



Recovery of rare earth elements from small scale consumer scrap magnets

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Abstract

This investigation deals with the recovery of rare earth elements (REE) from consumer scrap. High tech components are often dependent on REE to produce technologies such as magnets, energy saving bulbs or efficient batteries. To reduce the import pressure, it is necessary to develop a sustainable recycling process for Europe.

High performance-magnets are found in small scale applications like computer hard disk drives, actuators and medical device technologies. These magnets are mostly REE-Fe-B based. In total they consist of over 30 % of Neodymium, Praseodymium and Dysprosium. Today the yearly demand of REE oxides for magnets is estimated to be approximately 26.300 tons [1]. In future the demand for such high power magnets will increase, because of an increasing demand for hybrid and electrical vehicles. Due to the fact, that a pyrometallurgical refining of magnet scrap in order to remove more noble elements is not an option, a direct remelting process is not favorable. A high temperature conditioning step offers the chance to oxidize the REE into a leachable, REE rich slag. This phase can then be treated hydrometallurgically to extract the REE. The following separation technology is much easier in comparison to the primary extraction because only four out of all seventeen REE are in solution. This paper will present results of the thermal oxidation step as well as hydrometallurgical extraction experiments, which allow the recovery of REEs.

The full paper will be published soon after the conference in World of Metallurgy-Erzmetall.

1 Theoretical background for the planned recycling process

In comparison to iron, the REE have a more negative oxidation potential. Fig. 1b shows an Ellingham diagram for the single phase system Fe-Nd-O. According to the diagram, it is theoretically possible to very selectively oxidize Nd with oxygen or iron oxide. The oxidation potential, like most chemical properties, is very similar for all REE, i.e. a selective oxidation can be carried out for all REE in the system Fe-REE-O. For a precise process design, the phase diagram for the system Fe-Nd-O (Fig. 1a) shows the wide range of the partial pressure in which Fe and Nd₂O₃ coexist. Thermodynamic studies on the systems Fe-Dy-O and Fe-Pr-O calculate nearly the same



partial pressure ranges for the coexisting phases (Fe, REE₂O₃) [2], [3]. As a first step, a high temperature conditioning step to receive a marketable iron alloy and a REE₂O₃ rich slag phase seems to be theoretically possible.

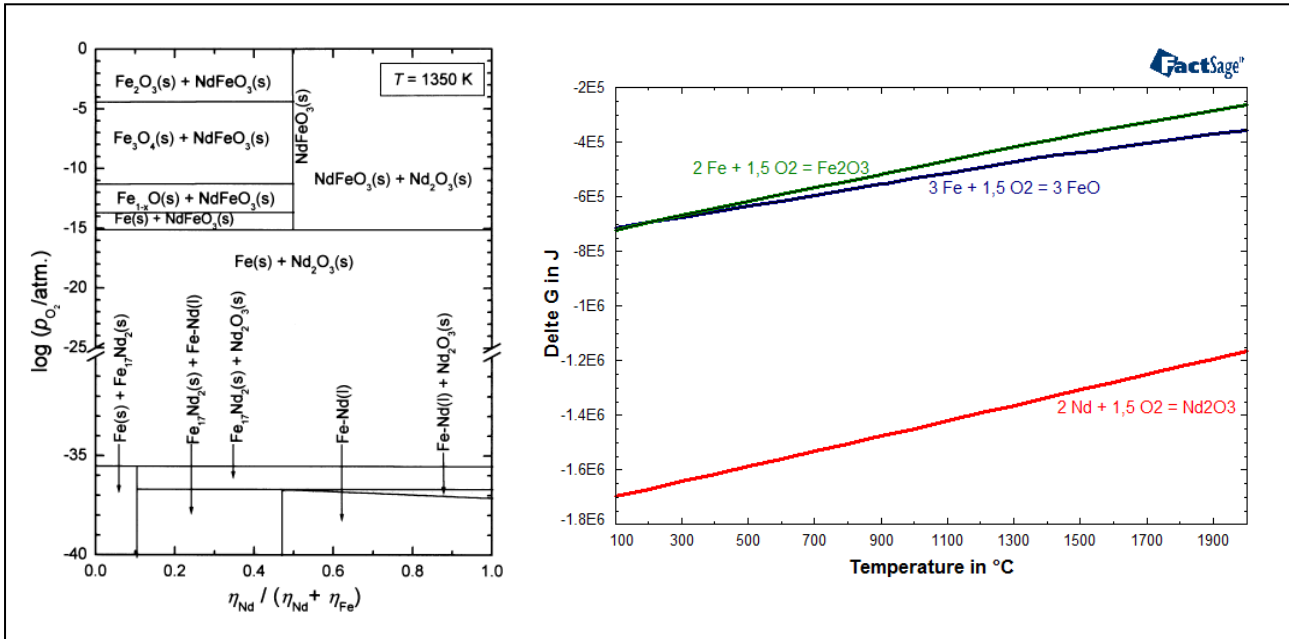


Figure 1: (a) Phase diagram of the Fe-Nd-O system at 1077 °C [4] (b) Ellingham diagram of the Fe-Nd-O system at 100 to 2000 °C (calculated with FactSage 6.3)

To obtain the REE at the required purity, hydrometallurgical processes are the best option today. Therefore, a leaching step to transfer the REE into an aqueous phase is intended. According to the literature, REE are soluble in acidic media like H₂SO₄ or HCl. Since metals like iron are also soluble in these media, it is necessary to previously remove these impurities. The aim is to produce a pure REE solution or concentrate, which can then be further treated by using simplified separation technologies according to the state of the art, e.g. solvent extraction (SX). Fig. 2 demonstrates the simplified process flow sheet. The dotted line demonstrates the case of direct leaching of magnet scrap, which is also a research aspect.

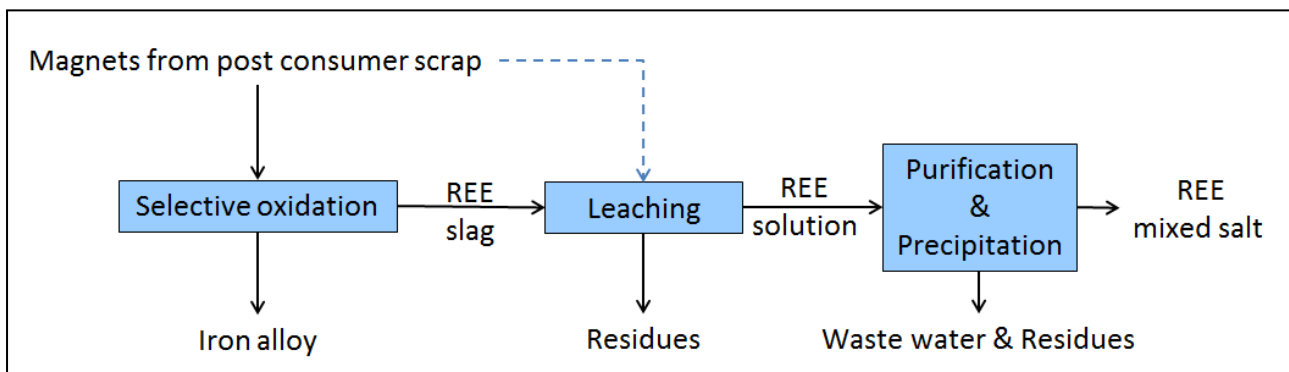


Figure 2: Planned process flow sheet

2 Experiments

For the experiments magnets from used hard disc drives were used. Fig. 3 shows a hard disc drive (HDD) with the magnets marked (a) and different magnets on the right side (b). The magnets strongly stick to each other, as can be seen in the figure. In the HDD the permanent magnets serve to position the read/write head across the spinning disk.



Figure 3: Hard disc drive with magnets marked (a); magnets of different hard disc drives sticking together (b)

The elemental analysis of the scrap is shown in Tab. 1. The element Pr is a substitution metal for Nd. Dy increases the temperature stability, whereas Tb serves to increase the coercivity. Further alloying elements are Cu and Co. They also improve the properties of the magnets.

Table 1: Elemental analysis of the used decoated and demagnetized magnet scrap

Fe	Nd	B	Pr	Dy	Co	Cu	Tb	Al
weight percentage [wt.-%]								
63,67	23,5	0,94	2,26	6,14	2,98	0,10	0,14	0,26

2.1 Pyrometallurgy

The magnet scrap (Table 1) is melted in a vacuum induction furnace (VIM) with an inert gas atmosphere to avoid the influence of air oxygen. The furnace atmosphere therefore is adjusted to a partial pressure of 700 mbar Ar. The oxygen needed to selectively oxidize REEs is calculated on the basis of the given composition. The addition can take place in different ways, either by adding oxygen in gaseous form mixed with argon or by adding iron oxide. Using the latter, the iron oxide will be reduced while REEs will be oxidized with the oxygen present. The addition can be carried



out either by mixing both components before inserting them into the furnace or by feeding the iron oxide to the molten magnet scrap. First experiments show strongly varying results, which will be discussed qualitatively.

Pre-tests have shown a fluctuation of the melting temperature in such an extent that melting of the magnet scrap partially has not been possible up to temperatures of 1 700 °C. Therefore, the process temperature has not been fixed during the test planning. One reason for this behavior can be the generation of an oxide layer on the surface of the magnet scrap. Hence, during the experiments the material is heated until a molten phase is visible or an obvious reaction occurs. Reactions with iron oxide prove to run exothermically, which can be seen in a marked rise of temperature. First chemical analysis results indicate that the neodymium content in the metal fraction can be reduced down to approximately 15 wt.-%, whereas iron is enriched. Fig. 4 shows the REM/EDX analysis of a sample after being selectively oxidized by iron oxide. The white spots consist of neodymium oxide, while the black phase contains almost exclusively iron. The grey phase constitutes unreacted magnet material.

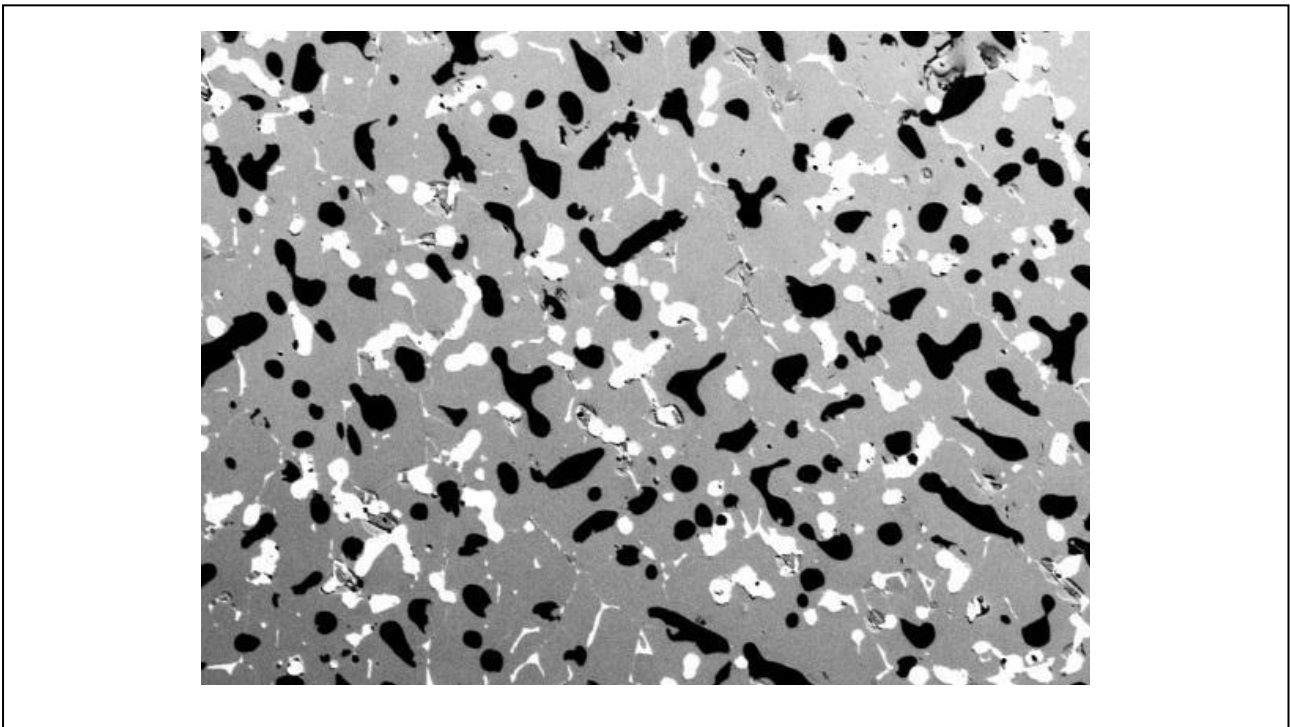


Figure 4: REM/EDX analysis of selectively oxidized magnet scrap

A separation between the metal and the slag phase has not been achieved so far, as solidification of the material occurs directly after the reaction is finished. The aim of following works is to secure a separation of metal and slag phases for example by providing an iron melt or adding slag forming components. The obtained slag can then be further treated hydrometallurgically.

2.2 Hydrometallurgy

Direct leaching experiments of magnet scrap on a laboratory scale show that the dissolution of the REE in sulfuric and hydrochloric acid is possible. During leaching, significant exothermic reactions and high acid consumptions can be observed due to the oxidation reactions of the metals. Different acid concentrations have been investigated for optimal REE leaching results. At a solid-liquid ratio of the concentrate to the leaching agent of 1:10, it is possible to dissolve the whole REE content with a 2 mol/L H₂SO₄ or a 3 mol/L HCl. Higher concentration of H₂SO₄ lead to REE yield losses. Lower acid concentrations lead to incomplete dissolutions because of the insufficient supply of H⁺-Ions that is needed for the oxidation reaction. In comparison to REE, high quantities of Fe dissolve as well. The metal yields of Fe, Dy, Nd, Pr and pH-values after three hour leaching time are shown in Fig. 5.

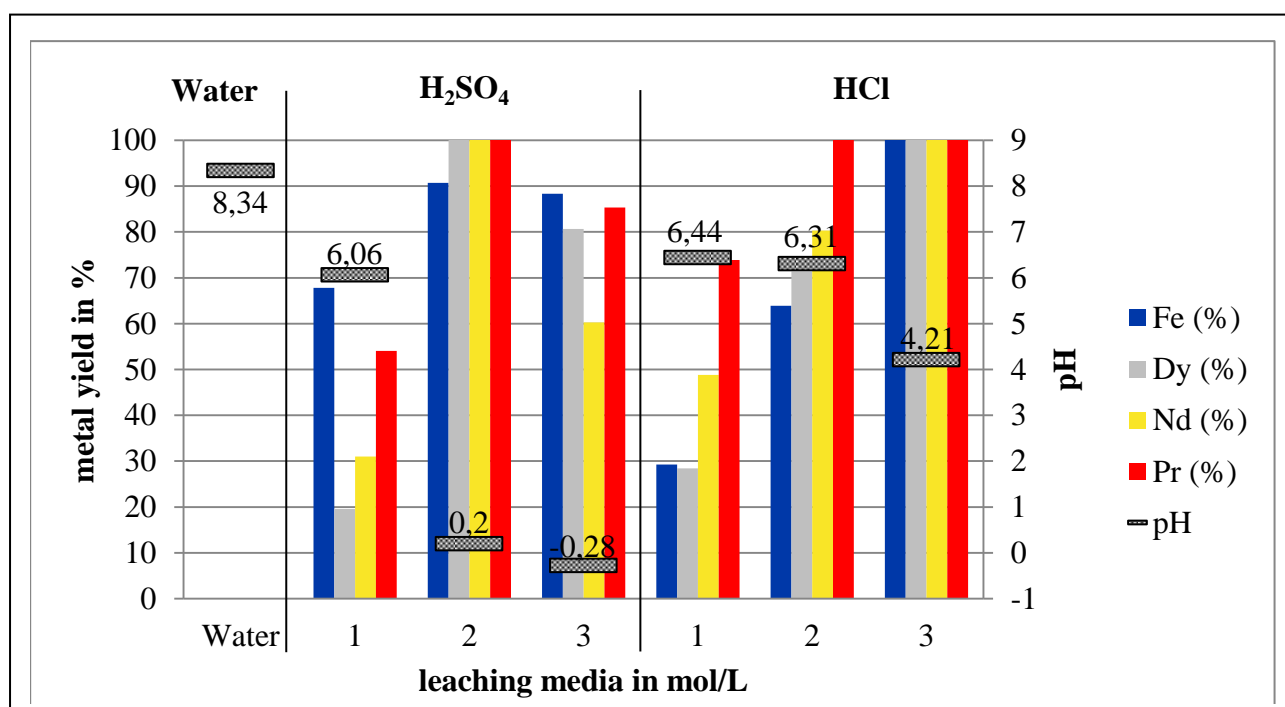


Figure 5: Metal yield of direct leaching experiments with different leaching media and concentrations

To separate impurities like iron from REE after leaching, a precipitation process with a pH adjustment by using a NaOH solution has been investigated. Results of ICP and XRF analyses are presented in Tab. 2. These results demonstrate that it is possible to precipitate a more than 95 wt.-% pure REE concentrate at pH 2 to 3, but only with a REE yield of 30 wt.-%. The rest of the elements remain in solution. Further investigations will focus on increasing the REE yield. Possibilities therefore are an optimization of the process parameters like temperature control or the use of additional precipitation agents like ethanol [5], [6].

Table 2: Results of ICP and XRF analyses of the pH precipitation process residues with the solution from the experiments with 2 mol/L H₂SO₄ (s/l ratio 1:10)



pH	REE (purity) in wt.-%	REE (yield) in wt.-%	contaminations in wt.-%	
			Fe	rest
2	98,47	29,82	0,31	1,23
3	97,23	32,23	1,49	1,28
6	83,42	28,01	10,69	5,89
7	86,12	59,55	9,44	4,44

4 Summary

The recent investigation shows that a selective oxidation of the present magnet scrap is possible. Further steps will deal with the optimization of process parameters to form a separable slag phase. Hydrometallurgical investigations show that Fe and REE are selectively separable but with a non-satisfying REE metal yield, which has to be increased hence. Thus, process optimization and further separation processes will be tested.

References

- [1] Goonan, T.G. (2011): Rare Earth Elements – End Use and Recyclability, U.S. Geological Survey Scientific Investigations Report 2011-5094, p. 15
- [2] Parida, S.C; Jacob, K.T; Venugopal, V. (2002): System Dy-Fe-O: thermodynamic properties of ternary oxides using Calvet calorimetry and solid-state, Solid State Sciences, 4: pp. 1245-1255, India
- [3] Tretyakov, Y.D; Sorokin, V.V; Erastova, A.P (1976): Phase Equilibria and Thermodynamics of Coexisting Phases in Rare-Earth-Element-Iron-Oxygen Systems, 18: pp. 263-269, U.S.S.R.
- [4] Parida, S.C. et al. (2002): Thermodynamic Studies on NdFeO₃(s); Journal of Solid State Chemistry, 164: pp. 34-41, Fig. 5; India
- [5] Sato, N.; Wei, Y.; Nanjo, M.; Tokuda, M. (1997): Recovery of Samarium and Neodymium from Rare Earth Magnet Scraps by Fractional Crystallization_ Fundamental study on the recycling of rare earth magnet (2nd Report), Journal of the Mining and Materials Processing Institute of Japan (MMIJ), 113, No. 12: pp. 1082-1086, Japan
- [6] Wei, Y.; Sato, N.; Nanjo, M. (1989): The Solubility of Sm₂(SO₄)₃ and Nd₂(SO₄)₃ in Sulfate Solutions_ Fundamental study on the recycling of rare earth magnet, Journal of the Mining and Materials Processing Institute of Japan (MMIJ), 105, No. 12: pp. 965-970, Japan