the process to enhance the efficiencies, mainly for Dysprosium and Terbium, as well as more leaching steps.

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