POSSIBILITIES OF NEODYMIUM RECOVERY FROM USED Nd-Fe-B MAGNETS

Mariola SATERNUS

Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, Katowice, Poland, EU
mariola.saternus@polsl.pl

Abstract

Today neodymium plays a very important role as a main component of Nd-Fe-B magnets, which are indispensable for clean energy application. Therefore, the short information about neodymium and its production in the last years are presented. The article briefly gives also the short characteristics of Nd-Fe-B magnets, as well as their appliances and methods of obtaining. For these magnets, the amount of production was compared in 1987-2016, and the main producers in 2015 are indicated. Perspectives for the production of Nd-Fe-B magnets in the following years are shown including the declining resources of rare earth metals and the simultaneous increase of their demand and taking into account the dominant producer and monopoly of China. The review of available methods of recycling of Nd-Fe-B magnets is presented focusing on hydrometallurgical and pyrometallurgical methods.

Keywords: Neodymium, Nd-Fe-B magnets, methods of Nd-Fe-B magnets recycling

1. INTRODUCTION

Neodymium belongs to the rare earth metals, which play significant role in today`s life (they are used for production of smart phones, digital camera, computer hard disks, fluorescent and light emitting diode lights, flat screen TV, computer monitors) [1]. **Figure 1** shows the percentage world demand by application for rare earth metals in 2015. Neodymium is an important element for such application like permanent magnet, Nd-alloy, battery, rare earth catalyst, automotive catalyst and semiconductor [2,3]. During the last 100 years it is observed the constant development of permanent magnets, from ferrites, Alnico, Sm-Co to Nd-Fe-B magnets [4, 5]. It is caused mainly due to their better properties and availability. Nd-Fe-B permanent magnets found application mainly in wind-energy generation, heavy/light green-hybrid vehicle, electrical storage device, electronics storage devices, notepad/laptop/computer hard drive, mobile telephones, medical devices, scientific instruments [6, 7]. **Table 1** shows the requirements for neodymium oxide in such application [8].

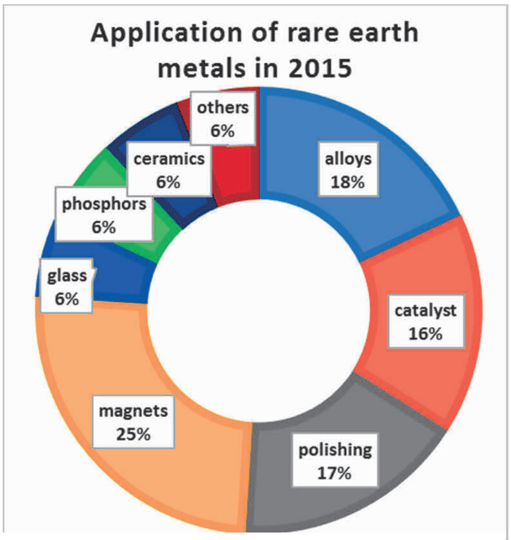

Figure 1 Percentage application of rare earth metals in 2015 [1]

Nd-Fe-B magnets have a higher remanence, a much higher magnetic coercivity and energy density (maximum energy product - BH_{max}), but often a lower Curie temperature compared to other magnets. Neodymium is often used with terbium and dysprosium to retain magnetic properties at high temperatures. Nd-Fe-B permanent magnets have different life cycles, depending on the application: from 2-3 years in consumer electronics to 20-30 years in wind turbines [9].

The production of Nd-Fe-B magnets has been constantly increasing (see **Table 2** [10, 11]). The global production of Nd-Fe-B magnets will grow by 4-5% per year. Thus, in 2020, it is estimated that the production size will increase to 120,000 tons. However, in the years 2021-2026, the estimated production of Nd-Fe-B magnets will remain stable, and even a slight downward trend is expected (up to -1% per year) [12], which will be caused by problems with neodymium availability and its high prices (see **Table 3** [13]). These estimations, however, may differ from reality, including due to the price inflation and the rare earth metals market.

Table 1 Demand for neodymium oxide for different application in 2010 and 2015 in tons [8]

Application	2010	2015	Application	2010	2015
Motors, industrial general auto	7122	10912	Sensors	982	720
HDD, CD, DVD	4117	7101	Hysteresis clutch	879	687
Electric bicycles	2549	3570	Generators	769	400
transducers, loudspeakers	2609	3118	Energy storage systems	670	1091
Unidentified and other	1995	2878	Wind power generators	583	4402
Magnetic separation	1466	1558	Air conditioning compressors	559	1091
MRI	1228	720	Hybrid and electric traction drive	214	2308
Torque-coupled drivers	1117	1091	Gauges, drives, brakes, etc.	2186	3113
Total	29046	44761			

Table 2 Production of Nd-Fe-B magnets in tons in years 1987-2016 [7, 10, 11]

Year	1987	2007	2015	2016
Nd-Fe-B production in tons	350	63,000	78,000	90,000

Table 3 Prices of neodymium oxides in tons in 2013-2017 [13]

Year	2013	2014	2015	2016	2017
Price, dollars per kg	65-70	56-60	39-42	38-40	56-59

In 2012, China produced about 80% of magnets, while in 2015, this value increased to 83% (see **Figure 2**). Since 1990 China has played a dominant role in the extraction and production of rare earth metals. The production of rare earth metal oxides in 2016 was around 126 000 tones. Currently, the main producers are: China (84%), Australia (11%) and Russia (2%) [14]. Thus, it is understandable that China is the main exporter of rare earth metals and also Nd-Fe-B magnets. Therefore, the forecast of the Nd-Fe-B magnets production must also be taken into account the difficulties in rare earth metals mining, environmental impact, mining dominance of China, fast-growing prices and huge demand [12]. It should be also mentioned that there are different methods of Nd-Fe-B magnets production: Nd-Fe-B alloys can be manufactured into resin bonded magnets (containing 10% epoxy resin) or into fully dense sintered magnets. Considering all above, it is obvious that in the nearest future the more and more focus will be put on the recovery rare earth metals such as neodymium and dysprosium from used Nd-Fe-B magnets.

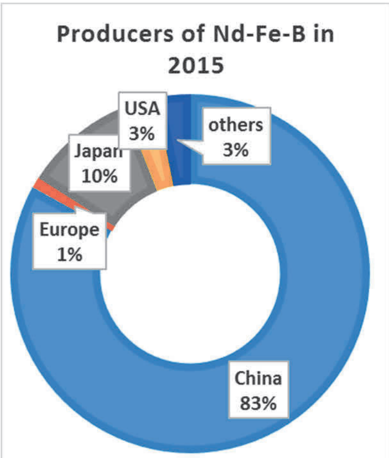

Figure 2 Main producers of Nd-Fe-B magnets in 2015 [7]

2. METHODS OF NEODYMIUM RECOVERY FROM USED Nd-Fe-B MAGNETS

At present the recovery of metals, especially critical and precious ones, from different waste materials become the necessity [14-16]. It eliminates many dangerous pollution generated during the production of primary metals in ore mining, leaching, solvent extraction. Recycling avoids also unwanted byproducts; however the recycling process is sometimes also not so easy as it may seem. Different recycling methods of Nd-Fe-B magnets have been carried out during the last 20 years [17-27]. Such magnets apart from iron and rare earth elements (REE) contain also a lot of additional materials such as organics (adhesive, oil) or coatings (especially nickel). The recycling methods of Nd-Fe-B magnets can be divided taking into account the final product (see **Figure 3**):

- waste-to-REE approaches, which can be mixture of rare earth metals or individual metal,
- waste-to-alloy approaches,
- direct reuse,
- magnet-to-magnet approach.

Considering different waste magnets it can be divided into: swarf originating from magnet manufacturing, small magnets in End-of-Life consumer products and large magnets in hybrid and electric vehicles or wind turbines [17]. Direct reuse can be used only for the large magnets. In all other cases, the pyrometallurgical and hydrometallurgical methods or gas-phase extraction or hydrogen decrepitation or others have to be used for further processing.

Magnet-to magnet approach allows for the ten or more metals present in sintered Nd-Fe-B magnets to be recycled simultaneously; it has a lot of advantages such as: simplicity, lower cost when compared to traditional recycling methods. It also allows for the development of a closed-loop recycling system for rare earth metals magnets, therefore reducing the emissions to the atmosphere. These methods also have good results on a commercial scale, additionally with improved magnetic performance (see **Table 4**).

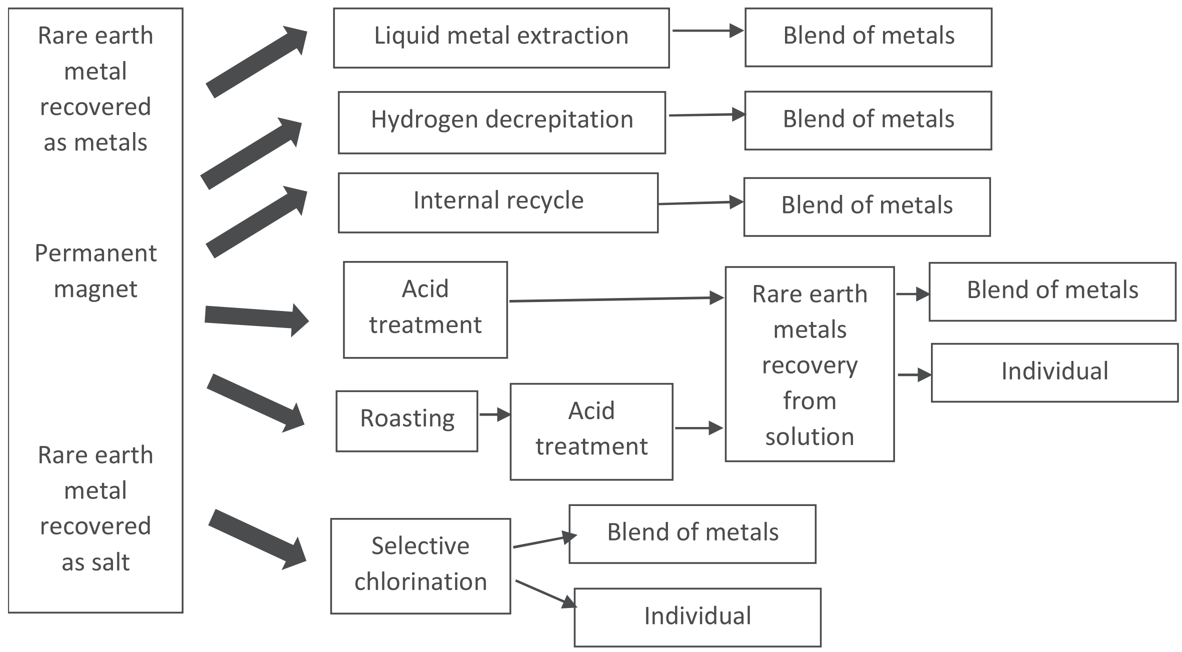

Figure 3 Diagram of various process options to recycle rare earth metals from permanent magnets [18]

2.1. Hydrometallurgical methods

During hydrometallurgical methods the waste magnets are treated by strong acids or basic solutions in order to selectively dissolve metals and then recovery of them using such processes as leaching, solvent extraction, ion exchange and precipitations. The first step includes dissolution of magnets applying different typical inorganics acids (see **Table 5**). However this process is non-selective, the all metals are present in concentrated leach solutions (40-60 g/L REE), which contain also a large amount of iron (100-120 g/L Fe), and then is available for metal recovery. For recovery neodymium from such solution and also other rare earth metals different methods are used; for example selective precipitation by double salt, fluoric acid or oxalic acid, followed by iron removal, or solvent extraction of iron, followed by solvent extraction for Nd or Dy. **Figure 4** shows exemplary route of hydrometallurgical treatment of waste Nd-Fe-B magnet.

Table 4 Comparison of properties and chemical composition of primary production of Nd-Fe-B magnets and Nd-Fe-B magnet-to magnet recycling [19]

Properties					
Magnet	Magnetic coercivity, *bHc* (kA/m)	Intrinsic coercivity, *iHc* (kA/m)	Energy density, BH_{max} (J/m^3)	Operating temperature, *T* (°C)	Remanence, *Br* (T)
Primary production	915	1512	270.5	180	1.2
Recycled magnets	1002	>1592	323.9	180	1.3
Chemical composition, wt. %					
Magnet	Fe	Nd	Dy	Pr	B
Primary production	66.88	18.00	6.15	4.60	1.02
Recycled magnets	64.57	21.63	3.96	6.43	0.93

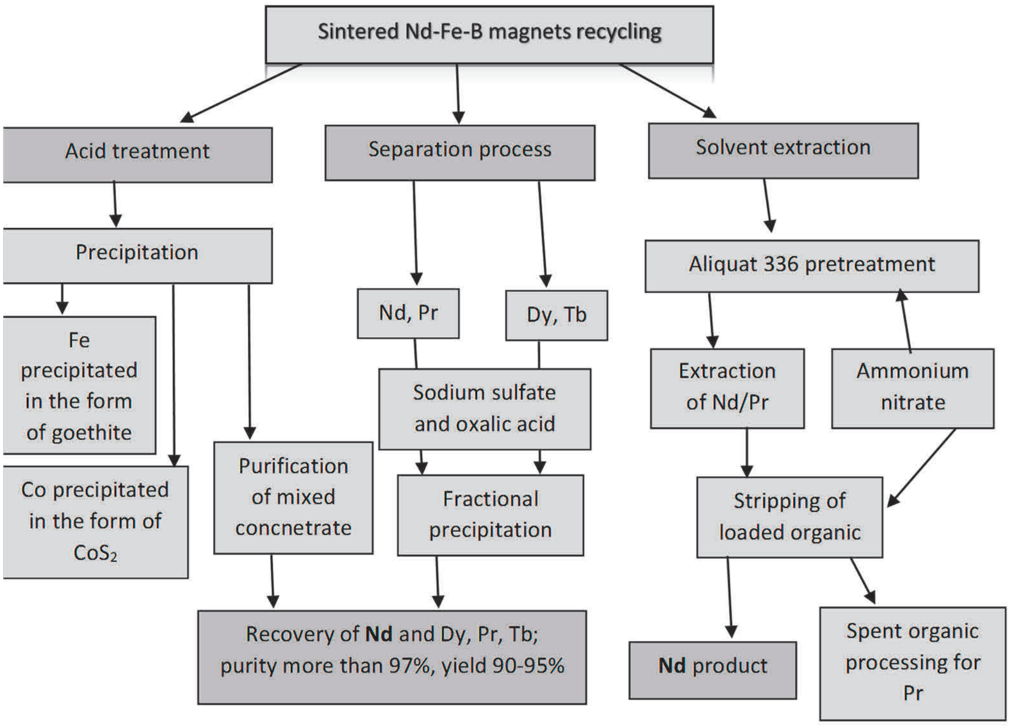

Figure 4 Scheme of possible hydrometallurgical recovery of neodymium from permanent magnets [20-23]

2.2. Pyrometallurgical methods

The pyrometallurgical methods have a bigger environmental impact than hydrometallurgical methods due to high material losses and electricity consumption; however still pyrometallurgical methods are treated as the alternative. Such methods enable to remelt the REE alloys or extract them from transition metals in the metallic state or to recycle rare earth metals of partly oxidized magnet alloys (respectively direct melting, liquid metal extraction, electroslag refining, glass-slag method - **Table 6** presents the short characteristic of the mentioned methods).

Table 5 Leaching process of permanent magnets in different acids [14, 24-27]

Applying medium	Characteristics
Ammonium chloride	chlorination with NH_4Cl; Nd-Fe-B primary phase was selectively converted to $NdCl_3$ together with α-Fe and Fe-B solid residues by chlorinating at 573 K for 3 h.
Hydrochloric acid and oxalic acid	Ni-coated Nd-Fe-B magnets are treated with 3 M HCl and 0.2 N oxalic acid solutions, h=3h, T = 283 K; as a results 99% of Nd is recovered as neodymium oxalate.
Hydrochloric acid	Leaching > 80% of Nd and Dy, roasted Nd-Fe-B magnets were selectively leached by 0.02 mol/L HCl solution in an autoclave at 455 K with the ultrasound applying.
Nitric acid	Nd-Fe-B magnet scraps was dissolved in nitric acid, then HF was added, which results in the formation of neodymium-iron fluoride double salt; then this salt was dried and calciothermically reduced to the metallic state.
Sulfuric acid	1 kg of Nd-Fe-B magnet scrap was dissolved in 10 l of 2M H_2SO_4; pH is low (0.2) to protect $Fe(OH)_3$ precipitation, then pH of the leach solution increased to 1.5 at which double salt of Nd is formed, then this salt is leached in HF to form NdF_3.

Table 6 Short characteristics of pyrometallurgical methods used for recycling permanent magnets [14, 17]

Methods	Characteristics
Electroslag refining	Applied for clean and big scrap, remelted as electrode or melted as an addition to liquid bath.
Direct melting	Scrap is decarbonized by heating, then heated in the atmosphere of H_2 to reduce Fe_2O_3, as a result oxides of rare earth metals are reduced by calcium.
Glass slag method	Nd-Fe-B scrap is melted with liquid B_2O_3, which selectively dissolves REE and show tendency to supercool to a glass; glass slag is dissolved in H_2SO_4, followed by selective precipitation.
Liquid metal extraction	For wide variety of scrap, producing very clean material; consist of selective dissolution of REE by a liquid alloy system, the REE and transition metals distribute themselves between two immiscible liquid metal phases.
Gas-phase extraction	To recover metals by chlorination and carbochlorination (Cl_2 and CO in N_2 stream), metals are transformed into volatile chloride and separated based on differences in volatility.

3. CONCLUSIONS

Taking into account the development of new technologies for which growing demand for the rare earth metals is observed, in the nearest future the production of the rare earth metals, especially neodymium should be increasing. It is possible to open new mines, however it is associated with high capital cost. Therefore, recycling of materials, containing such metals is highly desirable, and even not only economically but also environmentally more appreciated than exploitation of new mineral deposit. There are various recycling approaches for the recovery neodymium from Nd-Fe-B magnets, i.e. hydrometallurgical and pyrometallurgical methods. Both has some advantages and disadvantages. Today the more and more popular becomes magnet-to-magnet route using hydrogen decrepitation. This method is more favorable to environment than mentioned earlier methods and additionally more simple and cheapest than traditional recycling methods. Because up to 2011 less than 1% of rare earth metals were actually recycled [17]; thus improvement in recycling is necessity and should be drastically improved in the nearest future.

ACKNOWLEDGEMENTS

Work was supported by Polish Ministry of Science and Higher Education under BK221/RM0/2018.

REFERENCES

[1] HUMPHRIES, M. *Rare Earth Elements: The global supply chain*. Congressional Research Service. 2013.

[2] SATERNUS, M., WILLNER, J., FORNALCZYK, A. and ŚWIĘCICKA, Z. Available methods used for recovery of the rare earth metals from spent fluorescent lamp - review. In *METAL 2017: 27th International Conference on Metallurgy and Materials*. Ostrava: TANGER, 2017, pp. 1637-1643.

[3] DU, X. and GRAEDEL, T. Global rare earth in-use stocks in NdFeB permanent magnets. *Journal of Industrial Ecol*ogy. 2011. vol. 15, pp. 836-843.

[4] DUBUIS, J.-M. *Magnetic mechanism, magnet process, materials and evolutions*. Valeo Materials, 2012.

[5] SATERNUS, M. and ŁABUSZEWSKI, M. Comparison between NdFeB magnets and other permanent magnets - production and perspectives, *Hutnik*. 2018. vol. 3, pp. 68-74.

[6] PEIRÓ, L.T., MENDEZ, G.V. and AYRES, R.U. Material flow analysis of scarce metals: sources, functions, end-uses and aspects for future supply. *Environmental Science & Technol*ogy. 2013. vol. 47, pp. 2939-2947.

[7] BENECKI, W.T. *More than you ever wanted to know about the permanent magnet industry*. Magnetics, Orlando, USA, 2017.

[8] CONSTANTINIDES, S. *The demand for rare earth materials in permanent magnets*. COM2012, USA, 2012.

[9] YONGXIANG, Y., WALTON A., SHERIDAN R., GU K., GAUß R., GUTFLEISCH O., BUCHERT K., STEENARI B.M., VAN GERVEN T., JONES P.T. and BINNEMAN K. REE Recovery from End-of-Life NdFeB permanent magnet scrap: A critical review. *Journal of Sustainable Metal*lurgy. 2017. vol. 3, pp. 122-149.

[10] STRNAT, K.J. Modern permanent magnets for applications in electro-technology. In *Proceedings of the IEEE*. 1990. vol. 78, pp. 923-946.

[11] BENECKI, W.T. A producer`s and buyer`s perspective: the permanent magnet outlook. In *Magnetics Conference*, Denver, USA, 2008.

[12] http://www.pm-review.com/rare-earths-market-outlook-2026/, 28.01.2018.

[13] GAMBOGI, J. *US Geological Survey*. Mineral Commodity Summaries, January 2018, pp. 132-133.

[14] SATERNUS, M., WILLNER, J., FORNALCZYK, A. and LISIŃSKA, M. Rare earth metals - receiving and recovery from waste materials. *Przemysł Chemiczny*. 2017. vol. 96, pp. 1595-1599.

[15] SATERNUS, M., FORNALCZYK, A., WILLNER, J. and KANIA, H. Methods for silver recovery from by-products and spent materials. *Przemysł Chemiczny*. 2016. vol. 95, pp. 78-83.

[16] WILLNER, J. and FORNALCZYK, A. Electronic scrap as a source of precious metals, *Przemysł Chemiczny*. 2011. vol. 90, pp. 1000-1005.

[17] BINNEMANS, K., JONES, P.T., BLANPAIN, B., VAN GERVEN, T., YANG, Y., WALTON, A. and BUCHERT, M. Recycling of rare earths: a critical review. *Journal of Cleaner Production*. 2013. vol. 51, pp.1-22.

[18] FERRON, C.J. and HENRY, P. A review of the recycling of rare earth metals. In *COM 2013, MS&T*, 2013, pp. 517-531.

[19] JIN, H., AFIUNY, P., MCINTYRE, T., YIH, Y. and SUTHERLAND, J.W. Comparative life cycle assessment of NdFeB magnets: virgin production versus magnet-to-magnet recycling. *Procedia CIRP*. 2016. vol. 48, pp. 45-50.

[20] YOON, H.S., KIM, C.J., K.W., KIM, S.D., LEE, J.Y. and KUMAR, J.R. Solvent extraction, separation and recovery of dysprosium (Dy) and neodymium (Nd) from aqueous solutions: Waste recycling strategies for permanent magnet processing. *Hydrometallurgy*. 2016. vol. 165, pp. 27-43.

[21] YOON, H.S., KIM, C.J., CHUNG, K.W., LEE, S.J., JOE, A.R., SHIN, Y.H., LEE, S.I., YOO, S.J. and KIM, J.G. Leaching kinetics of neodymium in sulfuric acid from E-scrap of NdFeB permanent magnet. *Korean Journal of Chemical Engineering*. 2014. vol. 31, pp. 706-711.

[22] ZAKOTNIK, M., HARRIS, I.R. and WILLIAMS, A.J. Possible methods of recycling NdFeB-type sintered magnets using the HD/degassing process. *Journal of Alloys Compounds*. 2008. vol. 450, pp. 525-531.

[23] ELWERT T., GOLDMANN D., SCHMIDT F. and STOLLMAIER R. Hydrometallurgical recycling of sintered NdFeB magnets. *World of Metallurgy-Erzmetall*. 2013. vol. 66, pp. 209-219.

[24] JHA, M.K, KUMARI, A., PANDA, R., KUMAR, J.A., YOO, K. and LEE, J.Y. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy*. 2016. vol. 165, pp. 2-26.

[25] ITOH, M., MIURA, K. and MACHIDA, K. Novel rare earth recovery process on Nd-Fe-B magnet scrap by selective chlorination using NH_4Cl. *Journal of Alloys Compounds*. 2009. vol. 477, pp. 484-487.

[26] ITAKURA, T., SASAI, R. and ITOH, H. Resource recovery from Nd-Fe-B sintered magnet by hydrothermal treatment. *Journal of Alloys Compounds*. 2006. vol. 408, pp. 1382-1385.

[27] KOYAMA, K., KITAJIMA, A. and TANAKA, M. Selective leaching of rare-earth elements from an Nd-Fe-B magnet. *Kidorui*. 2009. vol. 54, pp. 36-37.