When materials become critical : lessons from the 2010 rare earth crisis

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Life cycle inventory of the production of rare earths and the subsequent production of NdFeB rare earth permanent magnets

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3.1 Introduction

In the past years the environmental damage caused by the production of rare earth elements (REEs) has received substantial media coverage. The use of REEs in sustainable energy technologies such as wind turbines and electric vehicles has given rise to newspaper articles with titles like 'clean energy's dirty little secret'.[1] These articles describe the appalling conditions under which rare earths are produced. Indeed, a quick search on the Internet will yield dozens of pictures of huge tracts of lands devastated by toxic wastewater, primitive metallurgical workshops and Chinese mine workers covered in radioactive mud.

These detrimental environmental effects of REE production are the official reason why the Chinese government has clamped down on its domestic production, introducing export quotas and forcing many of the smaller production facilities to close. Because China currently wields a near-monopoly over rare earth production (50% of worldwide mineral reserves and 86% market share),[2] this caused great upset in the rare earth market.[3] Numerous studies have pointed to REEs as being critically scarce materials,[4,5] especially in the context of a transition towards a global low-carbon energy system.[6] Recent publications have also focused on how global trade flows of REEs influence scarcity[7] and the possibility of recovering REEs from the bottom ash of municipal solid waste incinerators.[8]

The difficulties encountered in scaling up REE production outside of China, combined with the sharp increase in demand of technologies depending on these rare earth elements and increasingly tighter Chinese export restrictions led to a short-lived scarcity crisis in 2011, where, in the timespan of a few months, the price of certain REEs jumped more than tenfold. During this period numerous industrial and academic initiatives to recycle REEs were announced.[9-12]

Although recycling could help to alleviate scarcity of REEs,[13] it is not immediately apparent that it would also carry a significantly lower environmental burden. REEs are notoriously difficult to process,[14] and, depending on the choice of recycling technology, many of the most energy intensive processing steps would have to be performed on recycled material as well. Nevertheless, the environmental damage caused by primary production of REEs has not been a subject of more than cursory scientific investigation.[15,16] To our knowledge, the environmental impact of REE recycling is not discussed in scientific literature.

In our research we set out to quantify the environmental impact of producing 1 kg of neodymium magnets using virgin material, compared with producing 1 kg of neodymium magnets from recycled material. Magnets are the single largest application of rare earths, taking up 21% of the total rare earth production by volume and generating 37% of the total value of the rare earth market.[17] Although there are two types of rare earth permanent magnets (neodymium-iron-boron and samarium-cobalt), neodymium magnets are more powerful, resulting in the fact that samarium cobalt magnets play only a minor role in the market.[18]

3.2 Method

We used life cycle assessment (LCA) methodology to compare the environmental impact of producing 1 kg of neodymium (NdFeB) permanent magnets in China with 1 kg of equivalent magnets from recycled sources. We assumed these to be used for voice coil motors, as found in computer hard drives (HDDs), and weigh 10-20 grams.[19] The foreground processes covered the entire production chain of NdFeB magnets, from mining to the production of the magnets, but not the incorporation of these magnets into the final products. Capital goods were assumed to be of negligible impact, and therefore not included in the foreground processes.

We created the Life-Cycle Inventory (LCI) using CMLCA software, version 5.2 (www.cmlca.eu), combined with the ecoinvent 2.2 database (www.ecoinvent.ch) for the background processes. The impact assessment was done according to Guinée.[20]

The foreground processes are based on literature sources and interviews with experts.

One of the difficulties encountered in constructing a representative LCA is data availability. Many recent English language publications are based on process descriptions that are over twenty years old.[14,21] Although more recent techniques used for the production of rare earth elements are well described in Chinese literature, associated emissions and environmental damage are usually only referred to in anecdotal manner. Furthermore, there is significant uncertainty surrounding the state of technology in Chinese REE processes. In order to deal with these sources of uncertainty we constructed three scenarios. The baseline scenario is what we think is a realistic representation of the current state of the industry. When literature descriptions are open for interpretation we lean towards more advanced processing technologies, because of the strides China has made recently in consolidating the industry and closing old processing facilities.[22] Of the two alternative scenarios, high-tech represents the best available technology case while low-tech represents the more polluting processing technologies, the main differentiation being efficiency and emission controls.

The exact composition of NdFeB magnets varies by application. Elements such as dysprosium and holmium are added when the magnet is required to operate in a high temperature environment. Usually a mixture of neodymium (Nd) and praseodymium (Pr) is used as an alloying agent, instead of pure neodymium. Because Nd and Pr differ only one atomic number an extra solvent extraction step is needed to separate them. Therefore, in all but the most high-end application neodymium and praseodymium are not separated. However, because this has little influence on the production processes described here, as praseodymium will for all intents and purposes have the same properties as neodymium, we will refer to NdPr alloy as Nd. NdFeB magnets used in HDDs generally do not contain dysprosium, because HDDs are not designed to operate in high-temperature environments. Dysprosium use is not considered in our study.

Finally, it is important to note that during the different processing steps the chemical form of rare earth changes considerably. For instance, the mineral form bastnäsite is $RECO_3F$. During the sulphuric acid leaching step this is transformed to $RE_2(SO_4)_3$ and then to $RECl_3$. However, for sake of clarity we often refer to all of these different forms of rare earths as rare earth *oxides* (REO). This is also how these steps are referred to in the literature.

3.3 Life cycle inventory

In this section we discuss the life cycle inventory (LCI) in detail. Each subsection discusses one process of the LCA. Section 3.3.1 describes the conventional method of rare earths in China from mineral sources. Section 3.3.2 describes the production process used to transform neodymium oxide into an NdFeB magnet. Finally, section 3.3.3 describes two alternative recycling processes that could be used. Detailed information on the LCI, assumptions and allocation choices can be found in the supporting information.

3.3.1 Chinese rare earth production route

In this section we describe the processes used for the production of rare earth oxides (REO), based on the ore composition as found in the Bayan-Obo mine in Inner-Mongolia, China.

Ore removal from mine

Du and Greadel[23] estimate that two-thirds of the total Chinese REO production originates from the Bayan-Obo mine, making it the world's single largest source of REE's. Ore is recovered from the open pit mine using conventional surface mining techniques such as drilling and blasting. The mine contains 750 million tons of ore at 4.1% REO.[24]

Historically Bayan Obo was mined primarily for its iron contents. Rare earths were discarded with the tailings. With REO prices increasing and the Fe content of the ore decreasing this situation has changed. Even though the iron content of Bayan Obo ore is currently only at 30-35%, it is still being commercially recovered.[25]

Beneficiation of REO containing ore

The ore is transported 150 km from the Bayan-Obo mine to the city of Baotou, for further processing.[25] After transportation the rare earth containing minerals, mainly bastnäsite and monazite, are separated from the iron ore and other less valuable minerals. The ore also contains 0.04% ThO_2, which exposes workers to radioactive dust.[25]

First the ore is crushed and grinded to the required particle size, where 90% of the particles are smaller than 74 micrometre. This causes the grains of various minerals to be separated from each other. Magnetic separation is used to remove the iron bearing minerals, while other minerals are removed using a combination of froth flotation and table separation.[18] Table separation utilizes the difference in specific gravity of the various minerals. Froth floatation is a somewhat more complicated process where various chemicals are added to a mixture of finely grinded ore and water. Air is bubbled through the mixture. Certain minerals will attach to the bubbles and float to the surface. The resulting froth is then mechanically removed.

Several chemicals are needed for an efficient floatation process. Frothers are used to produce froth with the required properties, such as being strong enough to support the weight of the minerals, but not so strong as to be detrimental to further processing. Typically alcohols, pine oil or low molecular weight polypropylene glycols are used. Collector chemicals such as fatty acids give certain minerals hydrophobic properties and cause the mineral particle to be more likely to stick to an air bubble. Depressant chemicals such as sodium silicate have the reverse function. Using depressants and collectors in unison makes it possible to separate minerals that would normally both end up in the froth layer. There are many other factors of relevance, such as pH or particle size. The particle should be small enough for the bubble to be able to lift, but not so small as to not stick to the bubble at all.[26] Schüler et al.[18] estimate REO recovery rates of 40% for private and 60% for state-owned enterprises. We assume an average 50% REO recovery rate.

The end result of the beneficiation process is a concentrate containing 61% rare earth bearing minerals, consisting of 50 wt% bastnäsite and 20 wt% monazite with the balance consisting of other minerals, such as iron oxide and carbonates.[27]

Acid roasting

In the acid roasting process we model the production of 1 kg $RE_2(SO_4)_3$ from the 61% REO concentrate produced in the previous process.[27]

Bastnäsite ($RECO_3F$) is a carbonate that can be decomposed to REO and REOF, using high temperature oxidative roasting. Monazite ($REPO_4$) is a highly stable phosphate mineral structure that requires roasting with addition of strong acid or alkali agents. The goal of acid roasting is to remove the fluoride and carbonate so that only water-soluble rare earth sulphate remains, which is leached out of the ore in a later process.

Before the actual acid roasting the concentrate is first dried in a rotary kiln at 400 – 500 °C to less than 0.2% moisture. The subsequent acid roasting is done in a roasting kiln at 150 – 320 °C. The kilns are usually heated with heavy oil, kerosene, gas or coal.[27]

The roasted ore consists of spherical loose balls in 5 – 50mm in diameter. These will easily disperse into water forming slurry, which is important for the subsequent leaching step. More than 90wt% of the mineral particle size of the concentrate is less than 47_m in size.[27]

Other compounds such as ThO_2, CaO (CaF_2), Fe_2O_3 and BaO also consume acid, and HF will react with SiO_2 to generate SiF_4 in the off-gas.

Leaching

After acid roasting the ore will contain $RE_2(SO_4)_3$. This is mixed with cold water in a 1:9 solid/liquid ratio and stirred for four hours, during which the REO will dissolve in the water. Dissolution of $RE_2(SO_4)_3$ is an exothermic reaction. The solubility decreases with increasing temperature. For instance, at 20 °C, the average solubility is 86 g REO/l, while at 40 °C this decreases to 45 g REO/l.[27]

At this point the leachate will still contain impurities such as Fe, Th and P. MgO or $CaCO_3$ is added to adjust the pH of the leachate to 3.5-4.5 (literature does not state the pH before adjustment).[27] This causes the impurities to precipitate in the form of non-soluble hydroxides, phosphates, sulphates, silicates or complex salts.

After settling for 12 hours impurity levels are lower than 0.05 g/l for Fe and P, and lower than 0.01 g/l for Th. The leaching solution will contain $RE_2(SO_4)_3$ and H_2SO_4. At this point a molar excess of caustic soda (NaOH) is added, causing the REO to precipitate in the form of double salts. These precipitates are then washed and dried.[27]

In the final step of the leaching process a molar excess of HCl is added. This converts the salts into $RECl_3$, which can be used as input for the following solvent extraction process.

Solvent extraction

After obtaining a relatively pure 92% $RECl_3$ concentrate from leaching, the individual rare earths must be separated from each other. This is done using a process known as solvent extraction, which exploits the fact that different rare earths differ slightly in their basicity.

The leachate, containing ± 1 mol/l $RECl_3$, is mixed with an organic solvent. Different solvents can be used, such as P204, P507 and P350. Literature indicates that P204 – short for $(C_8H_{17})_2PO_2H$ – is currently most widely used for separating the light/middle weight REE's. By varying the pH, an individual REE can be selectively extracted from the leachate. This must be done in order of atomic weight, from light to heavy. Other parameters like HCl concentration and organic composition will also play important role in the REE separation. A small amount of kerosene is added to prevent emulsification of the two liquids.[27]

Because the difference in basicity between the $RECl_3$'s is minute, the process is repeated at least twelve times for each REE, with higher purities requiring more solvent extraction steps. At this point the separated $RECl_3$ solutions will still contain impurities such as iron and thorium. 0.8 mol/l HCl is added, causing the impurities to precipitate. This washing step is repeated eight times.

Subsequently an inorganic salt (e.g. ammonium bicarbonate) is added. The inorganic salt causes the rare earths to precipitate from the solvent in the form of $RE_2(C_2O_4)_3$ or $RE_2(CO_3)_3$. Finally, the precipitate is heated, causing the formation of rare earth oxides with a purity of up to 99.99%.[18]

3.3.2 NdFeB production route

In the following paragraphs we describe the most widely used industrial processes for making NdFeB permanent magnets, starting with the Nd oxide resulting from the Chinese primary production route described in the previous section.

Nd-oxide molten salt electrolysis

The most common industrial process for the production of metallic neodymium involves dissolving Nd_2O_3 into fluoride based molten salt (e.g. NdF_3-LiF), and electrolysing to produce pure liquid Nd metal. The process is similar to the Hall-Héroult process, used for aluminium production.

NdFeB alloying and strip casting

After obtaining metallic Nd an alloy of NdFeB must be made. In the past this was done using traditional casting methods. However, during this type of casting a small amount of iron is formed in between the NdFeB crystals. This so-called free iron is detrimental to the magnetic properties of the magnet and should be prevented. Additionally, iron is softer than NdFeB alloy, leading to problems later in the milling process. However, free iron is only formed at temperatures somewhat below the liquefying temperature of NdFeB alloy. Cooling the alloy very rapidly from a molten to a solid state can prevent the formation of free iron. For this reason, the most common casting process in industry is strip casting.

In strip casting a mixture of Nd, Fe and B is molten in an induction furnace. This is then poured over a fast spinning copper wheel. The copper wheel is water cooled, leading to cooling rates of 40.000 C°/s. As soon as the alloy hits the copper it solidifies and flies off the wheel, breaking up in flakes of a few mm thick and several cm long in the process. Not only do these flakes contain very low levels of free iron, they are also much easier to process than the solid slab of NdFeB alloy produced by traditional casting methods.

Casting the material increases the oxygen content of the alloy from a few hundred ppm to 2000-4000 ppm. Oxygen has a negative impact on the magnetic properties of the final magnet.

Hydrogen decrepitation

The structure of the strip casted NdFeB flakes consists of NdFeB crystals, forming 100-300 nm-sized grains. The space between the NdFeB grains is known as the grain boundary and is filled with metallic Nd.

When the flakes are exposed to hydrogen the Nd-rich grain boundaries form a hydride, which expands in volume. This causes the alloy to fall apart in a fine powder, where the particle size is equal to the size of the NdFeB grains. The NdFeB particles themselves form an interstitial hydride, where the hydrogen molecules don't actually react with the NdFeB but rather sit in the empty space in the crystal structure. This causes the NdFeB particles to crack, further reducing the average particle size. Together these reactions greatly reduce the amount of energy needed in the following jet milling process to reduce the particle size to the desired 5-7 micrometre range.

Sometimes the powder is then immediately de-gassed by heating it to 600 C, under a vacuum. This causes the particle volume to return to its normal size, which is better for the subsequent pressing process. However, this adds extra costs to the process and makes the material more hazardous to handle, because very fine non-hydride NdFeB powder is pyrophoric. If the material is not de-gassed the hydrogen is released in a later stage, during the sintering of the material.

Jet milling

The NdFeB flakes are milled into 5-7 micron particles using a process known as jet milling, or fluid energy milling. In this process the particles are fed into a cylindrical grinding chamber using compressed gas. Inside the chamber, the compressed gas forms a vortex in which the NdFeB flakes are grinded into ever-smaller sizes. Centrifugal forces cause the bigger particles to move to the outside of the vortex, while the smaller particles move to the centre. A strategically placed outlet removes particles at the desired particle size.

Aligning and pressing

The NdFeB particles need to be pressed before they can be sintered together. Additionally, the particles have a magnetic axis. The better the alignment of the particles when they are pressed, the better the final magnet will be resistant to demagnetisation.

The hydrogenated NdFeB particles are soft magnetic, meaning that they will magnetise under a magnetic field but will lose its magnetic properties as soon as the field is removed. This feature is used for alignment. The NdFeB powder is poured into a mould. The particles are then aligned using a short 4-8 tesla magnetic pulse.

There are two methods for pressing the powder: die setting, where the powder is put in a mould and pressed from the sides, or isostatic pressing, where the powder is put in a rubber mould in a vat with oil. The oil causes the powder to be evenly pressed everywhere. Die setting is cheaper and faster, but the alignment of the NdFeB particles is slightly changed because of the mechanical pressure. With isostatic pressing the alignment remains perfect. Both methods are used commercially.

Vacuum sintering

The blocks of aligned and compressed NdFeB particles are vacuum-sintered at pressures of 2-10 mbar. The temperature (1000 C°) is chosen so that the neodymium-rich phase between the NdFeB particles will liquefy, while the particles themselves remain solid. During sintering the material reaches its final density and all remaining hydrogen is removed.

Grinding and slicing

The sintered block of NdFeB alloy is sliced into rough shape and then grinded and polished into its final form, most commonly using the centreless grinding method. Grinding losses are highly dependent on the final shape of the magnet. For instance, if we assume that our reference flow of 1 kg NdFeB magnet would be a solid block there would be no losses at all at this stage. We will use an average loss rate for voice-coil motors, as used in hard disk drives (HDDs). Losses are estimated to be around 30-40% in China. Production in western countries is more efficient, with loss rates of 15-20%.[28]

The material lost during grinding and slicing can be recovered and re-used for production of magnets, albeit usually at a somewhat lower quality level.

Electroplating

NdFeB magnets are very susceptible to damage in a moist environment, because the Nd-rich phase in the grain boundaries of the NdFeB particles catalyse formation of hydrogen from water. The hydrogen then forms a hydride with the Nd-rich phase, which, similarly to the hydrogen decrepitation process, causes the magnet to disintegrate. For instance, if an uncoated NdFeB magnet would be used in a sea based wind turbine it would be destroyed in a matter of weeks. In these very demanding environments the magnets are laser welded into stainless steel canisters. Most magnets are used in less demanding environments, allowing coating with a nickel or nickel-copper-nickel layer. For our LCA we assume a nickel coating applied via electroplating, both because of data availability and because this is the most common coating for NdFeB magnets. Based on experiments we report that HDD neodymium magnets contain on average 10wt% nickel from their nickel coating.

Pulse magnetising and testing

After coating the NdFeB magnets are subjected to a strong (4-8 Tesla) magnetic field in order to magnetise them. Finally, magnets go through quality control. Depending on how strict the final requirements of the customers are up to 5% can be rejected. Before the dramatic price increases of rare earths these magnets would be discarded. Now they are recycled. Because only a small percentage is rejected and these magnets are recycled we neglect the rejecting of magnets in our LCA. Energy consumption of magnetization is likewise negligible.

3.3.3 Recycling processes

In this section we describe life cycle inventories of two proposed recycling routes. In the first route, NdFeB magnets are manually recovered from HDDs and recycled using a novel hydrogen decrepitating process, described in Binnemans et al.[19] In the second route HDDs are shredded, after which magnetic material is recovered and reprocessed into neodymium.

Recycling using manual dismantling

EoL HDDs can be found in general electronic scrap. Electronic scrap in the Netherlands is usually collected by municipalities, and then sold as container lots to waste management companies, who recycle it. Electronic scrap must be depolluted before further processing in order to remove toxic components such as batteries and printer cartridges. The scrap is spread over a conveyor belt and a team of workers manually removes hazardous components. HDDs are often readily accessible on the conveyor belt. Every 700 kg electronic scrap yields on average one HDD.[28] Since the electronic scrap must be depolluted anyway, this step incurs negligible marginal environmental costs.

The collected HDDs are manually dismantled and the magnets removed. This step is assumed not to have any environmental impact, because it only involves manual labour. We assume each HDD yields on average 15 grams of magnet.[28]

The NdFeB magnets are then put in a container with hydrogen gas. The hydrogen seeps into the grain boundaries, forcing them to expand, resulting in the disintegration of the magnet. This process is equivalent to hydrogen decrepitation during the virgin production process, except that the particle size of the product is much finer, because the powder from the recycled magnet has already been jet milled. Some additional milling is still necessary, but this can be done using a low energy milling process, saving energy compared to the jet milling process used during virgin production. Before milling the powder is sieved to remove the nickel coating. After milling the process steps are equivalent to primary magnet production.

Manual dismantling also benefits the recycling of the other components of the HDD – primarily printed circuit board and aluminium – since these are now less contaminated and could in theory be worth more, although this is currently not the case in the Netherlands.

Recycling using shredded HDDs

An alternative to manual dismantling is using shredders to liberate all the individual components of the HDD. However, this method results in the destruction of the magnet, not only leading to low recovery rates, but also oxidising the material and introducing many contaminants. This results in the necessity of many more processing steps, because the neodymium needs to be leached out of the HDD fragments.

After shredding the neodymium must be leached out of the material and then be reprocessed in almost the same manner that virgin material is processed. Several experiments were undertaken to determine the optimal leaching conditions. 99% of Nd can be recovered from the scrap if a molar excess of sulphuric acid is used. The mixture must be agitated to achieve optimal contact between the scrap and the acid. The Nd is leached relatively quickly, and after eight hours the highest leaching rate is achieved. Temperature has no influence on the leaching rate.[29]

3.4 Results

In this section we present our LCA results. We also report our findings of the environmental impact of the rare earth oxides (REO) production process, since this process is generic for many rare earths and may be of use. Because of the large uncertainties surrounding the primary production process we constructed three scenarios to explore the consequences of different levels of technology.

Section 3.4.1 presents our results on the REO production, 3.4.2 presents the results with respect to the NdFeB magnet production and finally section 3.4.3 contains a contribution and sensitivity analysis.

3.4.1 Production of rare earth oxides

In our LCA we modelled the production of REO with a process that is commercially used for the production of neodymium, cerium, lanthanum, praseodium, europium, gadolinium and samarium. Therefore our cradle-to-gate results for the production of 1 kg REO (99% purity) could be of use outside the context of NdFeB production. These are presented in Table 4. See supporting materials for more information.

Table 4 Characterised results (according to CML2001 impact assessment method) for 1 kg REO.

Name	1 kg REO, High-tech scenario	1 kg REO, baseline scenario	1 kg REO, Low-tech scenario	Unit
eutrophication potential	0.12	0.15	0.18	kg NOx-Eq
acidification potential	0.14	0.17	0.22	kg SO2-Eq
photochemical oxidation (summer smog)	5.3-E03	6.5-E03	85-E03	kg ethylene-Eq
climate change	12	14	16	kg CO2-Eq
Ionizing radiation	3.9E-08	4.1E-08	4.4E-08	DALYs
freshwater aquatic ecotoxicity	2.7	3.0	3.5	kg 1,4-DCB-Eq
stratospheric ozone depletion	2.5E-06	2.7E-06	3.0E-06	kg CFC-11-Eq
human toxicity	36	140	320	kg 1,4-DCB-Eq

3.4.2 NdFeB magnet production

In Table 5 we compare the environmental impact of our baseline scenario for the production of NdFeB magnets from virgin material with two recycling processes of NdFeB magnets found in HDDs.

Compared to the primary production process, recycling via hand picking scores significantly better with respect to most impact categories. This is caused mainly by lower energy use. Additionally, human toxicity is significantly lower, because this recycling process does not include the most polluting processing steps associated with virgin production. The same is true for the recycling of magnets via shredding. Although this recycling process is much more involved compared to recycling via hand picking, the processes related to mining and beneficiation are still avoided, resulting in lower environmental impacts.

Table 5 Characterised results (according to CML2001 impact assessment method) for NdFeB production.

Name	Primary NdFeB magnet, baseline	Recycled NdFeB magnet via hand picking	Recycled NdFeB magnet via shredding	Unit
eutrophication potential	1.9-E01	7.7-E03	3.2-E02	kg NOx-Eq
acidification potential	0.44	0.027	0.20	kg SO2-Eq
photochemical oxidation (summer smog)	1.7-E02	1.1-E03	8.0-E03	kg ethylene-Eq
climate change	27	3.3	10	kg CO2-Eq
Ionizing radiation	5.1E-08	2.0E-08	8.1E-08	DALYs
freshwater aquatic ecotoxicity	14	5.3	11	kg 1,4-DCB-Eq
stratospheric ozone depletion	2.6E-06	9.3E-08	1.0-E06	kg CFC-11-Eq
human toxicity	150	3.6	28	kg 1,4-DCB-Eq

The normalised results (presented in the supporting materials) indicate that for the primary production process the human toxicity component is by far the most relevant environmental impact. Both recycling processes also count human toxicity and freshwater aquatic ecotoxicity as their main impacts, but much less overwhelmingly so.

Figure 7-A shows the amount of neodymium lost along the primary processing chain. The largest losses occur during beneficiation, where 50% of the rare earth containing mineral is lost to tailings. Further losses amount to a total of 64% of the total input of neodymium in the production chain for neodymium magnets is lost. Note that losses during the grinding and slicing of NdFeB blocks are highly dependent on the final size and shape of the magnet, in this case voice coil assemblies used in HDDs.

Figure 7-B shows the neodymium losses along the production chain of the shredded recycling process. We would like to highlight that >90% of the magnetic material is lost during the shredding process.

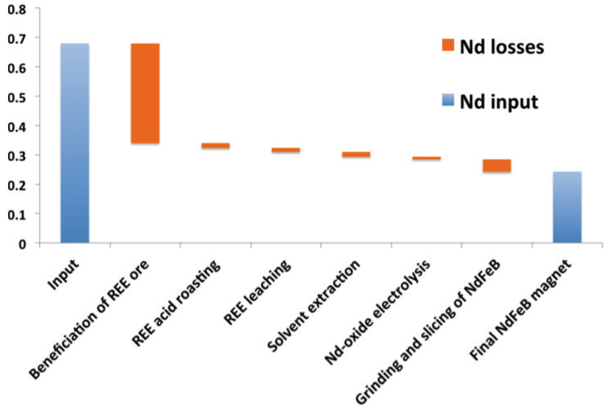

Figure 7-A Neodymium losses along the primary production chain in kg.

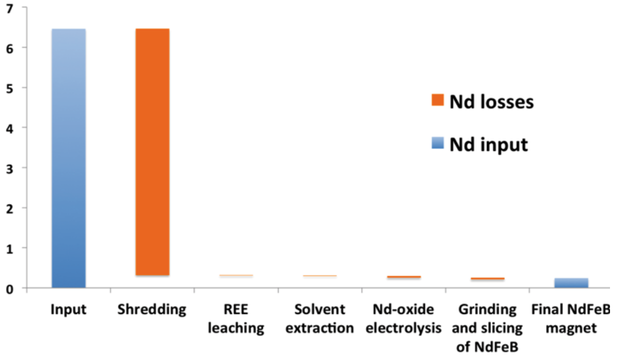

Figure 7-B Neodymium losses along the shredded recycling chain in kg.

3.4.3 Contribution and sensitivity analysis

This paragraph looks in more detail at our results of our LCA modelling. First we will look at scenario's covering different assumptions for the primary production process. Then we will highlight the biggest contributions to the LCA results.

Scenarios

Because of the large uncertainties surrounding the processes used for the production of Neodymium, we constructed three scenarios: a baseline scenario that represents the current state of the industry, a high-tech scenario that assumes best available technology and finally a low-tech scenario. The main differences between the scenarios are efficiencies of various processes along the production chain and differing emission controls. Table 6 shows our scenario results.

Table 6 results of LCA, different scenarios.

Name	[A1] High-tech, primary, NdFeB magnet	[A2] baseline, primary, NdFeB magnet	[A3] Low-tech, primary, NdFeB magnet	Unit
eutrophication potential	0.14	0.19	0.30	kg NOx-Eq
acidification potential	0.37	0.44	0.66	kg SO2-Eq
photochemical oxidation (summer smog)	1.4-E02	1.7-E02	2.6-E02	kg ethylene-Eq
climate change	21	27	41	kg CO2-Eq
ionizing radiation	4.1E-08	5.1E-08	7.2E-08	DALYs
freshwater aquatic ecotoxicity	13	14	20	kg 1,4-DCB-Eq
stratospheric ozone depletion	2.0E-06	2.6E-06	3.9E-06	kg CFC-11-Eq
human toxicity	42	150	470	kg 1,4-DCB-Eq
cumulative energy demand	260	330	490	MJ-Eq
Ore use (4.1% REO)	28	43	76	kg

Compared to baseline, the high-tech scenario requires 22% less energy and 35% less ore. This is reflected in most of the indicators, which are reduced in roughly the same amount. For the freshwater aquatic ecotoxicity indicator the difference is only 7%. This indicator is dominated by nickel use in the coating of the magnets. The high-tech and baseline scenario both use the same coating process, explaining the small difference. Human toxicity is reduced by 72%, due to the modelling of more robust emission controls.

The same trend is observed with the low-tech scenario, which requires 32% more energy and 77% more ore per kg of NdFeB compared to baseline. Most indicators also increase in this range. The exception is human toxicity, which increases by 68%, again caused by modelling the relative lack of emission controls.

Contributions

Regarding human toxicity, in the baseline scenario 81% is caused by emissions of hydrogen fluoride (HF), with the balance consisting of various smaller emissions of heavy metals. 93% of HF is emitted during acid roasting. The low-tech scenario shows the same structure, albeit with higher absolute numbers. In the high-tech scenario, only 52% of human toxicity is due to HF emission, with the balance relating mostly to heavy metal emissions. Of the shredded recycling process, 43% is related to HF emissions during solvent extraction. 36% is related to the emissions of heavy metals related to nickel electroplating, and the remainder to various smaller emissions.

Global Warming Potential (GWP) of all alternatives is almost exclusively due to energy use. In the baseline scenario, 48% of total GWP is due to electricity use of the foreground processes. 17% is attributed to the burning of diesel in electric generators in the mining process. The remainder is due to energy consumption elsewhere in the system. Similarly, eutrophication is mostly due to energy use, although this indicator is dominated (52%) by the emissions of nitrogen oxides of the diesel electric generating sets used during mining.

Acidification, photochemical oxidation, freshwater ecotoxicity and stratospheric ozone depletion all show a similar pattern in that ± 40% is due to the use of nickel in the electroplating process, and the remainder to various small emissions related to energy production. All alternatives show a similar structure, varying with the difference in energy use.

Finally, for the recycling via shredding scenario, we also explored the influence of using the British energy mix instead of the Chinese energy mix. This caused GWP, acidification and photochemical oxidation to increase by roughly half. Eutrophication potential doubled, while freshwater aquatic ecotoxicity, stratospheric ozone depletion and human toxicity hardly changed.

3.5 Discussion

In this chapter we investigated the environmental impact of the primary production process of 1 kg of NdFeB rare earth permanent magnet, and compared this with two alternative recycling processes.

Primary production process
For a technically advanced primary production process of NdFeB, most of the impacts are related to energy use. The outcome of our model is correspondingly sensitive to energy related emissions. Technically less advanced production processes also incur a large human toxicity penalty.

The issue of radioactive waste connected to rare earth production is important. Unfortunately a combination of uncertain data and a lack of appropriate characterisation factors means that the ionising radiation results should only be seen as a first attempt to quantify radioactive impacts during primary production.

Our scenarios from the sensitivity analysis highlight the importance of emission controls and process efficiency. They show a doubling of GWP emissions from the high-tech to the low-tech scenario, while the Human Toxicity indicator increases by an order of magnitude. Please note that the Human Toxicity indicator is very sensitive to hydrogen fluoride emissions during the acid roasting of REE containing ore. Although we are confident of the literature used to obtain our emission data, the characterisation factors associated with hydrogen fluoride are quite uncertain.[30]

We also want to highlight that in our baseline scenario 64% of the total neodymium input is lost along the production chain. 50% of the total loss occurs during the beneficiation process of REE containing ore, meaning that not only neodymium but also all other REEs contained in the ore are lost as well. An improvement to the recovery rate in this process has the potential to significantly reduce supply side constraint. Indeed, Peiró and Méndez[14] report that recovery rate is expected to rise to 75% by 2016.

Recycling process
We looked at two recycling processes. The first recycling process involves collecting HDDs from end-of-life computers, removing by hand the NdFeB magnets contained in HDDs and recycling these using a novel recycling process.[19]

Because this manual recycling process allows the recycled material to be utilised very late in the NdFeB magnet production process, it is very benign, using 88% less energy and scoring 98% lower on Human Toxicity than the baseline primary production process. The largest contribution to the environmental impact of this recycling process is from applying the nickel coating to the final magnet. However, this very positive result also reflects a lack of data on emissions related to this – for the time being – hypothetical recycling process.

The second recycling process involves collecting HDDs from end-of-life computers and shredding these, thereby completely destroying the HDD. Because the most polluting production steps can still be avoided, this less efficient manner of recycling still uses 58% less energy and scores 81% lower on the Human Toxicity indicator, compared to baseline primary production.

These results show that for recycling the choice of recycling method is of significant influence on the environmental impact. However, the most important difference between the two recycling processes is not adequately reflected in the environmental indicators: recycling through shredding results in a very significant (>90%) loss of NdFeB. Because the discussion on the use of rare earths is framed in terms of scarcity more than environmental damage, this is a serious issue not address through LCA.

We conclude that the value of recycling of neodymium is highly dependent on the method of recycling. Although from an environmental point of view recycling always be an improvement over primary production, the large losses of material incurred while shredding the material puts serious doubts on the usefulness of this type of recycling as a solution for scarcity. Furthermore, our LCA also shows that technological progress can make a significant difference in the environmental impact of producing neodymium magnets from primary sources.

Supporting Information Available
This information is available free of charge via the Internet at http://pubs.acs.org/ .

3.6 References

1. Margonelli, L. Clean Energy's Dirty Little Secret. *The Atlantic*. May 2009.
2. USGS National Minerals Information Center. *Mineral Commodity Summaries 2013*; Government Printing Office, 2013.
3. Japan Recycles Minerals From Used Electronics. *New York Times*. October 4, 2010.
4. EU. *Critical raw materials for the EU*; The Adhoc Working group on defining critical raw materials, 2010.
5. *Critical Materials Strategy*; U.S. Department of Energy, 2011.
6. Alonso, E.; Sherman, A. M.; Wallington, T. J.; Everson, M. P.; Field, F. R.; Roth, R.; Kirchain, R. E. Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean Technologies. *Environmental Science & Technology*. March 20, 2012, pp 3406–3414.
7. Nansai, K.; Nakajima, K.; Kagawa, S.; Kondo, Y.; Suh, S.; Shigetomi, Y.; Oshita, Y. Global Flows of Critical Metals Necessary for Low-Carbon Technologies: The Case of Neodymium, Cobalt, and Platinum. *Environmental Science & Technology*. February 4, 2014, pp 1391–1400.
8. Morf, L. S.; Gloor, R.; Haag, O.; Haupt, M.; Skutan, S.; Lorenzo, F. D.; Böni, D. Precious metals and rare earth elements in municipal solid waste – Sources and fate in a Swiss incineration plant. *Waste Management*. March 2013, pp 634–644.
9. Hitachi Develops Recycling Technologies for Rare Earth Metals. *www.hitachi.com*.
10. *Samenwerken aan Zeldzame Aarden*; TNO, 2012.
11. Improving reuse recycling. *https://cmi.ameslab.gov/research/improving-reuse-recycling*.
12. Darcy, J.; Dhammika Bandara, H.; Mishra, B.; Blanplain, B.; Apelian, D.; Emmert, M. Challenges in Recycling End-of-Life Rare Earth Magnets. *JOM*. October 3, 2013, pp 1381–1382.
13. Rademaker, J. H.; Kleijn, R.; Yang, Y. Recycling as a Strategy against Rare Earth Element Criticality: A Systemic Evaluation of the Potential Yield of NdFeB Magnet Recycling. *Environmental Science & Technology*. September 3, 2013, pp 10129–10136.
14. Talens Peiró, L.; Villalba Méndez, G. Material and Energy Requirement for Rare Earth Production. *JOM*. August 21, 2013, pp 1327–1340.
15. Tharumarajah, A.; Koltun, P. Cradle to gate assessment of environmental impacts of rare earth metals; 2011.
16. Althaus, H.-J.; Chudacoff, M.; Hischier, R.; Osses, M.; Primas, A. *Life Cycle Inventories of Chemicals*; ecoinvent report No. 8; Swiss Centre for Life Cycle Inventories: Dübendorf, 2007.
17. *Lanthanide Resources and Alternatives*; Oakdene Hollins, 2010.
18. Schüler, D.; Buchert, M.; Liu, D. I. R.; Dittrich, D. G. S.; Merz, D. I. C. *Study on Rare Earths and Their Recycling*; Öko-Institut e.V., 2011.
19. Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: a critical review. *Journal of Cleaner Production*. Elsevier July 15, 2013.
20. Guinée, J. *Handbook on Life Cycle Assessment*; Kluwer Academic Publishers, 2002.
21. Gupta, C. K.; Krishnamurthy, N. *Extractive Metallurgy of Rare Earths*; CRC press, 2004.
22. Zuo, Y. China ready to reconstruct rare earth industry. *english.peopledaily.com.cn*.
23. Du, X.; Graedel, T. E. Global In-Use Stocks of the Rare Earth Elements: A First Estimate. *Environmental Science & Technology*. March 25, 2011, pp 4096–4101.
24. Humphries, M. *Rare Earth Elements: The Global Supply Chain*; British Geological Survey, 2010.
25. *Radiation Protection and NORM Residue Management in the Production of Rare Earths from Thorium Containing Minerals*; Safety Reports Series No. 68; International Atomic Energy Agency: Vienna, 2011.
26. Introduction to Mineral Processing. *www.cpchem.com*.
27. Shi, F. *Rare Earth Metallurgy Technology*; Publisher of Metallurgical Industry: Beijing, 2009.
28. Sprecher, B.; Kleijn, R.; Kramer, G. J. Recovery Potential of Neodymium from Waste (working paper).
29. Abrahami, S. Rare-earths recovery from post-consumer HDD scrap, Delft University of Technology: Delft, 2012.
30. Frischknecht, R.; Jungbluth, N.; Althaus, H.-J.; Bauer, C.; Doka, G.; Dones, R.; Hischier, R.; Hellweg, S.; Humbert, S.; Köllner, T.; et al. *Implementation of Life Cycle Impact Assessment Methods*; ecoinvent report No. 3; Swiss Centre for Life Cycle Inventories: Dübendorf, 2007.