Current Status on Resource and Recycling Technology for Rare Earths

OSAMU TAKEDA and TORU H. OKABE

The development of recycling technologies for rare earths is essential for resource security and supply stability because high-quality rare earth mines are concentrated in China and the demand for rare earth metals such as neodymium and dysprosium, used as raw materials in permanent magnets (neodymium magnet), is expected to increase rapidly in the near future. It is also important to establish a recycling-based society from the perspective of the conservation of finite and valuable mineral resources and the reduction of the environmental load associated with mining and smelting. In this article, the current status of rare earth resource as well as that of recycling technology for the magnets is reviewed. The importance of establishing an efficient recycling process for rare earths is discussed from the characteristics of supply chain of rare earths, and the technological bases of the recycling processes for the magnet are introduced. Further, some fundamental researches on the development of new recycling processes based on pyrometallurgical process are introduced, and the features of the recycling processes are evaluated.

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I. INTRODUCTION

PROBLEMS related to, for example, economy and resource supply are generally the focus of studies on material flow and the recycling of metal resources. Rare metals, especially rare earths (or rare earth elements), are often a major topic in discussions of trade and economic challenges because they are intricately related to resource nationalism, territorial disputes, business issues in venture speculation, foreign and domestic affairs, and environmental burden.

In recent years, the heightened general interest in rare metals, which are often essential resources in high-tech industries, has led to rapid progress in quantity-based and economy-based analyses of the material flow of rare metals and related studies. Despite this progress, however, "the value of nature," which is the most important concept when considering the medium- to long-term outlook for the material flow of metal resources, is rarely discussed today.[1,2] The concept of "the value of nature," appropriateness of recycling rare metals, and future trends in material flow are omitted in this study because these topics have already been discussed in a previous article by the authors.[2]

Metals are extracted through a multi-step process that includes exploration, mine development, mining, smelting/refining, and processing before being used in industrial products. When such products are no longer valuable as industrial products, they become waste materials. Some of these waste materials are recycled and reused when they possess economic efficiency. However, it is often economically unfeasible to recycle rare metals from waste products, and these materials are frequently disposed of in landfills.

"Economic value" is typically used to evaluate the value of metals, particularly in countries that prioritize economic principles. As a result, rare earths contained in industrial products are typically not recycled. However, the environmental cost generated through the production of metals and the "fundamental value" (or value of nature) of the finite mineral resources from which those metals were initially produced should be considered. Therefore, fundamental issues, including the essential value of metals and the appropriateness of recycling those metals, should be discussed.

In the current economic system, the market prices of metals are based on the combined costs of exploration, mine development, mining, smelting, refining, processing, and distribution. Because metal consumers will attempt to acquire metals at the lowest cost possible, producers in a competitive environment will profit from producing those metals as cheaply as possible. Consequently, there are many instances in which no financial expenditures are made to prevent and/or to reduce pollution from mine development, mining, and smelting processes. This tendency is often particularly prominent in developing countries where economic growth is prioritized over environmental protection from the destruction associated with (or caused by) mining and smelting.

In 2002, the Mountain Pass mine in the United States, which is one of the finest rare earth mines in the world, was closed due to the prohibitive environmental costs from mining and smelting under strict environmental regulation. While other factors may have also

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contributed to this closure, the shutdown of the mining operation was directly caused by a lack of cost-competitiveness and not the depletion of the quantity or quality of ores.[3] In contrast, China has prioritized economic growth strategies and has succeeded in monopolizing the world market by producing and exporting rare earths at a very low cost, largely by disregarding environmental costs. This is an inevitable result under today's economic system, in which competitive principles determine the power balance for suppliers and price reflects apparent costs.

Due to the recent rapid rise in the price of rare earths following export regulations and price controls in China, the Mountain Pass mine resumed operation in 2011, and the development of rare earth mines has accelerated in countries other than China (*e.g.*, Australia and Vietnam). Because most of the rare earth ores in Australia contain radioactive elements such as uranium and thorium, radioactive waste is also frequently generated during the smelting process used to produce rare earths. Therefore, the Australian government may either impose strict environmental regulations for mining and smelting that generate radioactive waste within the country. This means that while the Australian government may allow mining and export of resources to acquire foreign currency, the country may also forbid or impose heavy penalties on the smelting process that generates radioactive waste within the country. Even if smelting is allowed in Australia, the country's strict environmental regulations, as in other developed countries, could be a deterrent for creating profitable businesses because these regulations would increase the environmental costs for waste disposal and treatment when mined ores are smelted locally.

Table I illustrates the significant differences in environmental and labor costs required for compliance with environmental regulations as well as the costs related to the energy and raw materials needed for smelting in various countries and regions. The costs related to the treatment of smelting wastes also differ depending on each country's environmental regulations.[4] Therefore, a business model is currently being developed in which rare earths are (1) mined in Australia; (2) exported overseas, primarily to developing countries with less stringent environmental regulations, for smelting and refining; and (3) re-exported to countries seeking rare earths at a low cost (see Figure 1).[4] Under this model, regional differences in environmental costs can lead to significant changes in the material flow of rare metals. If the regional disparity in environmental regulations is high, it is possible that the quantity and flow structure for rare earths could change significantly.

In developed countries such as Japan, the costs related to environmental regulations that are not seen directly by consumers are rarely considered. These countries are typically able to acquire the highest quality metals, alloys, and compounds at the lowest cost worldwide for the manufacture of high-tech products. This pattern is not limited to rare metals, and cases where environmental costs are disregarded can be seen for many international products.

II. PRODUCTION OF AND DEMAND FOR RARE EARTHS

In 2010, the estimated total production of sintered neodymium magnets was approximately 13,000 tons in Japan and 45,000 tons worldwide.[3,5] One problem associated with neodymium magnets is that their coercive force declines significantly at high temperatures, but the addition of the rare earths dysprosium and terbium can overcome this issue. This technological development has extended the application of neodymium magnets to power motors. Up to 10 mass pct of dysprosium is added into neodymium magnets so that these magnets can operate effectively at operating temperatures approaching 473 K (200 °C), as in the motors of hybrid electric vehicles (HEVs). However, the rise in price and concerns over supply instabilities for dysprosium have led to the reduced use of this rare earth in recent years, driving the development of dysprosium-saving technologies.[4] Yet, as the need for energy conservation grows, the demand for dysprosium-added neodymium magnets has also grown for use in the motors of next-generation vehicles, air conditioners, and electric generators. As Table II shows, a motor in an electric vehicle (EV) contains about 1.3 kg of magnet. Given the distribution of next-generation automobiles, it is expected that the market for high-performance magnets containing high volumes of dysprosium will also expand.[5,6]

Neodymium and dysprosium, raw materials used for neodymium magnets, are classified as rare earths. However, challenges related to the acquisition of these resources differ. Table III shows the major rare earth ores as well as the grades and compositional ratios for the rare earth oxides (REOs) in each ore.[5,7,8]

Table I. Comparison of Costs for Producing Metals and Alloys of Rare Earths[4]

	Japan	USA	China	Australia
Feed cost	× (high)	× (high)	◎ (very low)	○ (low)
Energy cost	× (high)	○ (low)	?	○ (low)
Environmental cost	× (very high)	× (high)	◎ (very low)	× (high)
Employment cost	× (high)	× (high)	○ (low)	× (high)

As Figure 2 illustrates,[5,8,9] ores such as bastnaesite and monazite, which produce light rare earths, are globally distributed and abundant. However, many of these rare earth ores contain naturally occurring radioactive materials (NORMs) such as uranium and thorium, whose ion radius that is similar to that of rare earth elements. NORMs and harmful substances that

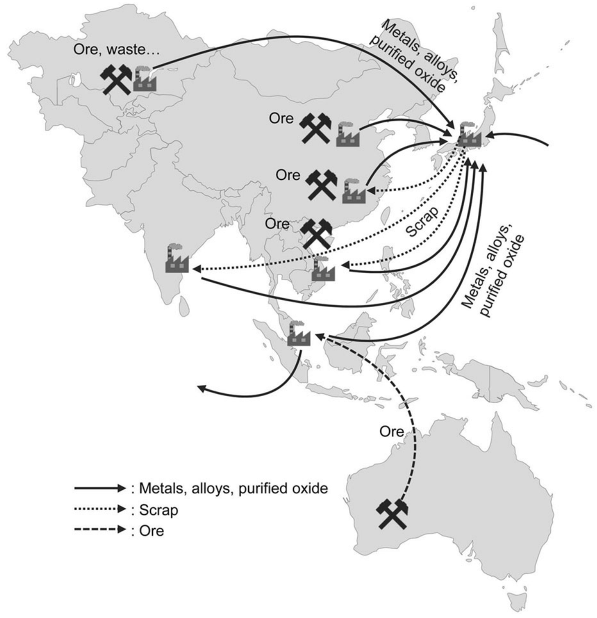


Fig. 1—Global material flow for production of metals and alloys of rare earths and waste treatment of the scrap.[4]

Table II. Mounted Weight of Nd Magnet in Products (Approximate Number)[5,6]

Product	Mounted Weight of Nd Magnet (kg/Unit)
HEV	0.25 to 1.25*
EV	1.3
Power steering	0.09
Air conditioner	0.12
Hard disk drive	0.01
Cellar phone	0.0005
Magnetic resonance imaging	1500

Low power motor: 0.25 kg/unit. High power motor: 1.25 kg/unit.
*Used amount of magnet depends on power of motor in HEV.

are concentrated through mineral dressing and smelting processes pose challenges to waste treatment when neodymium is produced from ores. On the other hand, the grades of heavy rare earths in ores are significantly lower compared to those of light rare earths (*e.g.*, neodymium). Furthermore, dysprosium and terbium are scarce. At present, heavy rare earths are produced from a special type of weathering deposit referred to as an ‘‘ion adsorption-style deposit’’ found in southern China. This is a special mineral deposit in which radioactive elements are washed away by weathering and heavy rare earths are preferentially ion-adsorbed into the clay layer. These heavy rare earths are condensed at the ground surface after many years when rare-earth-containing granite is weathered in a climate with high temperature and humidity levels (see Table III). The deposit contains very few radioactive elements and is a superior rare earth resource because rare earth elements in the ores can be easily separated and extracted through elution using eluting agent such as an ammonium sulfate. However, ion adsorption-deposits have been discovered only in southern China and certain parts of Southeast Asia to date, likely because they are formed under special climate and geological conditions. As Figure 2 shows, enormous amounts of rare earths still exist in reserves that are widely distributed worldwide. However, weak environmental regulations, superior deposits, and a cheap labor force in China have made other mines and smelting plants in other countries much less competitive economically. As a result, the production of rare earths is currently monopolized in China.

III. PROBLEMS AND SOLUTIONS RELATED TO RARE EARTH RESOURCES

As discussed previously, rare earths are relatively abundant mineral resources. Thus, problems related to

Table III. Composition of Rare Earth Ores[5,7,8]

Ore	Bastnaesite		Monazite	Ion Adsorption-Style Deposit
Ore Deposit (Country)	Bayan Obo (China)	Mountain Pass (USA)	Mount Weld (Australia)	Longnan (China)
REO grade in ore (wt pct)	6	8.9	11.2	0.05 to 0.2
Content ratio in REO (wt pct)				
La_2O_3	23.0	33.2	25.1	1.82
CeO_2	50.0	49.1	48.5	0.37
Pr_6O_{11}	6.20	4.30	5.30	0.74
Nd_2O_3	18.5	12.0	16.7	3.00
Sm_2O_3	0.80	0.79	2.20	2.82
Eu_2O_3	0.20	0.12	0.60	0.12
Gd_2O_3	0.70	0.17	0.90	6.85
Tb_4O_7	0.10	trace	0.10	1.29
Dy_2O_3	0.10	trace	0.20	6.67
Ho_2O_3	trace	trace	trace	1.64
Er_2O_3	trace	trace	trace	4.85
Tm_2O_3	trace	trace	trace	0.70
Yb_2O_3	trace	trace	0.10	2.46
Lu_2O_3	trace	trace	trace	0.36
Y_2O_3	trace	0.09	0.40	65.0

cf. Mixed ore of Bastnaesite and Monazite (Bastmonaziste) is also mined in Bayan Obo.

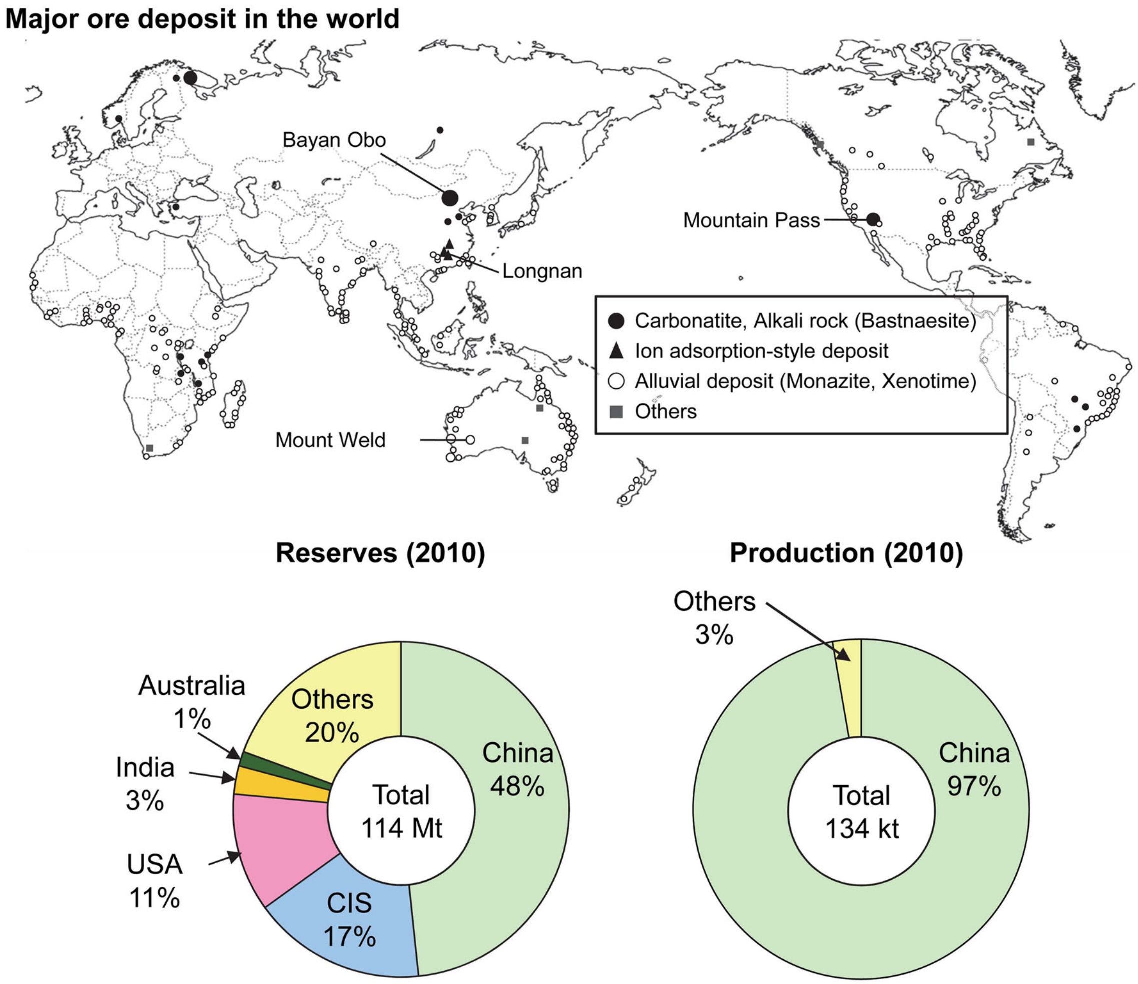


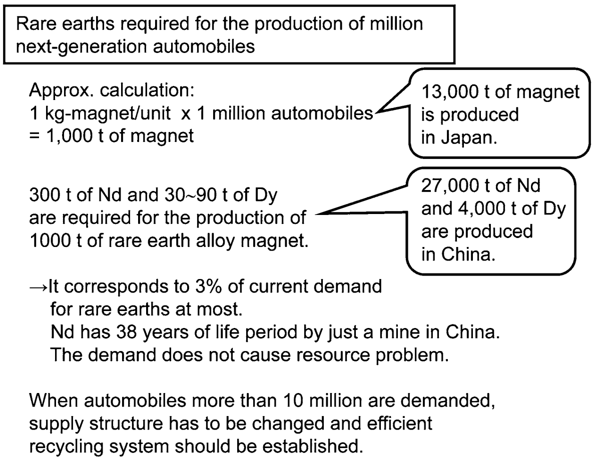
Fig. 2—Major ore deposit for rare earths and its reserves and production volume (oxide base).[5,8,9]

resource availability are not serious issues in the production of magnets for EVs and HEVs (see Figure 3[3,10]). However, as is the case for many other rare metals, problems involving speculation, political issues, and short-term supply shortages due to the suspension of mining and refining operations are common for rare earths. Since 2004, the Chinese government has strengthened regulations for exporting rare earth metals and compounds following more focused policies for the development of domestic industries, the increased domestic demand for rare earths, and the prioritization of environmental protection.[3] Such changes have led to a rapid rise in rare earth prices, particularly for heavy rare earths, which has caused Japanese industries that depend on rare earths to suffer serious supply shortages. By July 2011, the prices of neodymium and dysprosium reached 420 and 3,600 USD/kg (CIF Japan), respectively,[11] compared to 50 USD/kg for dysprosium a decade earlier. Although this dramatic price increase has been due in part to the use of dumping (*i.e.*, the export of a material at a price that is lower in the foreign market compared to that charged in the domestic market) for the acquisition of foreign currency, rare earth prices have generally been abnormal since export regulations were implemented.

To establish a stable, long-term supply of rare earth metals and their compounds, which is key for the production of neodymium magnets, a multifaceted and collaborative approach among industry, government, and academia is required to find solutions for (1) the diversification of supply sources, (2) stockpile build-up (resource buffer), (3) product recycling, reuse, and long-term use, and (4) the development of alternative materials and technologies.[3]

Several companies have secured overseas resource interest in order to diversify resource supplies. These efforts include the development of the Mount Weld mine in Australia[12] and the extraction of dysprosium from uranium smelting residues (wastes) in Kazakhstan.[13] However, because deposits that can produce dysprosium at a low cost are rare outside of China, it is not easy to reduce the worldwide dependency on China for this rare earth. Furthermore, because dysprosium is scarce, the development of technologies that can reduce the use of this rare earth in neodymium magnets, and the establishment of a legal system that permits national stockpiling at low prices are critical.

It is also important to look beyond economic considerations and to discuss the resource problem from the perspective of environmental protection. Managing the



Rare earths required for the production of million next-generation automobiles

Approx. calculation:
1 kg-magnet/unit x 1 million automobiles
= 1,000 t of magnet

13,000 t of magnet is produced in Japan.

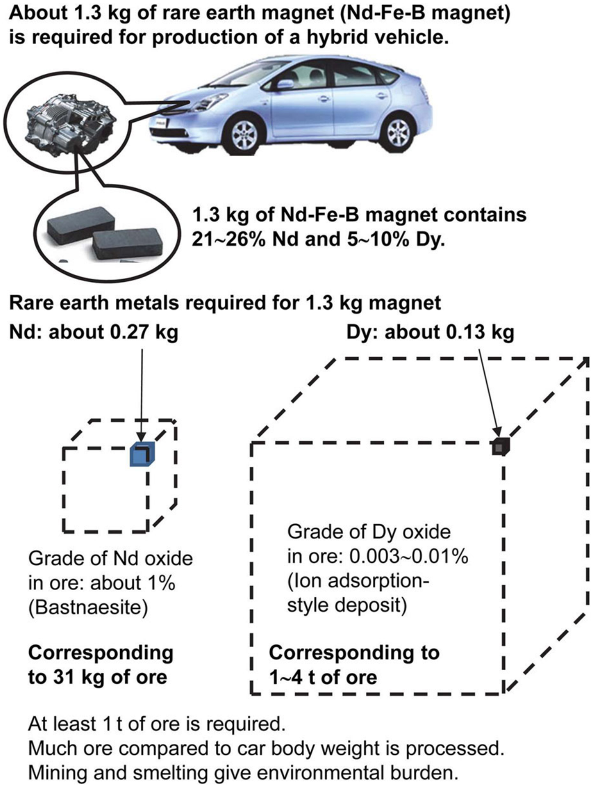
300 t of Nd and 30~90 t of Dy are required for the production of 1000 t of rare earth alloy magnet.

27,000 t of Nd and 4,000 t of Dy are produced in China.

→It corresponds to 3% of current demand for rare earths at most.
Nd has 38 years of life period by just a mine in China.
The demand does not cause resource problem.

When automobiles more than 10 million are demanded, supply structure has to be changed and efficient recycling system should be established.

Fig. 3—Approximate calculation of rare earths volume required for the production of next-generation automobiles.[3,10]



About 1.3 kg of rare earth magnet (Nd-Fe-B magnet) is required for production of a hybrid vehicle.

1.3 kg of Nd-Fe-B magnet contains 21~26% Nd and 5~10% Dy.

Rare earth metals required for 1.3 kg magnet

At least 1 t of ore is required.
Much ore compared to car body weight is processed.
Mining and smelting give environmental burden.

Fig. 4—Approximate calculation of volume of rare earth ore required for the production of next-generation automobiles.[3,5]

disposal of wastes, including NORMs, is an issue in many instances where rare earth ores are mined. The natural environment is destroyed even when using special ores such as the aforementioned ion adsorption-deposits containing trace amounts of uranium and thorium, because these ores are mined by injecting an extractant (eluting agent) directly into the ground. Although ion adsorption-deposits are rich in heavy rare earths, the grade of dysprosium in these ores is very low at about 30 to 100 ppm. Given that 1 to 4 tons of natural ore are processed per vehicle when dysprosium is extracted from ion adsorption-deposits (Figure 4),[3,5] the environmental destruction caused by mining and smelting cannot be ignored. The value of nature, which was formed by miraculous natural phenomena occurring over the course of millions of years, must be recognized, and the traditional perspective that places economic principles above all other considerations should be broken.[1,2]

Although not commonly discussed, the disposal costs of excess by-products may become significant when the demand for particular element, such as scarce dysprosium and terbium, grows; because the supply of rare earths produced from ores is regulated by the abundance ratio in the ores (see Table III) and this abundance ratio cannot be changed. An imbalance in the supply mechanism can result due to supply disruptions and price increases. For the effective utilization of resources, including by-products, the development of highly efficient recycling technologies is an extremely important technical issue.

IV. AN OVERVIEW OF THE PRODUCTION AND RECYCLING OF NEODYMIUM MAGNETS

Figure 5[14,15,25] illustrates the material flow for neodymium magnets, and the photographs in Figure 6 show the appearance at an electrolysis plant in southern China where rare earth metals and alloys are produced using fluoride molten salt electrolysis at approximately 1073 K (800 °C). Japan imports rare earth metals and alloys from China for raw materials. The processes used to produce magnets primarily consist of the melting of raw materials, the pulverization of alloys, shape forming, sintering, cutting, and magnetization. Although some of the rare earth metals and alloys used as raw materials are produced domestically from recycled products, the majority of these metals are imported from China.

A large amount of scrap is also generated in the manufacture of rare earth magnet alloys. Most of this scrap is comprised of "off-spec" products that contain high concentrations of impurities (*e.g.,* oxygen) and residues generated from alloy processing. In addition to sludge generated from the magnet cutting process, individual scrap that failed to meet stage-specific standards is also produced during the magnet manufacturing process. Therefore, yield rates are currently low at 50 to 80 pct when raw materials are converted into the final products.

Internally generated scraps (in-plant scraps) that are generated through the production process (prior to the incorporation of metals into final products) require minimal costs for recovery and separation, and this scrap typically contains large volumes of valuable rare earths. This scrap can be regarded as a very high-grade raw material if considered a mineral ore. However, scrap is generally treated by a wet (or hydrometallurgical) process, where scrap is dissolved with acid into an aqueous solution and then separated and refined to remove water and oil contaminants. In contrast, "off-spec" products

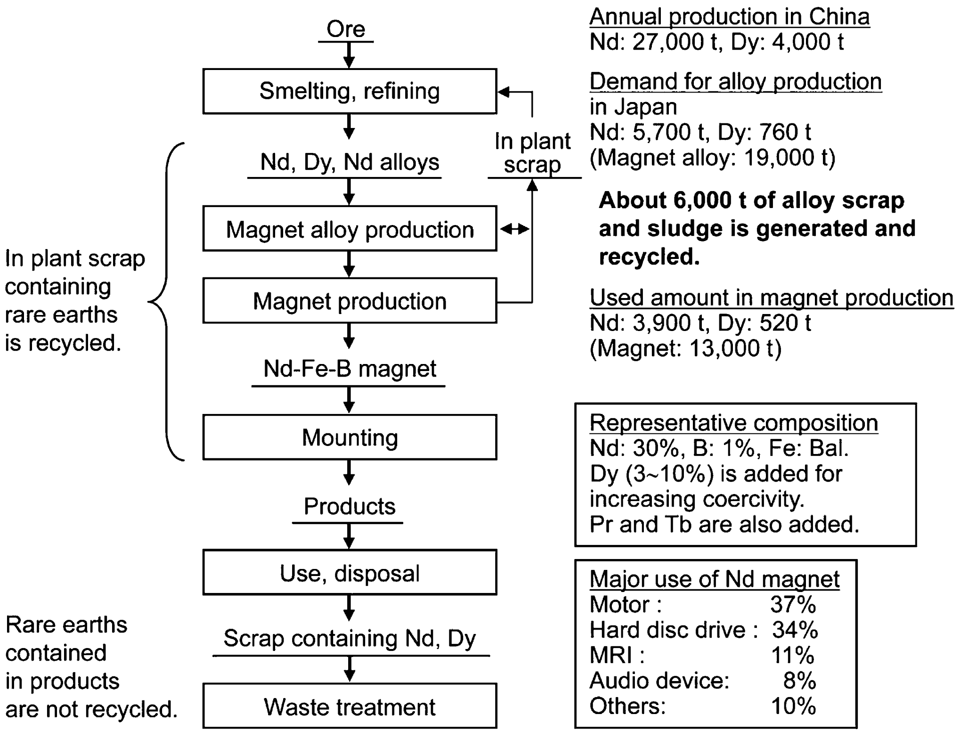


Fig. 5—Material flow of Nd and Dy in Nd magnet production.[14,15,25] (Number in figure is approximate value in 2010).

that are relatively less contaminated are sometimes re-melted at a high temperature and reused as raw alloys. Currently, technologies for the recovery and reuse of in-plant scrap generated from magnet production have already been established, allowing the scrap to be recycled at a high recovery rate. The recycling of scrap from neodymium alloy magnet production is often outsourced to foreign refineries due to issues related to treatment costs, but the flow of the scrap materials is unclear.

On the other hand, neodymium magnets that enter the market in a separate product are rarely recovered, primarily due to the high cost of recovery (except when recovered from large products like MRI magnets). However, product scrap is expected to be generated in the future at a constant volume through the utilization of relatively large magnets in EVs and HEVs. Therefore, an important challenge for the future will be to develop an efficient mechanism for recovering valuable elements such as neodymium and dysprosium from product scrap (*e.g.*, large motors).

Most of the scrap that contains rare earths in Japan is exported overseas and reprocessed through smelting for recycling purposes. However, the development of new technologies to efficiently recover, separate, and extract these materials for cyclical use is critical for securing a stable resource supply and for promoting environmental conservation.

V. RECYCLING TECHNOLOGIES FOR NEODYMIUM MAGNETS[15–17]

Recycling technologies for sintered Nd-Fe-B magnet are categorized and listed in Table IV.[15–17] It should be noted that this table contains some biases given that the table focuses primarily on high-temperature processes (that are the authors' specialty), even though various other approaches are probably being pursued. As the comparison with the material flow for magnet production in Figure 5 illustrates, recycling technologies for magnet alloys are broadly categorized into three groups: (1) "material recycling methods" in which scrap materials are charged into smelting processes as raw material, (2) "alloy recycling methods" in which the materials are regenerated into master alloys for magnet production, and (3) "magnet recycling methods" in which magnet alloys are reused in their current form. Because sludge from magnet production is often heavily contaminated with water and oil, the sludge is generally separated and refined after being dissolved with acid using a wet process. In contrast, studies are currently underway to find a recycling method in which less contaminated scrap, including substandard products, is reused as alloy material after being re-melted with flux. However, the practicality of this method remains unclear.

Recycling through the wet process[18–24] described in Figure 7 is a highly practical and widely accepted method for processing scrap, including sludge that contains rare earths (see Figure 8). However, this recycling method is a multistage process that requires dissolution with a strong acid and generates a large volume of waste from the difficult preparation of the dissolving solution. Accordingly, environment loads increase when a large amount of scrap is processed. Therefore, this method generates high waste treatment costs in developed countries that impose strict environmental regulations, and the economic rationality is high

Fig. 6—Photographs of molten salt electrolysis process for producing rare earth metals and alloys in a plant of China. (Courtesy of Dr. Eiji Nakamura of Santoku Co. Ltd.).

Table IV. Recycling Processes of Nd-Fe-B Magnet Scrap[15,16]

(1) Material recycling method
  Hydro-metallurgical method (Wet process)
    (1)-a Fluoride precipitation
    (1)-b Oxalates precipitation
    (1)-c Sulfate crystallization
    (1)-d Nitrate precipitation
  Pyro-metallurgical method (Dry process)
    (1)-e CVT (Murase *et al.* fundamental study)
    (1)-f Selective chlorination and distillation (Uda *et al.* fundamental study)
    (1)-g Selective extraction (Okabe *et al.* fundamental study) *etc.*
(2) Alloy recycling method
  (2)-a Electrolytic regeneration
  (2)-b Remelting by high frequency induction heating
    Remelting with flux
    Remelting by Arc melting
    Remelting by electron beam melting
    Remelting by zone melting *etc.*
  (2)-c Reduction and deoxidation with hydrogen and calcium
  (2)-d Deoxidation with calcium and halide flux
  (2)-e Electrochemical deoxidation
(3) Magnet recycling method
  (3)-a Magnet alloy recycling (regeneration of magnet by adding virgin material into scrap powder)
  (3)-b Cascade recycling (reuse to the lower spec application)

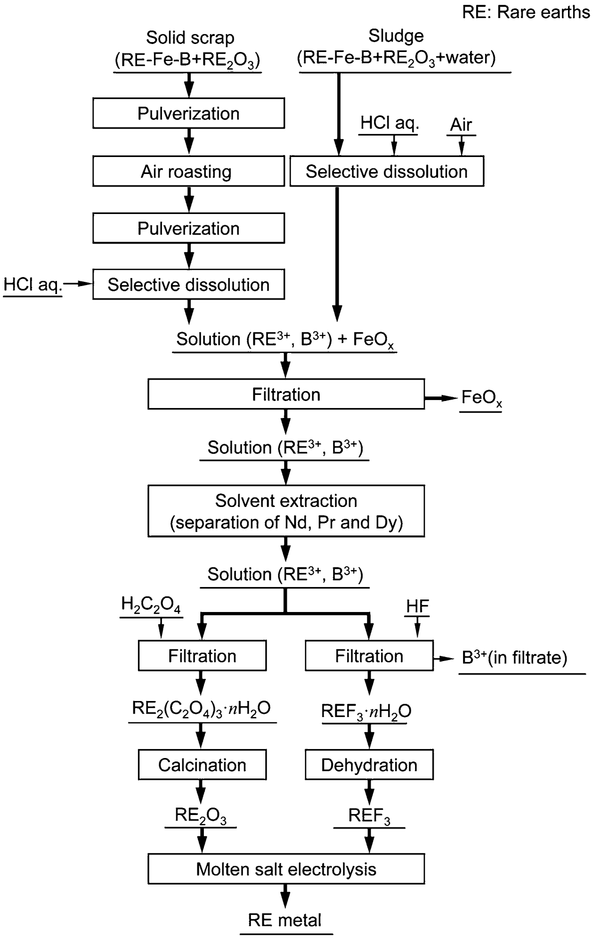


Fig. 7—Recycling process for rare earths from Nd-Fe-B magnet scraps based on hydrometallurgical method.[18–24]

for sending scrap generated in developed countries overseas. However, when recycling is considered a buffer for overcoming supply shortages, it is preferable to develop new technologies and to build an economic system where magnet scrap can be efficiently recovered and where valuable metals can be extracted for cyclical resource use.

The development of efficient recycling technologies is also important for rare metal resource conservation, and rare earth magnet companies are currently developing methods for recovering alloy scrap. However, few recycling technologies have actually been implemented in Japan to date due to numerous financial and technical issues.

Reviews on the recycling of neodymium magnets have already been published by Machida[26] and the authors.[15–17] Therefore, this section focuses on basic research to provide an overview of existing technologies and to introduce several recent studies. For the recycling of rare earths in general, refer to the reviews by Harada and Nakamura[19] and Tanaka *et al.*[20]

Sludge generated through the magnet production process often contains impurities (*e.g.,* carbon and silicon) derived from the cutting tools and is also often contaminated and oxidized by water and oil. Although

Fig. 8—Photographs of solvent extraction process for mutual separation of rare earths in a plant of China. (Courtesy of Prof. Atsushi Shibayama of Akita University).

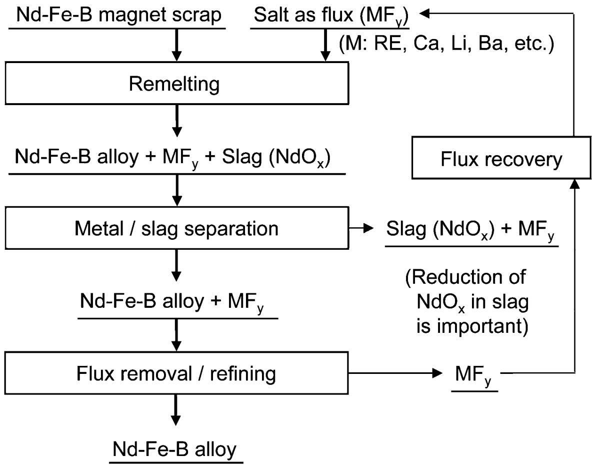


Fig. 9—Recovery process of Nd from Nd-Fe-B magnet scrap by remelting.[26,27,37–40]

the sludge is usually injected into the smelting process and then recycled as raw material, attempts have also been made to reuse the sludge as alloy.[27–29] Other methods include the regeneration of alloys by melting scrap with flux, improving the separation of slag and metal, and improving the deoxidizing ability of metallic calcium. The effectiveness of these methods has been demonstrated.[30–36] However, the practicality of these recycling technologies is unclear due to issues involving the balance between the cost and quality of the alloys regenerated, the yield ratio of rare earths, and the treatment of additional waste.

Previous studies on the recycling process for neodymium magnets include various examples, such as the wet process and the re-melting of alloys shown in Figure 7[18–24] and Figure 9,[26,27,37–40] respectively. Recycling through the wet process described in (1)-a through (1)-d in Table IV is a common treatment method for sludge-containing rare earths. However, this process requires dissolution with strong acids and a multistep process that employs oxalic and hydrofluoric acids, which generates a large volume of waste. As a result, this method is expected to cause heavy environmental burdens for treating a large amount of scrap.

Lyman and Palmer[41] attempted to recover rare earths by dissolving magnet scrap with sulfuric acid and then precipitating the rare earths as a double salt with sodium and ammonia in order to improve recycling yield through the wet process. Rare earth fluoride was recovered by adding hydrogen fluoride to the double salt. They claim that the filterability of the precipitates was improved compared to techniques where the fluorides were directly precipitated from an acidic solution containing rare earth ions. However, purity must be improved in this method because a small percentage of sodium often remains in the final fluoride product.

Sato *et al.*[42] successfully recovered neodymium after selective crystallization, where the magnet scrap was dissolved using a mixture of sulfuric and nitric acids and alcohol (ethanol) was added to decrease the solubility of the sulfate in neodymium. Because the addition of alcohol did not decrease the solubility of ferrous sulfate, the ferrous impurity was minimized to less than 1 pct. The further development of this approach for practical use can be expected in the future, because a sufficient level of separation was attainable with the simple operation of this method.

Koyama *et al.*[43] attempted to increase the leaching speed by using an autoclave during the selective dissolution and extraction of rare earths from magnet scrap with hydrochloric acid. Over 80 pct of the rare earths were leached in 2 hours at 453 K (180 °C). Elevating the leaching temperature both increased the speed and improved the selectivity of rare earth recovery because the range of pH in which solid Fe_2O_3 is stable expanded at a higher temperature, making it hard for iron to be soluble. As a result, the elution ratio for iron was minimized to less than 3 pct. This method is expected to be developed as a high-speed extraction method.

Tanaka *et al.*[44] tested the mutual separation of neodymium and dysprosium in the acidic solution using solvent extraction. After an organic phase was obtained by extracting both neodymium and dysprosium from the magnet scrap, neodymium was selectively stripped first with a low concentration acid, and dysprosium was then stripped with a higher concentration acid. As a result, the neodymium purity in the water phase reached 99.5 pct. This technique will likely be developed as an advanced separation method with high purification capacity.

On the other hand, the re-melting method shown in (2)-a through (2)-e in Table IV is a dry (pyrometallurgical) process, where fluoride is added as a flux and alloys are re-melted in order to remove impurities. Although this method yields minimal waste products, issues remain that are related to the partial oxidation of neodymium, the separation of the slag and alloy, and the control of impurity concentrations in the final alloy product (see Figure 9). In addition, the composition of alloys should be adjusted before reuse. At the current level of technology, the practical use of this method has rarely been achieved due to difficulties with the separation of the slag and metal generated by melting the scrap, low yield ratios for valuable metals in the regeneration process, and the generation of new wastes such as slag containing valuable metals from recycling. However, some alloy scraps generated from the magnet production process have been recycled recently using alloy re-melting methods.

Mainly for economic reasons, recycling processes for rare earths currently target cases where it is possible to predict the recycling and recovery routes of in-plant scrap as well as the types of impurities and their content, such as magnet scrap with familiar compositions. However, in order to consider the mass treatment of product scrap that will be generated in the future and the reuse of neodymium magnets, contamination by other metals (*e.g.,* iron, aluminum, and copper) and the variability of magnet alloy compositions must be taken into account. In some instances, dysprosium is added to neodymium magnets from the surface of the magnets by diffusing dysprosium or dysprosium compounds through grain boundaries.[40] Thus, it is preferable to isolate dysprosium from neodymium during the recycling process.

VI. BASIC RESEARCH ON PYROMETALLURGICAL RECYCLING TECHNOLOGIES FOR NEODYMIUM MAGNETS

New technologies for the low-cost, highly efficient recovery of rare earth metals from scrap have been developed worldwide. For example, Murase and coworkers[45–49] developed a new smelting process called the "chemical vapor transport method" as described in Figure 10. This method first causes aluminum chloride vapor to react with magnet alloy scraps at high temperatures to form a high vapor pressure complex that contains rare earths. This complex is then separated, and rare earths are recovered, using the difference in vapor pressures between the complexes.

Uda *et al.*[50,51] developed a selective reduction and distillation process that utilizes the disparities in vapor pressure caused by differences in the oxidation state between rare earth chlorides (or iodides). The principle behind separation and recovery in this method is identical to that of the chemical vapor transport (CVT) method, which uses the aforementioned disparities in vapor pressure. However, the process is innovative because it focuses on the substantial differences in vapor pressure among halides such as rare earth chlorides, in their divalent ($RECl_2$) and trivalent ($RECl_3$) states. This technique also substantially improves on the separation efficiency as indicated in Figure 11. Although it is difficult to separate and to refine rare earth elements simultaneously and given that tens to several hundreds of steps are required to conduct solvent extraction, the future development of this method is likely because it can efficiently and simultaneously separate rare earths using a high-temperature process that consists of one or a few steps.

As described in Figure 12, Uda[52] also developed a process in which neodymium in rare earth alloy sludge is selectively separated and recovered *via* chlorination with an iron chloride. As the schematic diagram for this reaction suggests, a chlorine-based recycling process can be developed in which only water and carbon are consumed in principle. Moreover, this technique only generates by-products that are comprised of carbon dioxide, hydrogen gas, and iron alloy, all of which have low environmental loads. REOs produced from this process can be used as raw materials for the electrolysis of oxide in molten fluoride.

Takeda and coworkers[53–56] conducted basic research on a new process that extracts neodymium metals directly from magnet alloy scrap without oxidation.

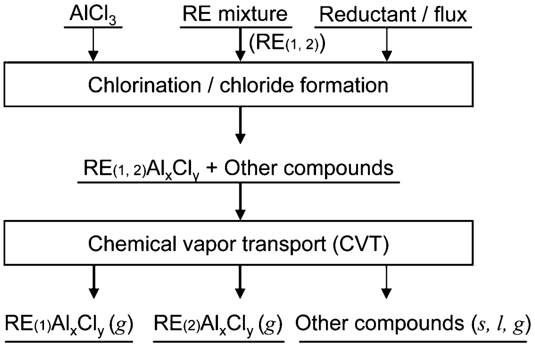


Fig. 10—Separation and refining process of rare earth compounds by CVT.[45–49]

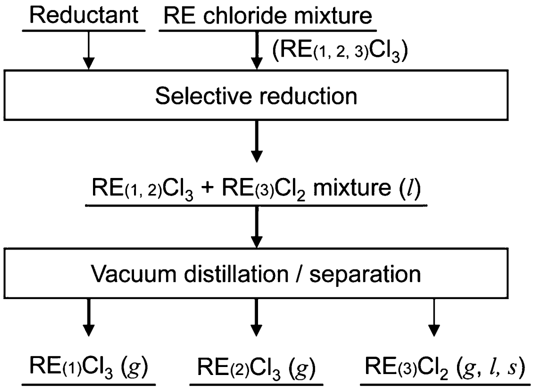


Fig. 11—Selective reduction and distillation process of rare earth chloride (or iodide) by utilizing difference of vapor pressure between multiple oxidation states.[50,51]

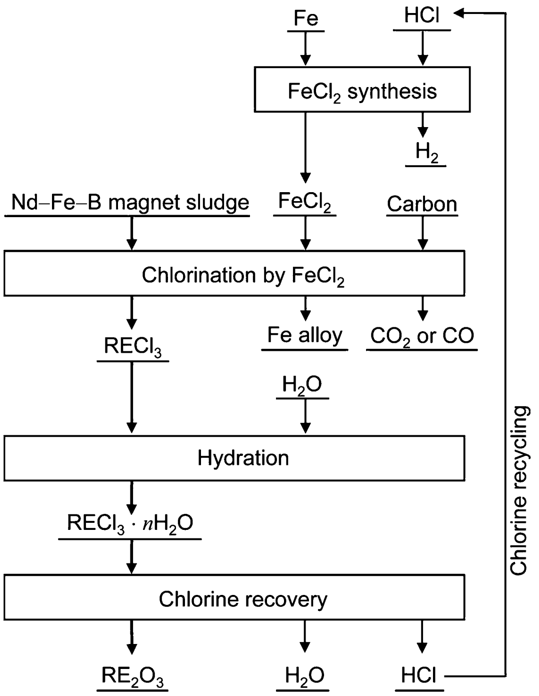


Fig. 12—Separation and recovery process of Nd from magnet alloy sludge by utilizing iron chloride as chlorinating agent.[52]

Figure 13 shows an example of a recycling technology in which neodymium is selectively extracted as a pure metal directly from an alloy, using molten magnesium and silver as extracting agents.[53–57] This method permits the use of magnesium and silver scraps as extracting agents, allowing the target rare earths to be selectively extracted, concentrated, and separated without oxidation. In addition, a new process is expected to be developed for the efficient separation and recovery of rare metals (*i.e.*, valuables) where wastes (*e.g.*, magnet and magnesium scraps) are effectively combined. Technologies that use molten metal as an extracting agent have higher operation costs compared to those that use the wet process. However, molten metal methods have advantages because waste solution treatment is not required, which is particularly important for recycling in developed countries with strict environmental regulations. Recently, Japanese companies and South Korean research institutions have made a variety of technological developments.[58,59]

Machida and coworkers[28,60–63] multifariously investigated a process in which magnet scrap is cascade-recycled (down-grade recycling). Although this method is advantageous for the efficient use of magnet scrap without consuming high amounts of energy, it can be difficult to balance the amount of generated scrap and the expected specification for cascade-recycled products with the actual demand. Previous studies have tested the use of magnet powders from scrap as a raw material. However, the effectiveness of such methods is not clear in terms of quality control.[64,65]

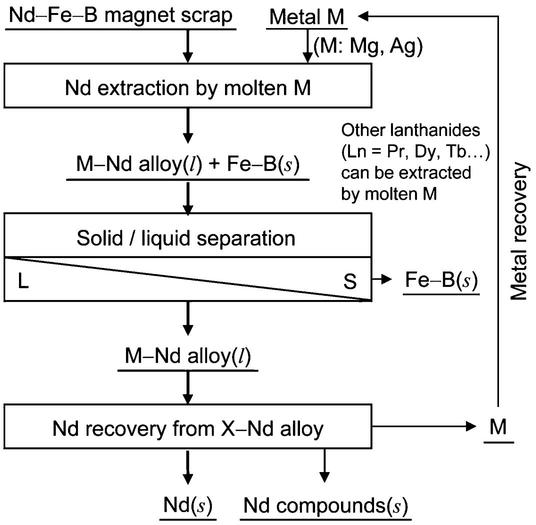


Fig. 13—Selective extraction process of Nd metal directly from Nd-Fe-B magnet scrap by utilizing molten metals as an extraction medium.[53–57,59]

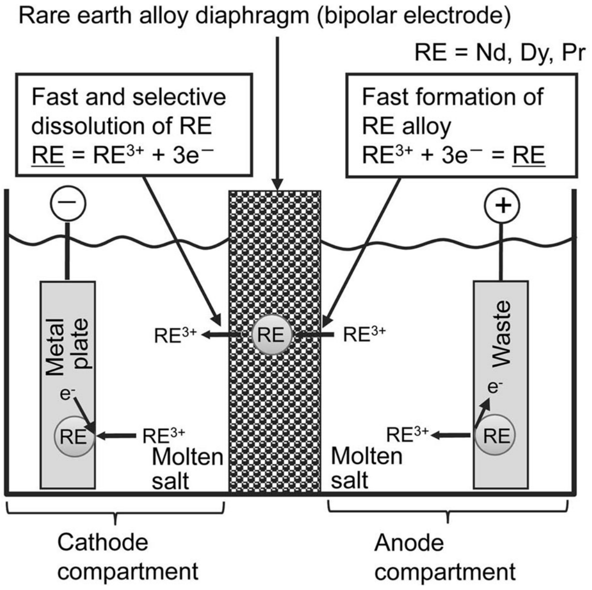


Fig. 14—Separation and recovery process of rare earth metals *via* molten salt electrolysis using alloy diaphragm.[66–70]

Recent studies on recycling technologies include rare earth metal separation and recovery using molten salt and an alloy diaphragm[66–70] and the refining of magnet alloys using molten fluoride.[71–73] Konishi and coworkers[66–70] developed an approach for separating and recovering rare earth metals using molten salt electrolysis and a bipolar alloy diaphragm. As Figure 14 shows, waste containing rare earths is used as the anode, and rare earths are anodically dissolved by molten salt electrolysis. Then, the rare earth ions are reduced on the anode compartment side of the alloy diaphragm. The rare earth ions reduced on the bipolar diaphragm react with the bipolar electrode, form rare earth alloys, and become diffused inside the diaphragm. The diffusing rare earth elements in the electrode are anodically re-dissolved on the surface of the cathode compartment side of the diaphragm. Finally, the rare earths precip-

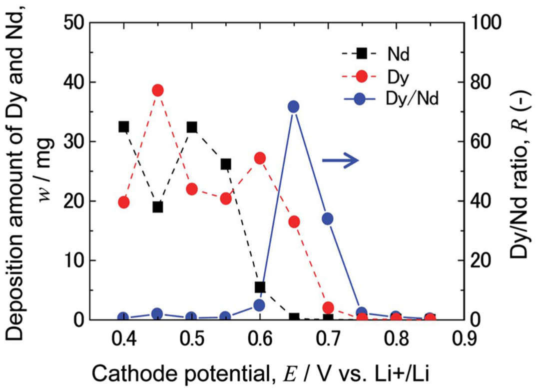


Fig. 15—Deposition amount of Dy and Nd in molten salt electrolysis using alloy diaphragm [723 K (450 °C)].[70]

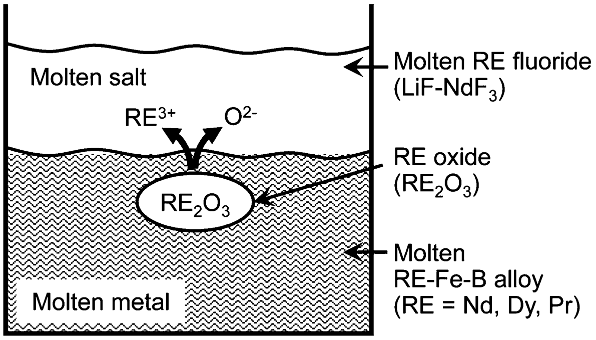


Fig. 16—Extraction process of RE oxide from magnet waste using molten fluoride.[71–73] (see Fig. 7 for process chart).

itate as a highly pure metal when the rare earth ions on the cathode compartment side are reduced on the cathode *via* molten salt. It has been experimentally demonstrated that dysprosium can be selectively separated from a mixture of dysprosium and neodymium by adequately controlling the electrolysis voltage (Figure 15[70]). Many issues still need to be resolved before this method can be implemented in a practical manner for treating actual scrap. Furthermore, practical use also appears to be limited by the current cell design. However, the process is advantageous because it allows for the simultaneous extraction and separation of materials.

As shown in Figure 16, Takeda *et al.*[71–74] developed a process in which molten fluoride is utilized to extract and to separate REOs, which become harmful for recycling when magnets are reproduced from magnet alloy waste. Alloys that are refined by removing oxides are used as a master alloy for magnets, and REOs extracted with fluoride are regenerated as rare earth metals with molten salt electrolysis. Because this process is relatively simple and consumes less energy by regenerating magnet alloys without oxidation, this approach is highly practical for industrial use. Figure 17 presents an example of the experimental extraction results,[74] where the oxygen concentration in the magnet alloy waste was reduced from 5,000 ppm to less than 200 ppm. Although many studies have been conducted in the past on similar refining processes that use flux for melting (see Figure 9), the concentration of impurities and the yield of the alloys have traditionally been a problem. The recent research by Takeda *et al.* experimentally demonstrated the approach's ability to produce alloys with low concentrations of impurities using molten fluoride. This approach will likely be developed as a recycling process with a short recycling path that does not require that wastes be fed back into the smelting process.

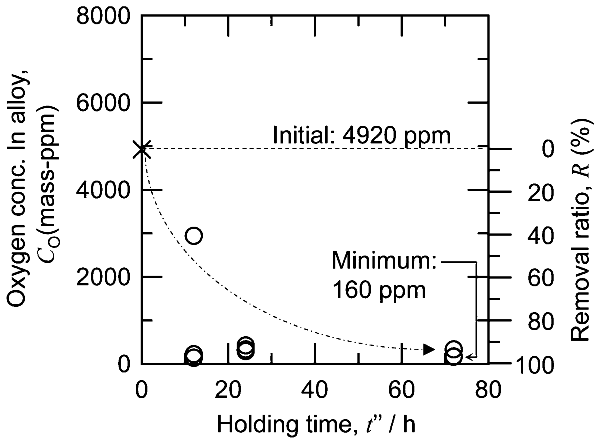


Fig. 17—Oxygen concentration in magnet alloy after extraction of oxide using molten fluoride [1503 K (1230 °C)].[74]

While recycling technologies that employ ionic liquids have also been investigated,[75] their effectiveness as an industrial process remains unclear to date.

Kubo *et al.*[76] investigated the rare earth recovery process using B_2O_3 as a flux. In this process, rare earths (RE) contained in neodymium magnet alloys are oxidized and extracted into the B_2O_3 flux. The rare earths are then separated and concentrated through the formation of RE_xO_y-B_2O_3 melt, which contains 50 mass pct RE_xO_y and B_2O_3 melt (immiscibility gap). Saito *et al.*[77] also investigated a similar recycling process. Kubo *et al.* efficiently removed iron in the magnet alloy as a molten Fe-C alloy by adding carbon in order to decrease the melting temperature of the iron alloy phase. The concentrations of rare earths (neodymium, dysprosium, and praseodymium) in the iron alloy were subsequently lowered to less than 0.01 mass pct, and almost all rare earths were extracted into the molten RE_xO_y-B_2O_3 phase. Finally, the rare earths were leached with hydrochloric acid and precipitated as an oxalate. This process is suitable for the large-scale treatment of magnet wastes containing iron.

Okabe and coworkers[78–80] recently conducted a basic study to develop a process where molten halide is used to recycle neodymium magnet scrap. As Figure 18 shows, molten salt (halide salt) such as chloride or iodide is used in this method to separate and to refine rare earths. In principle, rare earths in the magnet are selectively oxidized (*i.e.,* through chlorination or iodization), leached into the molten salt, and then separated by immersing the neodymium magnets into the molten salt. Because the reaction product is a rare-earth halide,

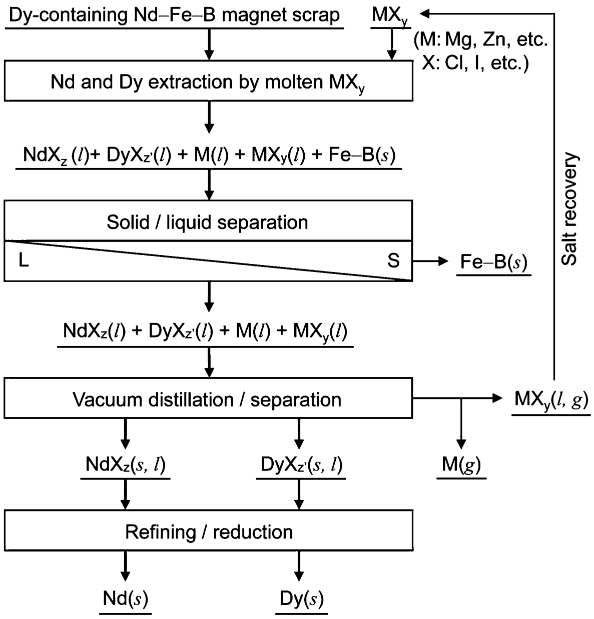


Fig. 18—Recovery process of rare earths from Nd-Fe-B magnet scrap by utilizing molten halide salt as an extraction medium.[78–80]

it is possible to separate rare earth compounds from the extraction medium in this process using the differences in vapor pressure, resulting in the simultaneous separation of rare earth elements. Thus, this process should be appropriate for treating large volumes of scrap. Based on a thermodynamic investigation, an extraction medium was chosen to selectively extract only rare earth elements from neodymium magnet alloys. Experiments were then conducted to extract and to separate rare earths from scrap using molten magnesium chloride ($MgCl_2$) as the extraction medium. The results of these experiments revealed that approximately 80 pct of neodymium and dysprosium could be efficiently extracted as a chloride from magnet alloy scrap following 12 hours of reaction.[78–80] A basic study was also conducted to evaluate a new recycling process that uses zinc iodide (ZnI_2) as the extraction medium. The results of this study showed that the process could selectively and efficiently extract neodymium and dysprosium from magnet alloys and that neodymium and dysprosium could be efficiently concentrated and separated by distilling the iodides.

Current recycling processes for rare earth metals and magnet wastes primarily employ the wet process. However, the use of pyrometallurgical processes could be preferable in developed countries, where environmental regulations require minimal waste solution discharge, or in a system where large volumes of scrap with the similar characteristics and quality are available.

The development of most of the recycling technologies discussed in this paper is currently still in preliminary stage (see Table V[74]). However, these technologies may be applied to new recycling processes where neodymium and dysprosium are directly extracted from magnet alloy scrap, as for EV and HEV motors. Constructing a new, environmentally friendly recycling process for magnet scrap that contains valuable rare metals (*e.g.*, dysprosium) is expected to be an important challenge in the future.

VII. CONCLUSIONS

Today's so-called "high-technology" cannot exist without rare metals. Japan has supplied high-performance industrial products to the world using high-tech products made with rare metals. However, mineral resources for rare metals are scarce in Japan, and most of the important rare metal resources are unevenly located in a few particular countries such as China. Therefore, securing a consistent, stable supply of rare metals is critically important for maintaining Japan's industrial competitiveness and national security. In general, developed countries must invest in resource recycling and advocate for changes in the industrial structure by cultivating manufacturing processes that do not rely on foreign resources, recycle rare materials, and minimize environmental wastes.

Japan is a leading producer of rare metals that are essential for the high-tech industry. Despite obstacles related to high labor and energy costs and strict environmental regulations, Japan produces large quantities of rare metals by importing mineral resources. In particular, Japan is competitive in the production of high-tech, electronic devices that require difficult refining processes, advanced manufacturing technologies, and high-purity rare metals and compounds. For Japan to maintain its top position in rare metal production and resource security, the development of new processes,

Table V. Examples of Research of Pyrometallurgical Recycling Processes for Nd-Fe-B Magnet[74]

Recycling as raw materials (Extraction type)
1. Extraction and separation of rare earths from waste using chemical vapor transport (Murase 1995[47])
2. Mutual separation of rare earths using selective reduction and distillation (Uda 2000[50])
3. Extraction and separation of rare earths using selective chlorination and distillation (Uda 2002[52], Shirayama 2008[78])
4. Extraction of separation of rare earth metals using molten metal as an extraction medium (Takeda 2006[56], Xu 2000[57], Chae 2014[59])
5. Electrochemical extraction and separation of rare earth metals using alloy diaphragm (Nohira 2010[67])

Recycling as magnet alloy (Refining type)
1. Refining of rare earth metals using electrochemical deoxidation (Okabe 1998[31], Hirota 1999[32])
2. Refining of alloy using oxidative decarburization and calcium reduction/deoxidation (Okabe 1998[31], Suzuki 2001[34])
3. Refining of alloy using molten fluoride flux remelting (Takeda 2009[71])

including the recycling of domestically accumulated scrap, is imperative.

Because the demand for rare earth elements such as neodymium and dysprosium, used as raw materials in permanent magnets, is expected to increase rapidly in the near future, the development of recycling technologies for these rare earths is essential for resource security. The use, demand, and importance of rare earth elements and their compounds will continue to expand through the 21st century, which will require the development of new recycling technologies that are suitable for various types of scrap. Given that high-quality rare earth mines are concentrated in China, advanced recycling technologies for rare earth elements such as neodymium and dysprosium and the reuse of products and scrap are critical for maintaining resource security and supply stability.[81]

In a country that strives to become a resource recycling-based nation, recycling technologies, social systems for rare metals, reliable resource buffers (buffering function), and the security of stable resource routes that allow for continuous supply and recycling are important.[82] Rare metal production from scrap using new recycling technologies would contribute to the conservation of finite and valuable mineral resources and to the establishment of a recycling-based society that can respond to environmental issues.

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