



The use of hydrogen to separate and recycle neodymium–iron–boron-type magnets from electronic waste



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ABSTRACT

The rare earth metals have been identified by the European Union and the United States as being at greatest supply risk of all the materials for clean energy technologies. Of particular concern are neodymium and dysprosium, both of which are employed in neodymium–iron–boron based magnets. Recycling of magnets based on these materials and contained within obsolete electronic equipment, could provide an additional and secure supply. In the present work, hydrogen has been employed as a processing agent to decrepitate sintered neodymium–iron–boron based magnets contained within hard disk drives into a demagnetised, hydrogenated powder. This powder was then extracted mechanically from the devices with an extraction efficiency of $90 \pm 5\%$ and processed further using a combination of sieves and ball bearings, to produce a powder containing <330 parts per million of nickel contamination. It is then possible for the extracted powder to be re-processed in a number of ways, namely, directly by blending and re-sintering to form fully dense magnets, by Hydrogenation, Disproportionation, Desorption, Recombination processing to produce an anisotropic coercive powder suitable for bonded magnets, by re-melting; or by chemical extraction of the rare earth elements from the alloy. For example, it was shown that, by the re-sintering route, it was possible to recover $>90\%$ of the magnetic properties of the starting material with significantly less energy than that employed in primary magnet production. The particular route used will depend upon the magnetic properties required, the level of contamination of the extracted material and the compositional variation of the feedstock. The various possibilities have been summarised in a flow diagram.

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1. Introduction

Rare earth magnets based upon neodymium–iron–boron (NdFeB) are employed in many clean energy and high tech applications, including hard disk drives (HDDs), motors in electric vehicles and electric generators in wind turbines.

In recent years, the supply of rare earth metals has come under considerable strain. China currently provides over 85% of rare earth metals to the world market but, in recent years, began to impose export quotas. This resulted in dramatic price fluctuations for the rare earth metals, in particular, neodymium, praseodymium and dysprosium, the rare earth constituents of NdFeB magnets. According to the [EU Critical Materials list \(2010, 2014\)](#) and the US

Department of Energy's energy critical element list (2010), the rare earth metals are classified as at greatest risk of supply shortages compared to those of all other materials used for clean energy technologies.

There are several ways in which these material shortages could be addressed including: (a) opening rare earth mines in countries outside of China, (b) using alternative technologies which do not contain rare earths (c) reducing the amount of rare earth metal used in particular applications such as magnets or (d) recycling the existing stock of NdFeB magnets contained within various types of equipment. It should, perhaps be emphasised that, none of these options are mutually exclusive.

However, with regard to option (a), the mining, beneficiation and separation of rare earth elements is energy intensive, results in toxic by-products from acid leaching processes and the primary ores are nearly always mixed with radioactive elements such as thorium ([Jordens et al., 2013; Zhu et al., 2015](#)). If alternative

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technologies are employed, as in option (b), compared to permanent magnet machines, this can often lead to a drop in efficiency which will effect CO₂ production (Widmer et al., 2015). It is possible to reduce some of the more scarce rare earth elements in magnets, as in option (c), however at present it is not possible to completely eliminate rare earths from magnets and achieve the same performance.

Despite the obvious need for a viable recycling route for rare earths, at present less than 1% of rare earths are currently recycled (Binnemans et al., 2013). With regard to recycling, option (d), much of the current stock of scrap NdFeB magnets is contained in obsolete HDDs, as the magnets used in electric vehicles and wind turbines are expected to be in service for at least 10 and 25 years respectively, and therefore as yet, unlikely to be available in significant quantities. Rademaker et al., 2013, predicted that in 2015, the HDD industry could source 64% of its NdFeB requirement from recycled HDD sources, which equates to approximately 11% of total NdFeB demand. However, Sprecher et al., 2014b, suggests lower figures of 57% and 3% respectively for the year 2017. In order to recycle NdFeB magnets from redundant electrical devices, several challenges need to be addressed, including the following:

- Collection and sorting of devices containing NdFeB.
- Identification of NdFeB in moving waste streams.
- Separation of NdFeB from the devices.
- Purification of the separated NdFeB.
- Re-processing of extracted materials into useful forms such as new magnets.

This paper outlines some possible methods for the separation, purification and re-processing of NdFeB magnets.

The work at the University of Birmingham has focussed primarily on HDDs as they are: (1) relatively easy to identify, (2) already separated from the device (such as a computer), (3) there is a rapid turnover of computers (~5 years) and (4) they are the largest single application of NdFeB magnets in electronic-type goods.

One of the biggest challenges associated with the recycling of NdFeB magnets from HDDs and any other form of electronics, is how to separate efficiently the magnets from the other components. There are two types of NdFeB magnet in a HDD; usually 2 fully dense sintered magnets in the voice coil motor (VCM) assembly and a resin bonded magnet in the spindle motor (See Fig. 1). The work outlined in this paper has focussed on the higher value sintered NdFeB magnets which, in total, weigh typically between 10

and 20 g for a 3½" HDD and 2.5 g for a 2½" HDD (Sprecher et al., 2014). It should be noted that the application of the HPMS process (Hydrogen Processing of Magnetic Scrap) allows the NdFeB-type magnets to be extracted without damaging the remainder of the device with regard to the possible recycling of the other components according to the WEEE legislation.

Manual separation of the sintered NdFeB magnets from the HDD would involve the removal of 8–10 security screws. The magnets are also coated with Ni (and occasionally with Ni–Cu–Ni), and glued into position between the plates of the VCM and they are in the fully magnetised state. At present, a large majority of HDDs are shredded in order to destroy any data on the disk. However, the magnets being extremely brittle, break up into granules/powder which remains permanently magnetised. Consequently, this powder is attracted to the other ferrous material including the shredder itself and is therefore very difficult to remove. The presence of this magnetised powder can adversely affect the operation of the shredder.

In the present work, hydrogen was employed, using the HPMS process, as a processing agent in order to extract selectively, NdFeB magnets from HDDs. Hydrogen is already used to process cast NdFeB in the Hydrogen Decrepitation (HD) process. The HD process is used extensively to reduce bulk (or strip) cast NdFeB ingots to friable, hydrogenated NdFeB granules/powder, prior to the production of jet milled powder which is then aligned, compressed and sintered to form fully dense sintered magnets (McGuinness et al., 1986). The hydrogen is then removed during the vacuum sintering process. Previous work at the University of Birmingham has shown that hydrogen can be employed to re-process uncoated scrap sintered magnets into powder which was then re-sintered to produce aligned, fully dense sintered magnets (Zakotnik et al., 2009) or subject to further HDDR processing to produce bonded magnets (Sheridan et al., 2012, 2014).

2. Materials and methods

The magnets employed in this study were (a) VCM magnets from the Philips factory (based in Southport UK) with a composition of Nd_{13.78}Fe_{75.51}B_{6.30}Dy_{0.66}Al_{0.76} (minor constituents not included) or (b) the magnets contained within obsolete 3½" HDDs sourced from redundant computers at the University of Birmingham (dating from 1996 to 2006). The HDDs were pre-processed by cutting off the corners, close to the VCM (using an industrial cropper). The sectioned HDDs were also distorted prior to hydrogen processing by pressing one side of the sectioned HDD in a uniaxial press in order to fracture the magnet into a few pieces (see Fig. 2).

Both the sectioned HDDs and the VCM magnets were processed in hydrogen at a pressure of 2 bar gauge (for between 2 and 4 h) and at room temperature (initially). Although, initially, the magnets were at room temperature, the absorption of hydrogen is an

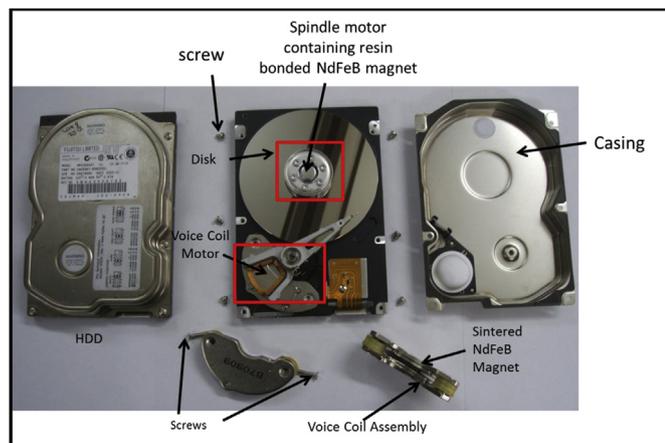


Fig. 1. Manually separated HDD, highlighting the voice coil motor assembly containing 2 sintered NdFeB magnets and the spindle motor containing a resin bonded NdFeB magnet.

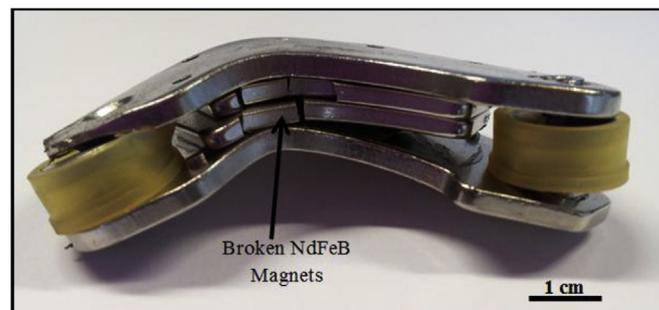


Fig. 2. Distorted VCM assembly.

exothermic process and consequently, there will be an increase in temperature. After hydrogen processing the sectioned HDDs were rotated in a porous drum in order to liberate the decrepitated magnetic powder. A combination of sieving and mechanical processing was employed in order to increase the fraction of NdFeB in the extracted materials.

Ion coupled plasma (ICP) spectroscopy and oxygen and carbon analysis (all performed at Less Common Metals, UK) were used to assess the composition of the extracted materials.

3. Results and discussion

Initial HPMS trials were performed on Ni-coated VCM magnets provided by Philips. It was evident that, on processing at room temperature and up to 10 bar hydrogen, and in the space of 4 h, on average, only 4 in 10 magnets decrepitated. This is likely to be the result of the number and character of pin holes in the electroplated coatings and/or to possible variations in the surface conditions of the underlying magnets. In order to guarantee that 100% of the magnets would react in hydrogen at 10 bar pressure, then, either the magnets needed to be heated to above 170 °C or, prior to hydrogen processing, the coating had to be ruptured. In the present work the magnets were fractured by distorting the VCM assemblies as shown in Fig. 2. The steel plates which surround the magnets are ductile whereas the NdFeB magnets are extremely brittle. Thus, on distortion of the VCM assembly within the HDD, the magnets break into several pieces. This was sufficient to create fresh surface without increasing significantly the surface area of the magnets and thus increasing the tendency to oxidise. In this condition it was shown that the VCM magnets could be exposed to air in the laboratory atmosphere for over 30 days and still all react on subsequent exposure to hydrogen.

Crucially, on reaction with hydrogen the NdFeB magnets become demagnetised (Harris and McGuiness, 1991), thus allowing the powder to be separated much more readily. During the HD-process, the Ni coating is converted to flake-like particles during the HD process with a wide range of particle sizes (150 µm – 3 mm). However, in the case of the Ni–Cu–Ni coatings, a markedly different behaviour was observed whereby the coating did not

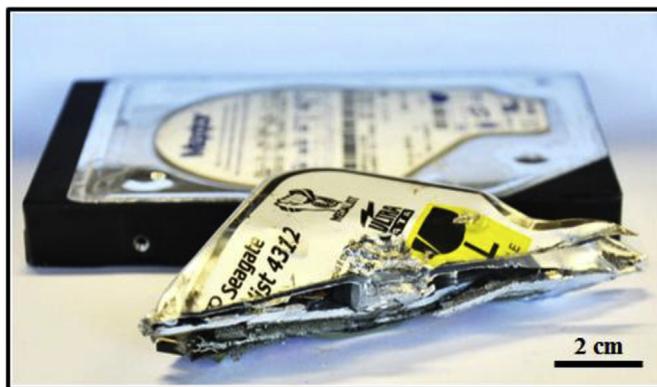


Fig. 4. Sectioned HDD.

fragment but separated as coiled sheets (as shown in Fig. 3) approximately 1 cm in length.

4. Processing of hard disk drives

Before the HPMS process was applied to HDDs, the HDDs were sectioned across the voice coil end of the device (Fig. 4). This had the dual effects of concentrating the NdFeB fraction of the waste product and opening up the HDD to provide a ready exit route for the hydrogenated powder. The remaining fraction of the HDD can therefore be shredded to destroy the data on the disk and subsequently recycled with other WEEE to recover the remaining valuable and/or critical material such as aluminium and components of the printed circuit boards.

Ten sectioned and distorted HDDs were placed in a hydrogen decrepitation vessel containing a rotating porous drum (Fig. 5). This was adapted from a unit designed for the production of sintered NdFeB-type magnets by the HD-process (McGuiness et al., 1986). The diameters of the holes in the drum were between 2 and 3 mm. The HDDs were processed in hydrogen for 2 h at room temperature and 2 bar gauge pressure. After this treatment the remaining

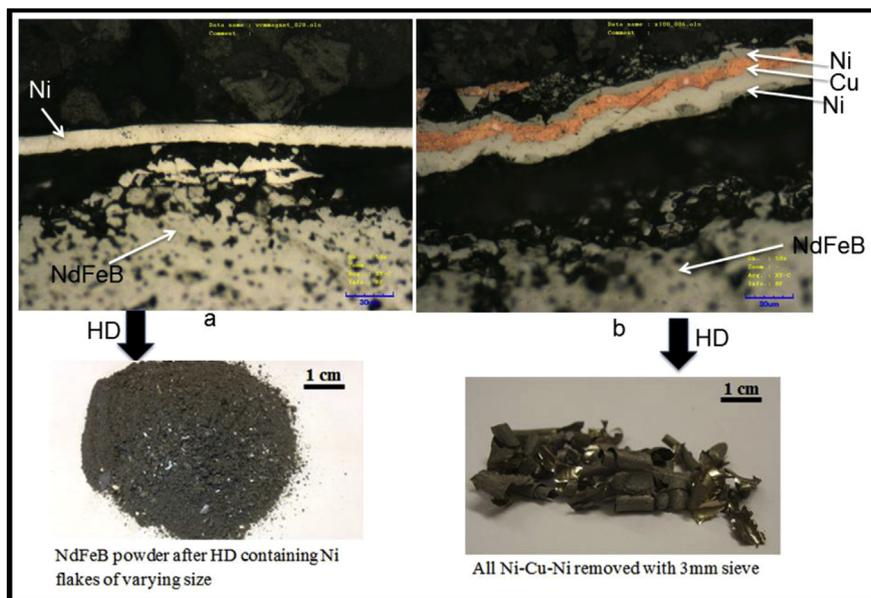


Fig. 3. Confocal laser microscope images of cross sections through a) Ni electroplated NdFeB magnet and b) Ni–Cu–Ni layer on NdFeB.

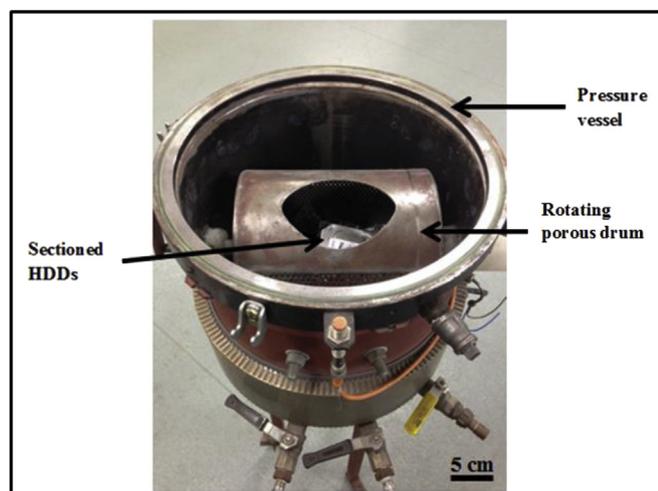


Fig. 5. Photograph of the proto-type separation apparatus based on an original HD-unit from Philips Southport (circa 1985).

gaseous hydrogen was evacuated and the drum rotated for 50 min at ~60 rpm. On rotation, a powdered feed of the magnet material was observed to fall immediately, through the port at the bottom of the vessel. In this experiment the vessel was left open to the air after HD processing in order to provide a direct observation of the effectiveness of the process. In the first five minutes of rotation, over 90% of the NdFeB-based material was removed from the HDDs.

The material extracted from the HDDs contained predominantly, hydrogenated NdFeB powder together with Ni flakes, pieces of plastic, sections of screws and fragments of electronic components, and some of these features can be seen in Fig. 6. By determining the mass of the extracted material compared to that of the NdFeB fraction which remained in the sectioned HDDs, it was possible to estimate an extraction efficiency of around $90 \pm 5\%$.

The material separated from the HDDs was processed further by sieving combined with mechanical agitation achieved by placing ball bearings onto the sieve stages. It was possible to extract nearly all of the contaminant particles using this technique. ICP and C-analysis of the residual, concentrated NdFeB fraction indicated 325 ppm Ni and 1779 ppm C. When the coating was removed prior to ICP analysis, the sintered magnets themselves contained an average of around 300 ppm Ni and 600–700 ppm of C. The higher Ni content is not significantly higher than the base alloy and is

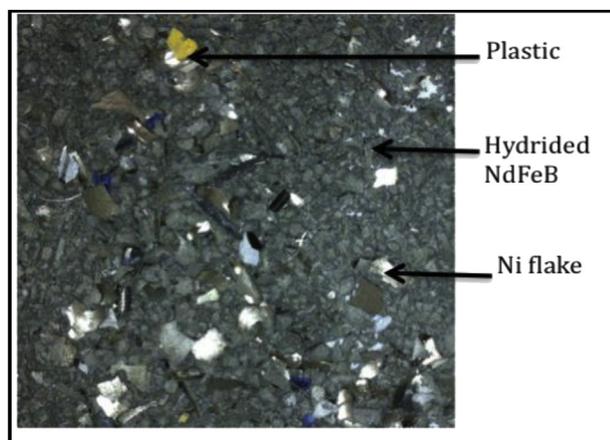


Fig. 6. Material extracted from porous rotating stage.

unlikely to present a problem for downstream re-manufacturing processes at this level. At this stage the origin of the additional carbon is not clear but could be due, in part at least, to the presence of polymers (such as adhesives) in the HDD or due to contamination from the cropper used at an industrial site. Further work is currently underway in an attempt to resolve this question.

5. Re-processing routes

As outlined in Fig. 7, once the material is extracted from the HDDs there are several possible re-processing routes for the extracted hydrogenated powders.

It is possible that procedures could be developed to extract the Nd from the hydrogenated alloy and, in this case, the extracted NdFeB would act as a type of rare earth-rich ore. However, unlike many mined sources, it would only contain 2–4 of the rare earth elements and would not contain any radioactive material (primarily thorium) therefore alleviating the ‘balance problem’ as described by Falconnet, 1985. The hydrogenated material has a high surface area which would lend itself to pyrometallurgical and hydrometallurgical chemical processes, as described by Binnemans et al., 2013. However, these processes will require a significant input of energy and therefore increased cost and possibly increased CO₂ emissions. The extracted elements would also have to be re-cast with the other constituents to produce the required NdFeB-type alloy and then hydrogen processed and jet milled to produce material suitable for sintering into new magnets. The hydrogenated powder is also likely to require degassing prior to any refining process.

Another possibility is to degas the hydrogenated alloy powder, pelletise and then melt and cast the material. It should then be possible to remove any surface oxide from the melt and therefore reduce the overall oxygen concentration in the resultant material. However this would require inert sample transfer and, to a large extent, the composition of the final cast material would be determined by that of the input scrap.

Yet another re-processing route would be to directly re-use the extracted hydrogenated NdFeB alloy to produce new sintered magnets. Previous work at the University of Birmingham (Burns et al., 2000; Zakotnik et al., 2009; Walton et al., 2012, 2014; Rivoirard et al., 2000) has shown that it is possible to recover around 90% of the magnetic properties by lightly milling the powders and then re-sintering. The extracted hydrogenated NdFeB powder already has a fine, aligned microstructure, retained from the starting material, and therefore much less milling is required than in the case of the cast and subsequently hydrogenated NdFeB-type alloy. By processing in this way it is possible to produce new magnets with fewer processing steps and hence with significantly less energy and hence cost than those for the complete sintering route. It was estimated by Sprecher et al., 2014a, using Life Cycle Analysis (LCA) that the direct re-sintering route would use 88% less energy than primary magnet manufacture due to the avoidance of high energy processing steps such as beneficiation, acid roasting, solvent extraction and jet milling. Human toxicity is also significantly reduced due to the absence of radioactive substances in the hydrogenated alloy compared to virgin production. The disadvantages of using the re-sintering route is that the composition of the final magnets will, to a great extent, be controlled by that of the input scrap and, on additional powder processing, the oxygen content of the magnets will increase. The higher oxygen content would result in a deterioration in the sinterability and hence in the magnetic properties. However, previous work (for example, Kianvash et al., 1999; Mottram et al., 2001; Zakotnik et al., 2009) in these laboratories has shown that this effect can be overcome by the blending of additional Nd in the form of NdH₂.

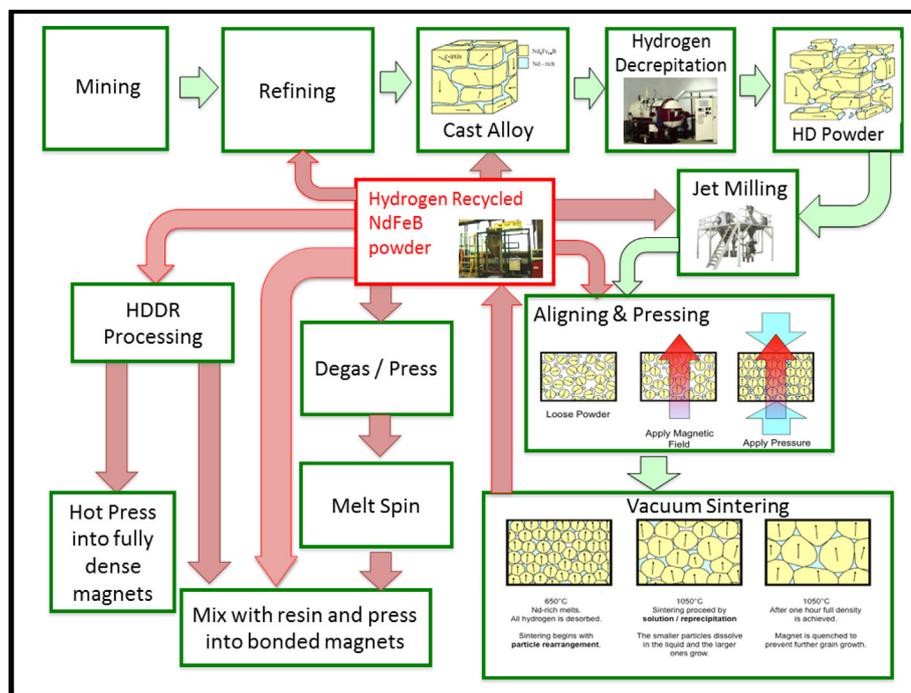


Fig. 7. Schematic of possible re-processing routes. Green boxes show primary route for manufacturing a sintered NdFeB magnet. Red boxes and arrows demonstrate where the hydrogen extracted powder can be fed back in to recycle the material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It is also possible to reprocess the extracted hydrogenated NdFeB into powder suitable for the production of coercive, anisotropic HDDR powder (Sheridan et al., 2012, 2014; Gutfleisch et al., 2012), which can be employed to make polymer bonded magnets or hot pressing to produce fully dense material (unpublished work).

The separation processes outlined in this paper have been carried out at low pressure and initially at room temperature so that, as with the HD-process for the manufacture of sintered NdFeB-type magnets, the process can be readily scaled-up. Thus, in the Magnetic Materials Group at the University of Birmingham, a 300 L capacity reactor has been constructed and assembled to process, in a single run, up to 500 sectioned hard disk drives. The scaling up was funded by the UK Waste Resources Action Program (<http://www.wrap.org.uk/>) and this work now forms part of the FP7 Remanence project (<http://www.project-remanence.eu/>). It should also be noted that hydrogen process gas could be recycled, possibly by employing a suitable metal hydride store to absorb the degassed hydrogen. This hydrogen could then be re-employed in the recycling process or used to generate electricity in a PEM fuel cell or a gas turbine. Under the conditions described in this paper, hydrogen would only react selectively with the NdFeB magnets and not with magnets based upon SmCo (2:17), SrFe₁₂O₁₉ and AlNiCo. With this in mind, it should be possible to use the HPMS route to separate NdFeB magnets from mixed feedstocks of material containing several types of magnets.

6. Conclusions

This paper shows that hydrogen is a very effective agent in extracting NdFeB magnets from HDDs using the HPMS process and that this technique can also be applied successfully to other devices such as electric motors, generators and actuators [to be published]. By concentrating the extracted materials using further sieving and mechanical separation steps, it is possible to reduce the contaminants to a level whereby the extracted NdFeB powder can be used

directly to form new magnetic materials. Fig. 7 shows that there are a number of viable routes to re-process the extracted materials into new magnets. The chosen route will depend upon the magnetic properties required by the final magnet, the contamination level of the extracted NdFeB and the compositional variation of the scrap feedstock. The HPMS process could well be driven by both economic and legislative processes aimed to create a sustainable supply of REEs for countries outside of China and to reduce the demand on natural geological resources. The main highlight of this paper is that the HPMS process has been shown to be cost effective with a much lower environmental footprint compared to primary production of NdFeB magnets, particularly when short loop recycling processes are employed (e.g. re-sintering). Further work is required on LCA with regard to all of the downstream re-manufacturing options. A US Patent has been granted on the HPMS process.

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