

RECYCLING RARE-EARTH-METAL WASTES BY PYROMETALLURGICAL METHODS

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Recycling secondary raw materials that contain rare-earth metals (REMs) can have a significant impact on the available supply of these valuable and scarce metals in the marketplace. The current use of pyrometallurgical methods to recover REMs from these materials is analyzed, with the focus being on such waste products as high-coercivity magnets and nickel-metal-hydride batteries. The analysis includes a discussion of the advantages and disadvantages of several pyrometallurgical processes, including melting, electroslag remelting, extraction with the use of molten magnesium, high-temperature treatment using halides and chlorides of metals, and the electrolysis of molten salts. Data are presented on the successful commercial use of pyrometallurgical processes in the recycling of REMs.

Keywords: rare-earth metals, waste products, pyrometallurgy, melting, electroslag remelting, extraction with molten magnesium, high-temperature chlorination and fluorination.

The recycling of waste products that contain rare-earth metals (REMs) can have a significant effect on the current critical shortage of supplies in the REM market. The entire recycling process, beginning with the collection of the waste products and ending with the manufacture of a final product that is in demand in the market, is a complex series of problems. In this article, we will limit the discussion to the high-temperature methods that can be used to return these valuable metals to the production process. The focus will be on recycling wastes generated in the production of high-coercivity magnets, batteries, and secondary raw materials. This includes scrap metal from used magnets, fluorescent lamps, catalysts, and consumer electronics. Hydrometallurgical methods are being used to recycle even highly contaminated and oxidized REM scrap [1], but there are obviously too many operations involved in dissolving the metals and then returning them to the metallic state. The attendant high energy costs and large quantities of reagents that are used have always motivated recyclers to search for alternative recycling methods. Results from studies of pyrometallurgical processes used to recycle waste products from REM production have been reported in a number of publications by Japanese, Chinese, and European authors, but this information is unfortunately often difficult to access due to the language barrier. Our goal here is to survey international experiences from the study and use of pyrometallurgical processes to recycle REMs. For convenience in the exposition of this subject, the information is organized based on the main type of technology that is used in the recycling operation.

Melting. For materials that are magnetic, have a chemical composition which satisfies the requirements established for such materials, and have physical parameters that deviate from the norm, it is best to perform the recycling operation by remelting them. A description was given in [2] of an attempt that was made to use this approach in the case of a sintered NdFeB powder magnet alloy with a protective nickel coating (oxygen content was less than 0.1 wt.%). Melting was followed by spinning with the drum surface rotating at a linear speed of 16 m/sec, which produced a material suitable for isotropic magnets having characteristics very close to those of industrial magnets of the same type. The fact that the properties of alloys obtained from unused REMs are comparable to those of alloys obtained from recycled REMs was noted in [3], where a hydration-grinding-dehydration process was employed to obtain magnetically anisotropic powders suitable for use in the

production of highly textured polymer-bound magnets. These magnets have characteristics that are rated somewhat lower than the characteristics of standard magnets but they can still be used in electric motors. The studies [4–6] examined the production of powders of brittle REM alloys in a mixture with iron-group metals. The powder and the mixture are obtained without the need for preliminary treatment by hydrogen, separation of the materials into fractions, the use of coarse and fine fractions, or other processing steps. Despite the obvious advantages of this technology – its simplicity and the absence of chemicals and waste products – its use is limited to a very small circle of waste products.

Extraction of REMs with the use of molten magnesium. As early as the 1960s, a prototype of this process was studied in [7, 8] for recovering silver from lead ores. At that time, a lead-zinc alloy was used as the extractant. The method was later developed further by the authors of [9] for use on NdFeB-magnet waste, and the extractant was now liquid magnesium. Neodymium has unlimited solubility in liquid magnesium, in contrast to liquid iron, and that makes it possible to selectively extract it. The neodymium-magnesium alloy that was formed was subjected to vacuum distillation in order to obtain magnesium and neodymium as separate products. Nickel, conversely, forms several compounds with magnesium, and this makes it possible to recover both valuable components from spent batteries for repeat use in the production of new batteries. In both cases, magnesium is returned to the extraction cycle [10]. The choice of magnesium as the extractant to recycle magnetic scrap is based on its strong affinity for neodymium, the low ductility of the alloy that is formed, the absence of reactions with iron, the high vapor pressure at temperatures above 1073 K, the moderate melting point (922 K), and the possibility of recycling it after condensation. An interesting equipment setup was discussed in [11] for using magnesium to recycle neodymium-bearing scrap having a neodymium content of up to 31%, a boron content of 1%, and iron as the remaining component. The magnesium is evaporated from a tantalum crucible located on the bottom of a hermetic argon-filled retort that is placed inside a furnace with a controllable temperature. Condensing on a conical condenser installed in the top part of the retort, magnesium flows downward and sprays onto crushed REM-bearing scrap located inside a special steel cage positioned directly under the condenser. Passing through the layer of scrap and becoming saturated by neodymium that is undergoing diffusion in the liquid magnesium, the product from the reaction of these elements flows into the crucible along with magnesium. The magnesium then evaporates again and is returned to the process cycle. The vapor pressure of neodymium in the process is very low (10^{-6} atm at 1300 K; for the sake of comparison, the vapor pressure of magnesium is 0.73 atm). Thus, neodymium accumulates in the crucible. In contrast to the earlier technology which involved placing scrap in a crucible with molten magnesium, in the method just described only pure magnesium participates in the extraction process. This makes it possible to avoid the difficulties that arise in the extraction of neodymium as it accumulates in the liquid phase of a magnesium-neodymium melt.

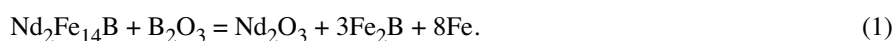
The lower part of the retort was heated to 1073–1273 K, while controlled air cooling was used to keep the temperature in the top part of the retort to 1002–1207 K. Residues of magnesium were removed from the extracted neodymium by vacuum distillation. The purity of the resulting neodymium was (wt.%) 97.7; the iron content was 0.72, boron content <0.002; and magnesium content <0.001. More than 90% of the neodymium was recovered. The fact that the iron content exceeds the values which correspond to the constitution diagram is attributable to an increase in the solubility of iron in the magnesium alloy as neodymium accumulates in the latter. Another variant of the process entails the combined melting of magnesium and scrap in an induction furnace with an inert atmosphere and subsequent vacuum distillation of the magnesium. REM recovery in this case has been greater than 98% and the neodymium which has been obtained has been used to make alloys of type $RE_2Fe_{14}B$, which have properties comparable to those of magnets made from pure metals [12]. In the autumn of 2012, the Ames Laboratory (U.S.) reported [12] that it was ready to experimentally demonstrate an improved method of recovering neodymium, praseodymium, and dysprosium from magnet scrap by using molten magnesium as the extractant. It is expected that this process will have an increasingly broad range of application.

Processes that use molten magnesium to extract useful components from rare-earth-metal scrap are relatively simple to realize and have good prospects for future practical use. However, they are energy-intensive, lack the universality of hydrometallurgical processes, and cannot be used on wastes that have a high oxygen content.

(Electro)slag remelting. If the metal that is to be recycled is in the form of relatively large lumps and the metal is sufficiently pure, then it can be recycled by electroslag remelting. In this process, the scrap is either employed as a consumable electrode in an electric-arc refining operation or is added to a melt [14]. A reactive flux composed of $CaCl_2$, CaF_2 , and RE_2F_3

is used to remove C, N, O, Li, Na, and Al. It is important to maintain a large metal-slag phase boundary during the holding and crystallization periods in order to effectively transfer the impurities to the slag phase. It was proposed in [9, 15] that this process be used on scrap with a high oxygen content (wt.%: Fe 55.6, Nd 20.6, Dy 4.2, Pr 5.27, B 0.80, Co 0.78, Al 0.25, C 0.58, O 11.9). The scrap charge should be held in a graphite crucible at 1823 K, which ensures good separation of the metallic and oxide phases that contain the REMs. Calculations have shown that only 4.94% oxygen is needed to completely oxidize all of the REMs in the scrap. Thus, the process has been carried out in an argon atmosphere. The effectiveness of the separation process is determined mainly by the melting point of the oxides of the rare-earth metals. The authors mention that the method cannot be used to recycle fine powder, chips, or wastes from grinding operations. In our opinion, these three types of waste products are more efficiently recycled by using a melt of the system LiF–BaF₂–REF₃. Such melts are employed in the electrolytic production of individual REMs, master alloys, and mischmetal. The solubility of a mixture of REM oxides in a melt of the given system at 915°C is 1.6 wt.% [16], which ensures the removal of most of the oxide film from the surface of scrap without affecting the metal itself.

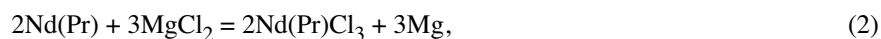
One other pyrometallurgical process was proposed in [17] – keeping molten scrap from NdFeB magnets in contact with boron trioxide at 1650 K. Study of the products obtained by this method confirmed the occurrence of the following reaction:



The metallic phase obtained from the experiment had the following composition, wt.%: 0.01 Nd, 95.86 Fe, 3.82 B; slag containing 25.80 Nd and 0.23 Fe. It was noted in [18] that the production of magnets generates scrap in amounts corresponding to only several percent of the magnets' weight but also results in the formation of sludge (wastes from comminution and other processing operations) in amounts corresponding to several tens of percent. The sludge cannot be directly returned to the production cycle because it has been contaminated with oxygen (up to 3.8 wt.%). It has been proposed that the sludge be recycled with the use of molten calcium in the method that is employed for processing samarium-cobalt magnet wastes.

The survey [5] included mention of several studies in which REM wastes were recycled by using vitrifying slags. However, the practical use of this method is problematic. Among its shortcomings are the impossibility of using it on finely dispersed or heavily contaminated scrap and the lack of a means to effectively separate the REMs from transition metals. Also, electric power consumption is high and new types of wastes are formed in the process. However, these problems do not preclude the use of electroslag remelting in the closed-cycle production of alloys of certain compositions.

Chlorination, fluorination. Previous experience with the recycling of natural rare-earth raw materials was used as the basis in [19] for chlorinating magnet scrap and sludge with elemental chlorine. As anticipated, the REMs were readily separated from the iron and cobalt in subsequent processing stages. An original approach was described in [20], where it was proposed that iron-neodymium-boron scrap be recycled by using a melt of magnesium chloride. The amount of melt used was in excess of the stoichiometric amount for the displacement reaction. As a result of the reaction, represented schematically in the form:

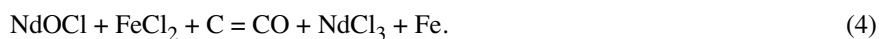


iron and boron remain in the metallic phase while the REMs are transferred to the melt in the form of chlorides. Separation of the solid and liquid phases and subsequent vacuum distillation yields an iron-boron alloy, in addition to usable magnesium, magnesium chloride, and chlorides of neodymium and dysprosium. The chlorides can then be reduced to obtain neodymium and dysprosium. Holding the scrap in the melt at 1273 K for 12 h results in the recovery of 90% of the neodymium and 87% of the dysprosium.

An attempt was made in [18] to selectively chlorinate oxidized neodymium-bearing magnet waste (containing alloying additions of Co, Dy, and Al and covered by a thin layer of Ni or Al) under milder conditions with the use of FeCl₂. A thermodynamic analysis made it possible to determine the temperature range (the range between the melting point and boiling point of iron dichloride – respectively equal to 950 and 1297 K) in which REMs can undergo chlorination by the below reaction without affecting iron-group metals:



The addition of activated charcoal to the charge makes it possible to surmount the problems connected with the presence of oxygen impurities in the system



The resulting REM chlorides were separated from the reaction products by vacuum distillation. The chlorides of aluminum and boron formed during the first stage of the process were easily separated from one another during the distillation operation thanks to the lower boiling point. Pyrohydrolysis of REM chlorides makes it possible to return hydrogen chloride to the production process and use it to chlorinate a new batch of iron, thus closing the production cycle. The author of [18] also stated that it might be possible to use this technology to recycle samarium-cobalt alloys and “bound” magnetic alloys. Magnets made with bound magnetic alloys are impregnated with epoxy resins instead of undergoing sintering. During heat treatment of the magnets the resins decompose and form volatile organic compounds and carbon, which is used in the process. Thus, the process being proposed is a closed-cycle production process (1073 K, 12 h) in which 96% of the neodymium and 94% of the dysprosium are recovered in the form of chlorides. The followed vacuum distillation with a yield of 76% allowed to get a neodymium and dysprosium chloride mixture of 99.2% purity.

Wastes from grinding operations performed during magnet production undergo recycling in the patent [21]. The recycling operation entails drying, oxidation at 550–650°C, magnetic separation of the resulting mixture of oxides, fluorination of the mixture with elementary fluorine at 200–350°C, and out-of-furnace metallothermic reduction of the resulting mixture of fluorides to obtain master alloys and magnetic alloys. The level of REM extraction is 90–95%, and the concentrations of carbon, boron, and silicon are simultaneously reduced to very low values. The main alloying elements – terbium, dysprosium, titanium, cobalt, and others – are transferred from the grinding wastes to the alloy and master-alloy ingots and thus do not have to be specially added to the material. A later patent [22] issued to the same researchers proposes that after oxidation scrap be rid of impurity elements by chemical methods and only then subjected to fluorination. The literature also contains information on the recycling of magnet scrap by chlorination in an AlCl_3 melt with the use of NH_4Cl , as well as the use of a carbonyl-based process to separate iron and selectively oxidize neodymium with oxygen at reduced pressure [5, 6].

Among the advantages of pyrometallurgical processes are the minimal use of water, the absence of liquid waste products, the smaller (compared to hydrometallurgy) number of stages in the process, the possibility of obtaining REMs in the form of metals, and the high degree of reagent regeneration. Shortcomings common to all pyrometallurgical methods are high energy use, the fact that they can only be used for a limited range of waste products, the length of the processes, the sometimes unsatisfactory purity of the final products, and the formation of solid waste products (in some cases). Despite these problems, a Japanese company is already using a process of this type and the Alcoa Company is performing research on it [23]. These developments definitely represent a step in the right direction, since until recently REMs were lost with the slag when discarded nickel-metal-hydride batteries containing 36–42% nickel, 3–4% cobalt, and 8–10% of a mixture of lanthanum, cerium, neodymium, and praseodymium were used in the production of stainless steel alloyed with nickel.

It has been reported [5] that the companies Umicore and Rhodia have jointly developed a technology for recovering REMs from used NiMH batteries. The technology is based on an ultra-high-temperature (UHT) process invented by Umicore [24] and on proprietary information provided by Rhodia. The flow of metals being recycled contains 1 g of REMs from AAA batteries, 60 g from batteries used in manual instruments, and 2 kg from batteries used in hybrid automobiles. The essence of the process consists in the use of plasma heating in a shaft furnace to melt a charge made up fluxes, coke, iron, and battery scrap which contains nickel and/or cobalt. The products of the process are an alloy which contains nickel, cobalt, and iron, iron-bearing slag, and a gas phase formed as a result of injection of the melt by a mixture of oxygen and air. Additional heat generated by the combustion of a plastic and an organic electrolyte lowers the energy costs of the process. Following the logic of the authors of the invention, when wastes that contain REMs in addition to nickel and cobalt are recycled the REMs should end up in the slag phase. The slag can then be processed by hydrometallurgical or other types of methods. REM concentrate will be recycled at Rhodia’s factory in La Rochelle (France), which long ago successfully introduced liquid-phase extraction processes. A pilot unit built by the company in Hoboken (Belgium) and having a capacity of 7000 tons/yr began operation in September 2011. The unit can recycle 150,000 hybrid-automobile batteries or 250 million mobile-telephone batteries, and it

can also be used to recycle lithium-ion batteries by a process that the company developed. The use of this process is especially attractive in light of the highly competitive market for the two aforementioned types of batteries.

The company Umicore is focusing on the fine purification of the gas phase in pyrometallurgical processes, which prevents the emission of fluorine, dioxins, and volatile organic compounds into the atmosphere. At the end of April 2012, the companies Honda and Japan Metals & Chemicals began working jointly on a project to recover REMs from used NiMH storage batteries. A special recycling plant has already been built and begun operation in Japan, the expectation being that the recovery of REMs from used parts of electric vehicles will soon be carried out on a massive scale. Only a little is known about the details of the process, which involves dismantling and disassembly, calcination, comminution, melting, and extraction. The products are nickel (or cobalt) and REMs [25].

Electrometallurgy. Although it is somewhat artificial to classify electrometallurgical processes as belonging to the realm of pyrometallurgy, such a classification can be justified by the fact that lanthanides are deposited on the cathode in metallic form only via the electrolysis of molten salts in a process that is similar to the electrolytic production of aluminum. Among the other processes that can be placed in this class is a method invented to recycle REM scrap by subjecting it to chlorination in a melt of chlorides of sodium and potassium and then extracting the REMs through electrolysis [26]. As might be expected, the current yield and the amounts of rare-earth metals recovered have been small because the metal deposited on the cathode reacts with its own salt and alkali chlorides in the melt. The previously mentioned study [6] included descriptions of processes for recovering REMs from scrap in a melt of salts by performing electrolysis with bipolar electrolytes and with a controlled potential. Research in this area is being carried out in Japan and Norway, where specialists in the given field have become well-known for their achievements in the high-temperature electrochemistry of ionic melts. The problems that are characteristic of the given method: high energy use, the need to recycle the anode gases, and the difficulty in obtaining metals in highly pure form. We believe that a more competitive method is electrorefining in melts, which yields finished products in the form of high-purity REMs [27]. However, the low values obtained in this case for current yield and productivity will be factors that slow the practical introduction of this process.

Conclusions. International experiences in the development and use of pyrometallurgical processes for the recovery and repeat use of rare-earth metals (REM) from secondary raw materials have shown the promise of these technologies, particularly in regard to REM-bearing magnetic and battery materials. Depending on the type of waste products being recycled, it may be possible to perform the recycling by remelting and spinning, extraction with liquid magnesium, electroslag remelting, chlorination or fluorination, or electrolytic extraction involving the use of salt melts. The most universal methods are those in the fourth group just mentioned, although the final product in this case is in the form of REM halides. If the goal is to arrange for an REM which is in factory wastes to be returned to the production cycle in the form of metal, then preference should be given to extraction with liquid magnesium. If it is necessary to obtain an REM in highly pure form, the most promising method is electrorefining in salt melts.

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