



(51) International Patent Classification:

C22B 59/00 (2006.01) C22B 3/24 (2006.01)
C22B 3/32 (2006.01)

(21) International Application Number:

PCT/US2016/041685

(22) International Filing Date:

11 July 2016 (11.07.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/191,238 10 July 2015 (10.07.2015) US

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77204 (US).(74) Agent: STROZIER, Robert W.; P.O. Box 429, Bellaire,
TX 77402-0429 (US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
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PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: AN IMPROVED PROCESS FOR THE RECOVERY OF RARE EARTH METALS FROM PERMANENT MAGNETS

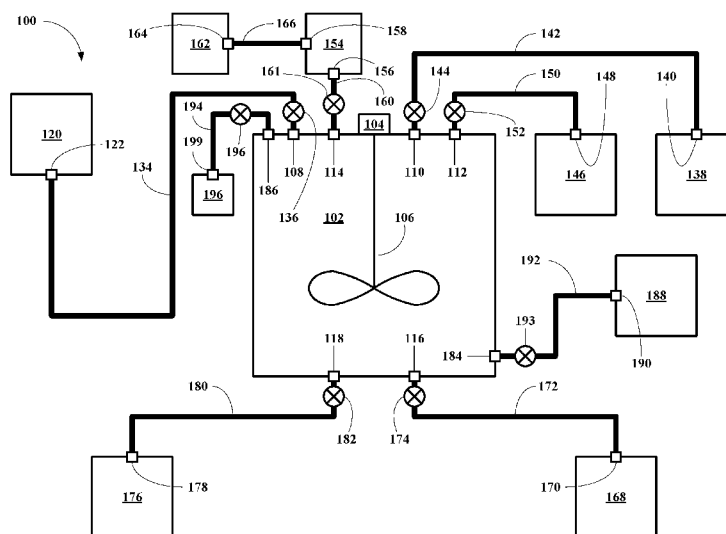


FIG. 1A

(57) Abstract: Systems and methods for recovering rare earth metals from rare earth metal-containing magnets includes fragmenting or commutating the magnets, contacting the commutated magnets with a mixture of low molecular weight carboxylic acids such as formic acid and water, and removing or extracting non-rare earth metal carboxylate phases such as an iron carboxylate (formate) phase from a rare earth metal carboxylate (formate) phase, using a solvent such as water.

TITLE: **AN IMPROVED PROCESS FOR THE RECOVERY OF RARE EARTH METALS FROM PERMANENT MAGNETS**

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ASSIGNEE: **THE UNIVERSITY OF HOUSTON SYSTEM**

RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of United States Provisional Patent Application Serial No. 62/191,238, filed 07/10/2015 (10 July 2015).

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] Embodiments of the present invention relate to systems and methods for recycling rare earth elements from end-of use products containing rare earth magnets.

[0003] More particularly, embodiments of this invention relates to systems and methods for recycling rare earth elements from end-of use products containing rare earth magnets, especially neodymium-iron-boron (NdFeB) magnets, where the methods include the steps of optionally fragmenting or commutating the magnets, contacting the commutated magnets with a mixture of formic acid and water to form rare earth metal (**REM**) formate precipitates (**REM(HCOO)₃**), separating the filtrate, which is impregnated with non-rare earth metal (**NREM**) components including iron formates (**Fe(HCOO)₂**) and borate/boric acid (**BO₃⁻/H₃BO₃**) by a solid-liquid separation, and purifying the precipitated **REM(HCOO)₃** by washing with excess water, and calcining the recovered **REM(HCOO)₃** products to rare earth oxides (**REM₂O₃** and **REM₆O₁₁**).

2. Description of the Related Art

[0004] NdFeB permanent magnets are fundamental components for various clean energy and high technology applications. NdFeB magnets are used, for example, in electric motors, wind turbines, missile guidance systems, hard drives, speakers, and many other existing and new technologies. The rare earth metals (**REMs**) in NdFeB magnets may also include, but not limited to, combinations of neodymium (Nd), praseodymium (Pr), Dysprosium (Dy), and Terbium (Tb). In some context Gadolinium (Gd) and Samarium (Sm) may also present. Nd and Dy, the primary rare earth components of NdFeB magnets are classified as two of the most critical rare earth elements in terms of supply risk and importance to advance technological fields by the U.S. Department of Energy.¹ In 2015, global demand for neodymium and dysprosium is projected to rise to 45,500MT with an imminent supply shortage of 34,700MT global production.²

[0005] Currently, the primary source for Nd and Dy are from rare earth element mining companies. The global rare earth supply, however, has not been increasing as quickly as the rise in demand due

to long lead times, trade policies, environmental concerns, and other factors effecting rare earth mining. Thus, recycling of NdFeB magnets to recover Nd and Dy is considered an attractive approach to mitigate the global rare earth supply shortage. Although commercial scale waste NdFeB magnets recycling efforts are almost non-existent to date, several research projects on NdFeB magnets recycling have been reported.

[0006] Prior art and literature on methods for rare earth magnet recycling mostly comprise of hydrometallurgical methods³ and pyrometallurgical methods.⁴ Recently, hydrogen decrepitation (HD) methods,⁵ gas-phase extraction methods,⁶ and hydrothermal methods⁷ were proposed as alternate approaches. The different recycling routes have, however, different advantages and disadvantages, described in greater detail elsewhere.⁸

[0007] Hydrometallurgical processes are by far the most common and main methods for recycling rare earths. Hydrometallurgical methods are employed mostly in commercial processes of rare earth recovery from primary mineral ores or scrap generated during the magnets manufacturing. A typical hydrometallurgical rare earth recovery process involves strong acid digestion steps which use hydrochloric acid, nitric acid or sulfuric acid to leach the rare earths, followed by a solvent extraction of the rare earth components or by a precipitation of the rare earth components using a suitable precipitating agent such as oxalate, fluoride or double salt sulfate.

[0008] The use of strong acids and the large amounts of chemicals required in hydrometallurgical processes have significant adverse environmental and economic impacts. The processes result in large amounts of liquid acid waste which causes significant waste disposal issues. During the extraction step, an excess amount, about 10 times or more of the stoichiometric amount of acid is used to enhance the stripping effect. Some of the chemicals used in the recovery processes such as fluorides, nitrates and sulfates, generate toxic, strongly oxidizing or air-polluting gases such as HF, NO₂, SO₂ and H₂S. From the economic perspective, obtaining high-purity single rare earth products is a common problem. In current processes co-precipitation of contaminants along with the rare earth phases is commonly observed. Most of these co-precipitated phases are not easily removable. Several other steps such as re-dissolution and re-precipitation are needed to purify the rare earth phases. The overall process is complex and multi-step resulting in longer lead times, low yields and high production costs. As a consequence it is hard to implement such methods in industrial rare earth recycling processes.

[0009] The methods disclosed in the prior art for NdFeB magnet recycling are mainly the methods for rare earth recovery from the pre-consumer production scrap or sludge. The end-of-use magnet scrap recycling is minimally researched or disclosed in the prior art. Thus, the effect of other waste materials such as the protective coating of the magnets on the recycling process is not well known.

In an ideal approach, the rare earth elements need to be selectively recovered, leaving behind all the other waste materials. Given the fact that protective coating consists of nickel and copper metals, it is nearly impossible to avoid these metal ions dissolving in the leaching solution. This makes the recycling of post-consumer NdFeB magnets more complex given the need to avoid all other elements including Fe, B, Ni, and Cu in the final rare earth product.

[0010] In a previous patent application US9376735B2 issued June 28, 2016 entitled "Methods and Systems for Recovering Rare Earth Elements" to Jacobson and Samarasekera, we disclosed methods and systems for recovering or extracting rare earth elements under mild conditions using a rare earth element crystallization approach. We used a crystallization medium under solvothermal conditions sufficient to form rare earth element crystals capable of gravity separation and purification. This previous invention used formamide with the addition of small amounts of formic acid and water as the dissolution and crystallization medium. Several other metals for rare earth metal recovery have been proposed such as US20110023660A1 published February 3, 2011 entitled Method and Apparatus for Recovery of Rare Earth Element, US005429724A published July 4, 1995 entitled Neodymium Recovery Process, and US6533837B1 issued March 18, 2003 entitled Method of Recovering and Recycling Magnetic Powder from Rare Earth Bond Magnet.

[0011] While several methods have been represented above, there is a significant need for better approaches for the efficient, economical and more environmental friendly recycling of rare earth elements.

SUMMARY OF THE INVENTION

[0012] Embodiments of the present invention provide methods for recovering rare earth metals (**REMs**) from waste magnets comprising contacting a rare earth metal-containing magnet material with a reactant composition including a low molecular weight carboxylic acid and water under reaction conditions sufficient to dissolve or extract and concurrently precipitate rare earth metals from the rare earth metal-containing magnet material forming a precipitate including rare earth metal carboxylates and non-rare earth metal components, and removing the non-rare earth metal components from the rare earth metal carboxylates with water to form a purified rare earth metal carboxylate product.

[0013] Embodiments of the present invention provide methods for recovering rare earth metals (**REMs**) from rare earth containing magnets, where the methods include a reaction step, where rare earth metal containing magnets are reacted with a formic acid/water mixture to dissolve rare earth metals and non-rare earth metals from the magnets forming rare earth metal (**REM**) formates and non-rare earth metal (**NREM**) formates and/or other **NREM** components. The **REM** formate precipitates, while the **NREM** formates and/or other **NREM** components are more soluble and either

remain in solution or form part of the precipitate. The methods also include filtrating the precipitates from the reaction mixture and washing the precipitate with a solvent to extract any remaining non-rare earth metal formates in the precipitate leaving a purer rare earth formate product, where the solvent is characterized in that the **NREM** formates and/or other **NREM** components are more soluble in the solvent than the **REM** formates. The methods of this invention are economical due to the minimum number of process steps and minimum chemical usage. As the reaction involves a metal reacting with an acid, the reaction generates a stoichiometric amount of hydrogen gas. The hydrogen gas may be disposed of by controlled burning in a combustion unit, feed to a hydrogen fuel cell for energy production, used in a hydrogenation reaction, or captured and stored for subsequent use. Thus, in certain embodiments, the hydrogen gas may be used as a fuel source to supply some or all of the energy needed to heat the reaction vessel.

[0014] The methods of this invention were successfully tested using NdFeB magnets recovered from hard disk drives, but may be used with any type of **REM** containing magnet products. The methods of this invention may be performed with or without any pretreatment steps, such as demagnetization or protective coating removal. Thus, the methods of this invention are simpler, less environmentally destructive or disruptive, and/or are a more economical approach for recovering rare earth elements from the **REM** containing magnets such as NdFeB magnets. The experiments have shown that the methods of this invention are capable of recovering at least 75% of the **REMs** present in the **REM** containing magnet materials. In certain embodiments, the recovery rate is as least 80% of the **REMs** present in the **REM** containing magnet materials. In other embodiments, the recovery rate is as least 85% of the **REMs** present in the **REM** containing magnet materials. In other embodiments, the recovery rate is as least 90% of the **REMs** present in the **REM** containing magnet materials. In other embodiments, the recovery rate is as least 95% of the **REMs** present in the **REM** containing magnet materials. Chemical analysis of the final rare earth product phases has shown that the methods of this invention are capable of recovering **REM** formates in greater than 90% purity, for example about 99% purity relative to the **NREMs**.

[0015] Embodiments of the present invention provide systems comprising a reaction vessel including a rare earth metal containing-magnet material input connect to a rare earth metal containing-magnet material source, a low molecular weight carboxylic acid input connected to a low molecular weight carboxylic acid source, a water input connected to a water source, a waste liquid outlet connected to a waste liquid receiver and a rare earth metal product outlet connected to a rare earth metal product receiver, where an amount of the rare earth metal containing-magnet material, the low molecular weight carboxylic acid and the water are added to the reaction vessel to form a reaction mixture and the reaction mixture is held under reaction conditions sufficient to dissolve or extract the rare earth

metals to form rare earth metal carboxylates along with non-rare earth metal carboxylate hydrates that precipitate out of the reaction mixture, and a separating vessel to separate the precipitate from the liquid and to wash the precipitate with a solvent to remove the non-rare earth metal carboxylate hydrates to form a purified rare earth carboxylate product.

[0016] Embodiments of the present invention provide systems for recovering **REMs** from **REM** containing magnet materials, where the systems include a reaction subsystem, a separation subsystem, and extraction subsystem. The reaction subsystem includes at least one reaction vessel for contacting a **REM** containing magnet materials with an aqueous formic acid solution or a mixtures of formic acid and water as a reactant composition to dissolve and/or extract the **REMs** contained in the **REM** containing magnet materials. The separation subsystem includes at least one separation vessel for removing a precipitate from a liquid. The extraction subsystem includes at least one extraction vessel for removing or extracting residual **NREM** formates from **REM** formates. The systems and methods operate on the basis of the differential solubility of the **REM** formates compared to the **NREM** formates in the solvent used to remove or extract residual **NREM** formates from the precipitate resulting in a substantially pure **REM** formate product. In certain cases, the magnets are coated with a protective coating, typically a copper nickel coating comprising either layers of Cu and Ni or a Cu/Ni alloy. These coatings minimally dissolve in the formic acid/water mixture and most remain behind in the precipitate and do not appear to interfere with the extraction and/or dissolution process, but the coating pieces in the precipitate may be readily removed magnetically.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawings in which like elements are numbered the same:

[0018] **Figure 1** depicts a first embodiment of a system of this invention.

[0019] **Figure 2** depicts a second embodiment of a system of this invention.

[0020] **Figure 3** depicts a third embodiment of a system of this invention.

[0021] **Figure 4** depicts a fourth embodiment of a method of this invention.

[0022] **Figure 5** depicts powder X-ray patterns (PXRD) of (a) as synthesized solid product of the reaction. Solid phase consists of a mixture of $\text{REM}(\text{HCOO})_3$, where **REM** is a rare earth metal, and $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (b) simulated PXRD pattern of $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (c) simulated PXRD pattern of $\text{Nd}(\text{HCOO})_3$; and (d) nearly-pure $\text{REM}(\text{HCOO})_3$ phase after $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ removal.

[0023] **Figures 6a&b** depicts SEM micrographs and EDX analysis of; (a) as-synthesized rare $\text{REM}(\text{HCOO})_3$ crystals; (b) a rare earth metal oxide product after annealing.

DEFINITIONS OF TERM USED IN THE INVENTION

[0024] The following definitions are provided in order to aid those skilled in the art in understanding

the detailed description of the present invention.

[0025] The term "about" means that the value is within about 10% of the indicated value. In certain embodiments, the value is within about 5% of the indicated value. In certain embodiments, the value is within about 2.5% of the indicated value. In certain embodiments, the value is within about 1% of the indicated value.

[0026] The term "substantially" means that the value is within about 5% of the indicated value. In certain embodiments, the value is within about 2.5% of the indicated value. In certain embodiments, the value is within about 1% of the indicated value. In certain embodiments, the value is within about 0.5% of the indicated value. In certain embodiments, the value is within about 0.1% of the indicated value.

[0027] The term "**REM**" means a rare earth metal and **REMs** means rare earth metals selected from the group consisting of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and/or Sc.

[0028] The term "w/w" means weight of magnet materials per weight of dissolving acid or weight of magnet materials to weight of water or weight of dissolving acid to weight of water.

[0029] The term "w/v" means weight of magnet material per volume of solvent.

[0030] The term "v/v" means volume of solute per volume of solvent.

[0031] The term "w/v ratio" means ratio of weight of magnet material to volume of dissolving solvent system.

[0032] The term "v/v ratio" means volume of solute to volume of solvent, here volume of water to dissolving acid.

[0033] The term "wt.%" means weight percent.

[0034] The term "vol.%" means volume percent.

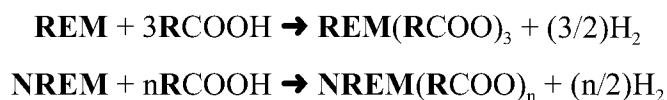
DETAILED DESCRIPTION OF THE INVENTION

[0035] The inventors have found that the present systems and methods overcome the problems discussed above producing an efficient approach to recover rare earths from rare earth metal (**REM**) containing magnet materials such as NdFeB waste magnet materials using an aqueous carboxylic acid solution as the only chemical reagent for dissolving out the **REMs** from the magnets, with or without prior pre-treatment, to form a precipitate from which residual non-rare earth metal (**NREM**) components are removed by solvent washing or extraction leaving a purer **REM** product. In the present invention, post-consumed NdFeB waste magnets were directly contacted and/or reacted with an aqueous acid solution such as an aqueous formic acid solution. The **REMs** were then recovered as insoluble **REM** carboxylates such as **REM** formates of the general formula **REM**(HCOO)₃. Throughout the processes, the carboxylic acid acts both as a leaching agent and a precipitating agent. The extraction and/or dissolution of **REMs** from the magnets and the precipitation

of the **REM** carboxylates occur concurrently and/or simultaneously, thus the process may be classified as a one-pot synthetic approach to **REM** recovery from **REM** containing magnet materials. One especially effective carboxylic acid is formic acid also the smallest carboxylic acid. Formic acid has a low toxicity and a minimal environmental impact. By using stoichiometric amounts of formic acid to react with the **REMs** in the magnet materials, the amount of acid waste generated from the processes may be reduced, minimized, substantially eliminated, or completely eliminated. Besides the formation of **REM** and non-rare earth metal (**NREM**) carboxylates such as formates of iron, nickel or other transitions metals, and borates/boric acid the reaction generates stoichiometric amount of hydrogen gas (H_2).

[0036] In the case of the carboxylic acid being formic acid, several different **REM** formates have been described in the literature. Simple anhydrous **REM** compounds having general formula $REM(HCOO)_3$, have been known for many years and are well characterized structurally.⁹ The compounds have a neutral framework structure composed of REM^{3+} ions coordinated by the oxygen atoms of the formate ligands. The REM^{3+} ions are coordinated by nine oxygen atoms in a tricapped trigonal prismatic geometry. The oxygen atoms of the formate ligand differ; one forms μ^2 -bridges between neighboring REM^{3+} ions, while the second is mono-coordinating. The space group is non-centric.

[0037] The reactant compositions of the present invention comprise an aqueous solution of formic acid or other low molecular weight carboxylic acid. The reaction is characterized by the following reactions of formic acid and **REMs**:



where **REM** is a rare earth metal, **R** is a hydrogen atom or an alkyl group having between 1 and 3 carbon atoms, and **n** is an integer having value between 2 and 3. In certain embodiments, the **REM** is Nd and the **NREM** is Fe and **R** is a hydrogen atom and **n** is 2. As the reaction generation stoichiometric amount of hydrogen gas, the hydrogen gas may be disposed of by controlled burning in a combustion unit, feed to a hydrogen fuel cell for energy production, used in hydrogenation reaction, or captured and stored for subsequent use. Thus, in certain embodiments, the hydrogen gas may be used as a fuel source to supply some or all of the energy needed to heat the reaction to vessel.

[0038] The reaction mixture may be characterized by two ratio: a ratio of magnet material to formic acid and a ratio of formic acid to water or by a single ratio of magnet material to formic acid to water. These ratio are best expressed on a w/w basis. The stoichiometric reactant ratios may be calculated by assuming an irreversible reaction. Based on the balanced equation, the theoretical ratio of magnet materials to formic acid may be calculated as 1:1.44 w/w. Based on the solubility data of

$\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ at 25°C , the theoretical amount of water required to dissolve all the $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ can be calculated as 1:30 w/w magnet materials to water. Thus, the ratio of magnetic material to formic acid to water is 1:1.44:30 w/w. In general operation, the ratio of magnet material to formic acid to water is between about 1:1:20 w/w to about 1:2:50 w/w. In other embodiments, the magnet material to formic acid to water ratio is between about 1:1.2:20 w/w and about 1:1.8:50 w/w. In other embodiments, the magnet material to formic acid to water ratio is between about 1:1.3:20 w/w and about 1:1.6:50 w/w. In other embodiments, the magnet material to formic acid to water ratio is between about 1:1.4:20 w/w and about 1:1.5:50 w/w. In other embodiments, the magnet material to formic acid to water ratio is between about 1:1.4:20 w/w and about 1:1.5:40 w/w.

REACTION CONDITIONS OF THE INVENTION

[0039] The parameters or reaction conditions used in the examples of the reaction processes of this invention including at least reaction temperature, reaction pressure, reaction time, and stirring rate. In general, the reaction temperature is between about 25°C and about 120°C . In certain embodiments, the reaction temperature may be any discrete temperature in the range between about 25°C and about 120°C . In other embodiments, the reaction temperature may be selected from the group of selected from 25°C , 50°C , 75°C , 100°C , and 120°C . In general, the reaction pressure is between about 1 atmosphere and about 5 atmospheres. In other embodiments, the reaction pressure is between about 1 atmosphere and 2 atmospheres. In other embodiments, the pressure is ambient pressure. In general, the reaction time is up to 24 hours or more. In certain embodiments, the reaction time is between about 3 hours and 24 hours. In other embodiments, the reaction time is any discrete time period in the range between 3 hours and 24 hours. In other embodiments, the reaction time is selected from the group consisting of 3 hours, 6 hours, 9 hours, 12 hours, 15 hours, 18 hours, 21 hours, and 24 hours. In general, the rate of stirring is up to 500 rpm or more. In other embodiments, the stirring rate is between about 100 rpm and 500 rpm. In other embodiments, the reaction time is any discrete stirring rate in the range between 100 rpm and 500 rpm. In other embodiments, the stirring rate is selected from the group consisting of 100 rpm, 150 rpm, 200 rpm, 250 rpm, 300 rpm, 350 rpm, 400 rpm, 450 rpm, and 500 rpm.

[0040] Once the rare earth metals are separated as $\text{REM}(\text{HCOO})_3$ product, the precipitate may be converted to economically valuable mixed rare earth oxides through a calcination step. The calcination may be performed by heating $\text{REM}(\text{HCOO})_3$ product to a calcination temperature in the range between about 750°C and about $1,000^\circ\text{C}$ for a calcination time between about 3 hours and about 5 hours.

[0041] It should also be noted that the invention may also be applied to the recovery of REMs from

other **REM** magnet materials including, but not limited to, Samarium-Cobalt (Sm-Co) magnet materials.

SUITABLE REAGENTS AND COMPONENTS OF THE INVENTION

[0042] Suitable reagent used for this processes of this invention include low molecular weight carboxylic acids of the general formula RCOOH or R-C(O)-OH , where **R** is H or an alkyl group having between 1 and 3 carbon atoms. Exemplary examples include, without limitation, formic acid (HCOOH or H-C(O)-OH) representing the smallest member of the carboxylic acids useful in the present invention, acetic acid (CH_3COOH or $\text{CH}_3\text{-C(O)-OH}$), propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$ or $\text{CH}_3\text{CH}_2\text{-C(O)-OH}$), other low molecular weight carboxylic acids, or mixtures and combinations thereof. Formic acid is a weak organic acid and is considered to be a reagent having low toxicity and environmentally friendly solvent due to its low environmental impact. Due to its relatively high hydrogen content, formic acid has been proposed as a valuable, safe and economical hydrogen carrier. Formic acid may be catalytically decomposed to yield hydrogen and carbon dioxide, while in the present invention, the reaction are controlled to yield metal formates and hydrogen gas. Under proper reaction conditions formic acid ionizes to formate anions (HCO_2^- or H-C(O)-O^-) and hydrogen ions (H^+). In this invention, we disclose the use of formic acid as an effective reagent for the recovery of rare earth components from magnets such as NdFeB magnets as rare earth formates of the structure (**REM**(HCOO)₃).

[0043] Suitable rare earth metals (**REMs**) to be extracted by the methods and systems of this invention include, without limitation, Lanthanum (La), Cerium (Ce), praseodymium (Pr), neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), Lutetium (Lu), and mixtures or combinations thereof.

[0044] Suitable non-rare earth metals or elements (**NREMs**) to be extracted by the methods and systems of this invention include, without limitation, iron (Fe), nickel (Ni), copper (Cu), boron (B) other transitions metals generally associated with materials that include **REMs**, and mixtures or combinations thereof.

DETAILED DESCRIPTION OF THE SYSTEM AND METHOD FIGURES

First Embodiment

[0045] Referring now to **Figure 1A**, a first embodiment of system of this invention, generally **100**, is shown to include a heated reaction vessel **102** including a motor **104** and a paddle stirrer **106**. The reaction vessel **102** also includes a **REM** containing magnet material inlet **108**, a water inlet **110** and a formic acid inlet **112**. The reaction vessel **102** also includes a gas outlet **114**, a waste liquid outlet **116** and a **REM** product outlet **118**.

[0046] The system **100** also includes a **REM** containing magnet material source vessel **120** having a **REM** containing magnet material outlet **122**. The outlet **122** is connected to the inlet **108** via a **REM** containing magnet material conduit **134** having a **REM** containing magnet material conduit valve **136**.

[0047] The system **100** also includes a water source vessel **138** having a water outlet **140**. The water outlet **140** is connected to the water inlet **110** via a water conduit **142** having a water conduit valve **144**. The system **100** also includes a formic acid source vessel **146** having a formic acid outlet **148**. The formic acid outlet **148** is connected to the formic acid inlet **112** via a formic acid conduit **150** including a formic acid conduit valve **152**.

[0048] The system **100** also includes a hydrogen gas bubbler **154** having a hydrogen gas inlet **156** and a hydrogen gas outlet **158**, where the gas outlet **114** is connected to the hydrogen gas inlet **156** via a hydrogen gas conduit **160** having a hydrogen gas valve **161**. The system **100** also includes a hydrogen gas utilization or storage unit **162** having a hydrogen gas inlet **164** connected to the hydrogen gas outlet **158** via a second hydrogen gas conduit **166**. In certain embodiments, the hydrogen gas utilization or storage unit **164** may be a combustor, where the heat produced may be used to heat the reaction vessel **102** to a desired elevated temperature. In other embodiments, the hydrogen gas utilization or storage unit **162** may be a hydrogen fuel cell for generating electrical power that may be used to heat the reaction vessel **102** or to power the reaction controllers and other electrical equipment associated with the systems. In other embodiments, the hydrogen gas utilization or storage unit **164** may be a hydrogen gas storage vessel, where the hydrogen gas is stored for latter use such as combustion in combustors or fuel cells or in hydrogenation reactions or in any other process that uses hydrogen gas as a reagent.

[0049] The system **100** also includes a waste liquid vessel **168** having a waste liquid inlet **170**, where the waste liquid outlet **116** is connected to the waste liquid inlet **170** via a waste liquid conduit **172** having a waste liquid conduit valve **174**. The system **100** also includes a rare earth product vessel **176** having a rare earth product inlet **178**, where the rare earth product outlet **118** is connected to the rare earth product inlet **178** via a rare earth conduit **180** having a rare earth conduit valve **182**.

[0050] The system **100** operates as follows. Rare earth containing HDD magnets are loaded into the vessel **120**. The valve **132** is opened and the magnets enter the commutating unit **124**, where the magnets are commutated into a particulate magnet input material. The commutating may be accomplished by grinding, cryogenic grinding, pressure fracturing, shredding, any other commutating technique or mixtures and combinations thereof. The valve **136** is opened and the particulate magnetic input material is supplied to the reactor vessel **102**. Once a desired amount of the input material is added to the reactor **102**, the valve **136** is closed and a mixture of water and formic acid is added to

the reactor **102**, where the relative amount of water and formic acid are controlled by the valves **144** and **152**. Once the designated amount of water and formic acid are added, the valves **144** and **152** are closed. The reaction vessel **102** is stirred and maintained at a temperature of about 100°C. Gas evolved during the reaction exits the reaction vessel **102** into the hydrogen gas bubbler **154**. After the desired reaction time, waste liquid is withdrawn from the reaction vessel **102**, by opening the valve **174** into the waste liquid vessel **168**. After the waste liquid is removed, the valve **174** is closed. The solids in the reaction vessel **102** are washed with water by open the water valve **144** until substantially all or all non-rare earth precipitate is dissolved by the added water. Once the non-rare earth precipitate has been dissolved away, the water valve **144** is closed and the rare earth product valve **182** is opened transferring the product into the product vessel **176**. Thus, the major part of the reaction occurs in the reaction vessel **102**. The generated hydrogen gas proceeds through the bubbler **154** and into the hydrogen gas utilization or storage vessel **162**.

[0051] In certain embodiments, the reaction vessel **102** will be purged with an inert gas such as nitrogen, argon, methane, hydrogen, or mixtures and combinations thereof to remove unwanted oxygen gas to minimize metal oxidation especially iron oxidation to the ferric oxidation state. Thus, the reaction vessel **102** may further includes an inert gas inlet **184** and a purge gas outlet **186**. The reactor vessel **102** also includes an inert gas vessel **188** having an inert gas outlet **190** connected to the inert gas inlet **184** via an inert gas conduit **192** having an inert gas valve **193**. The inert gas fed into the reactor vessel **102** passes through the reaction medium removing unwanted gases and exits the reactor vessel **102** through the purge outlet **186** through a purge conduit **194** having a purge valve **196** into a purge vent **198** having an inlet **199**. The inert gas may be used at different stages of the reaction to purge gases from the reaction medium.

Second Embodiment

[0052] Referring now to **Figure 1B**, a first embodiment of system of this invention, generally **100**, is shown to include a heated reaction vessel **102** including a motor **104** and a paddle stirrer **106**. The reaction vessel **102** also includes a particulate **REM** containing magnet material inlet **108**, a water inlet **110** and a formic acid inlet **112**. The reaction vessel **102** also includes a gas outlet **114**, a waste liquid outlet **116** and a **REM** product outlet **118**.

[0053] The system **100** also includes a **REM** containing magnet material source vessel **120** having a **REM** containing magnet material outlet **122**. The system **100** also includes a commutating unit **124** having a **REM** containing magnet material inlet **126** and a particulate **REM** containing magnet material outlet **128**. The **REM** containing magnet material outlet **122** is connected to the magnet inlet **126** via a magnet conduit **130** having a magnet conduit valve **132**. The particulate magnet outlet **128** is connected to the particulate magnet inlet **108** via a particulate magnet conduit **134** having a

particulate magnet conduit valve **136**.

[0054] The system **100** also includes a water source vessel **138** having a water outlet **140**. The water outlet **140** is connected to the water inlet **110** via a water conduit **142** having a water conduit valve **144**. The system **100** also includes a formic acid source vessel **146** having a formic acid outlet **148**. The formic acid outlet **148** is connected to the formic acid inlet **112** via a formic acid conduit **150** including a formic acid conduit valve **152**.

[0055] The system **100** also includes a hydrogen gas bubbler **154** having a hydrogen gas inlet **156** and a hydrogen gas outlet **158**, where the gas outlet **114** is connected to the hydrogen gas inlet **156** via a hydrogen gas conduit having a hydrogen gas valve **161**. The system **100** also includes a hydrogen gas utilization or storage unit **162** having a hydrogen gas inlet **164** connected to the hydrogen gas outlet **158** via a second hydrogen gas conduit **166**. In certain embodiments, the hydrogen gas utilization or storage unit **162** may be a combustor, where the heat produced may be used to heat the reaction vessel **102** to a desired elevated temperature. In other embodiments, the hydrogen gas utilization or storage unit **162** may be a hydrogen fuel cell for generating electrical power that may be used to heat the reaction vessel **102** or to power the reaction controllers and other electrical equipment associated with the systems. In other embodiments, the hydrogen gas utilization or storage unit **162** may be a hydrogen gas storage vessel, where the hydrogen gas is stored for latter use such as combustion in combustors or fuel cells or in hydrogenation reactions or in any other process that uses hydrogen gas as a reagent.

[0056] The system **100** also includes a waste liquid vessel reaction vessel **168** having a waste liquid inlet **170**, where the waste liquid outlet **116** is connected to the waste liquid inlet **170** via a waste liquid conduit **172** having a waste liquid conduit valve **174**. The system **100** also includes a rare earth product vessel **176** having a rare earth product inlet **178**, where the rare earth product outlet **118** is connected to the rare earth product inlet **178** via a rare earth conduit **180** having a rare earth conduit valve **182**.

[0057] The system **100** operates as follows. **REM** containing HDD magnets are loaded into the vessel **120**. The valve **132** is opened and the magnets enter the commutating unit **124**, where the magnets are commutated into a particulate magnet input material. The commutating may be accomplished by grinding, cryogenic grinding, pressure fracturing, shredding, any other commutating technique or mixtures and combinations thereof. The valve **136** is opened and the particulate magnetic input material is supplied to the reactor vessel **102**. Once a desired amount of the input material is added to the reactor **102**, the valve **136** is closed and a mixture of water and formic acid is added to the reactor **102**, where the relative amount of water and formic acid are controlled by the valves **144** and **152**. Once the designated amount of water and formic acid are added, the valves **144** and **152** are

closed. The reaction vessel **102** is stirred and maintained at a temperature of about 100°C. Gas evolved during the reaction exits the reaction vessel **102** into the hydrogen gas bubbler **154**. After the desired reaction time, waste liquid is withdrawn from the reaction vessel **102**, by opening the valve **174** into the waste liquid vessel **168**. After the waste liquid is removed, the valve **174** is closed. The solids in the reaction vessel **102** are washed with water by open the water valve **144** until substantially all or all non-rare earth precipitate is dissolved by the added water. Once the non-rare earth precipitate has been dissolved away, the water valve **144** is closed and the rare earth product valve **182** is opened transferring the product into the product vessel **176**. Thus, the major part of the reaction occurs in the reaction vessel **102**. The generated hydrogen gas proceeds through the bubbler **154** and into the hydrogen gas utilization or storage vessel **162**.

[0058] In certain embodiments, the reaction vessel **102** will be purged with an inert gas such as nitrogen, argon, methane, hydrogen, or mixtures and combinations thereof to remove unwanted oxygen gas to minimize metal oxidation especially iron oxidation to the ferric oxidation state. Thus, the reaction vessel **102** may further includes an inert gas inlet **184** and a purge gas outlet **186**. The reactor vessel **102** also includes an inert gas vessel **188** having an inert gas outlet **190** connected to the inert gas inlet **184** via an inert gas conduit **192** having a inert gas valve **193**. The inert gas fed into the reactor vessel **102** passes through the reaction medium removing unwanted gases and exits the reactor vessel **102** through the purge outlet **186** through a purge conduit **194** having a purge valve **196** into a purge vent **198** having an inlet **199**. The inert gas may be used at different stages of the reaction to purge gases from the reaction medium.

Third Embodiment

[0059] Referring now to **Figure 2**, a first embodiment of system of this invention, generally **200**, is shown to include a reaction subsystem **202**, a separation subsystem **250**, and an extraction subsystem **270**.

Reaction Subsystem

[0060] The reaction subsystem **202** includes a single reaction vessel **204**, a REM containing magnet material source vessel **206**, a formic acid source vessel **208**, and a water source vessel **210**. The magnet material source vessel **206** is connected to the reaction vessel **204** via a magnet material conduit **212** having a magnet material valve **214**. The formic acid source vessel **208** is connected to the reaction vessel **204** via a formic acid conduit **216** having a formic acid valve **218**. The water source vessel **210** is connected to the reaction vessel **204** via a water conduit **220** having a water valve **222**. The reaction vessel **204** also includes a hydrogen gas utilization unit **224** connected to the reaction vessel **204** via a hydrogen gas conduit **226** having a hydrogen gas valve **228**. The reaction vessel **204** also includes an inert gas source **230** connected to the reaction vessel **204** via an inert gas conduit **232**

having an inert gas valve **234**. The reaction vessel **204** also includes a purge gas vent **236** connected to the reaction vessel **204** via a purge gas conduit **238** having a purge gas valve **240**. The reaction vessel **204** also includes a reaction mixture conduit **242** having a reaction mixture valve **244**.

Separation Subsystem

[0061] The separation subsystem **250** is shown here to comprise a single separation vessel **252** and a liquid receiving vessel **254**. The reaction mixture conduit **242** connects the reaction vessel **204** and the separation vessel **252** and is used to transport the reaction mixture from the reaction vessel **204** to the separation vessel **252**. The separation vessel **252** is connected to the liquid receiving vessel **254** via a liquid conduit **256** having a liquid valve **258**. The separation vessel **252** also includes a solids conduit **260** having a solids valve **262**.

Extraction Subsystem

[0062] The extraction subsystem **270** is shown here to comprise a single extraction vessel **272**, a solvent source vessel **274**, a liquid vessel **276**, and a product vessel **278**. The solids conduit **260** connects the separation vessel **252** and the extraction vessel **272** and is used to transport the solids from the separation vessel **252** to the extraction vessel **272**. The separation vessel **272** is connected to the solvent source vessel **274** via a solvent conduit **280** having a solvent valve **282**. The separation vessel **272** is also connected to the liquid vessel **276** via a liquid conduit **284** having a liquid valve **286**. The separation vessel **272** is also connected to the product vessel **274** via a product conduit **288** having a product valve **290**.

Fourth Embodiment

[0063] Referring now to **Figure 3**, a second embodiment of system of this invention, generally **300**, is shown to include a reaction subsystem **302**, a separation subsystem **346**, an extraction subsystem **350**, and a recovery and recycle subsystem **380**.

Reaction Subsystem

[0064] The reaction subsystem **302** includes a single reaction vessel **304**, a magnet source vessel **306**, a formic acid source vessel **308**, and a water source vessel **310**. The magnet source vessel **306** is connected to the reaction vessel **304** via a magnet conduit **312** having a magnet valve **314**. The formic acid source vessel **308** is connected to the reaction vessel **304** via a formic acid conduit **316** having a formic acid valve **318**. The water source vessel **310** is connected to the reaction vessel **304** via a water conduit **320** having a water valve **322**. The reaction vessel **304** also includes a hydrogen gas utilization unit **324** connected to the reaction vessel **304** via a hydrogen gas conduit **326** having a hydrogen gas valve **328**. The reaction vessel **304** also includes an inert gas source **330** connected to the reaction vessel **304** via an inert gas conduit **332** having an inert gas valve **334**. The reaction vessel **304** also includes a purge gas vent **336** connected to the reaction vessel **304** via a purge gas conduit

338 having a purge gas valve **340**. The reaction vessel **304** also includes a reaction mixture conduit **342** having a reaction mixture valve **344**.

Separation Subsystem

[0065] The separation subsystem **346** is shown here to comprise a single separation vessel **348** and a liquid receiving vessel **350**. The reaction mixture conduit **342** connects the reaction vessel **304** and the separation vessel **348** and is used to transport the reaction mixture from the reaction vessel **304** to the separation vessel **348**. The separation vessel **352** is connected to the liquid receiving vessel **350** via a liquid conduit **352** having a liquid valve **354**. The separation vessel **352** also includes a solids conduit **356** having a solids valve **358**.

Extraction Subsystem

[0066] The extraction subsystem **360** is shown here to comprise a single extraction vessel **362**, a solvent source vessel **364**, and a liquid vessel **366**. The solids conduit **356** connects the separation vessel **348** and the extraction vessel **262** and is used to transport the solids from the separation vessel **348** to the extraction vessel **362**. The separation vessel **362** is connected to the solvent source vessel **364** via a solvent conduit **368** having a solvent valve **370**. The separation vessel **362** is also connected to the liquid vessel **366** via a liquid conduit **372** having a liquid valve **374**. The separation vessel **262** is also includes a product conduit **376** having a product valve **378**.

Recovery and Recycle Subsystem

[0067] The recovery and recycle subsystem **380** is shown here to comprise a single a recovery and recycle vessel **382**, a recycle formic acid vessel **384**, and a rare earth metal product vessel **386**. The recovery and recycle vessel **382** is connected to the recycle formic acid vessel **384** via a recycle formic acid conduit **388** having a recycle formic acid valve **390**. The recovery and recycle vessel **382** is connected to the rare earth metal product vessel **386** via a rare earth metal product conduit **392** having a product valve **394**.

Fifth Embodiment

[0068] Referring now to **Figures 4**, a third embodiment of system of this invention, generally **400**, is shown to include a commutating subsystem **402**, a reaction subsystem **416**, a separation subsystem **438**, an extraction subsystem **454**, and a recovery and recycle subsystem **476**.

Commutating Subsystem

[0069] The commutating subsystem **402** includes a commutating unit **404** and a magnet source vessel **406**. The magnet source vessel **406** is connected via a magnet source conduit **408** having a magnetic source valve **410**. The commutating unit **404** also includes a particulate magnet material conduit **412** having a particulate magnet valve **414**.

Reaction Subsystem

[0070] The reaction subsystem **416** includes a single reaction vessel **418**, a formic acid source vessel **420**, and a water source vessel **422**. The commutating unit **404** is connected to the reaction vessel **404** via the particulate magnet conduit **414**. The formic acid source vessel **420** is connected to the reaction vessel **418** via a formic acid conduit **424** having a formic acid valve **426**. The water source vessel **422** is connected to the reaction vessel **418** via a water conduit **428** having a water valve **430**. The reaction subsystem **416** also includes a hydrogen gas utilization unit **432** connected to the reaction vessel **418** via a hydrogen gas conduit **434** having a hydrogen gas valve **436**. The reaction subsystem **416** also includes an inert gas source **438** connected to the reaction vessel **418** via an inert gas conduit **440** having an inert gas valve **442**. The reaction subsystem **416** also includes a purge gas vent **444** connected to the reaction vessel **418** via a purge gas conduit **446** having a purge gas valve **448**. The reaction vessel **418** also includes a reaction mixture conduit **450** having a reaction mixture valve **452**.

Separation Subsystem

[0071] The separation subsystem **454** is shown here to comprise a single separation vessel **456** and a liquid receiving vessel **458**. The reaction mixture conduit **450** connects the reaction vessel **418** and the separation vessel **456** and is used to transport the reaction mixture from the reaction vessel **418** to the separation vessel **456**. The separation vessel **456** is connected to the liquid receiving vessel **458** via a liquid conduit **460** having a liquid valve **462**. The separation vessel **456** also includes a solids conduit **464** having a solids valve **466**.

Extraction Subsystem

[0072] The extraction subsystem **468** is shown here to comprise a single extraction vessel **470**, a solvent source vessel **472**, and a liquid vessel **474**. The solids conduit **464** connects the separation vessel **456** and the extraction vessel **470** and is used to transport the solids from the separation vessel **456** to the extraction vessel **470**. The separation vessel **470** is connected to the solvent source vessel **472** via a solvent conduit **476** having a solvent valve **477**. The separation vessel **470** is also connected to the liquid vessel **474** via a liquid conduit **478** having a liquid valve **479**. The separation vessel **470** also includes a product conduit **480** having a product valve **481**.

Recovery and Recycle Subsystem

[0073] The recovery and recycle subsystem **482** is shown here to comprise a single a recovery and recycle vessel **484**, a recycle formic acid vessel **486**, and a rare earth metal product vessel **488**. The product conduit **480** connects the extraction vessel **470** to the recovery and recycle vessel **484** and is used to transport the product to the recovery and recycle vessel **484**. The recovery and recycle vessel **484** is connected to the recycle formic acid vessel **486** via a recycle formic acid conduit **490** having a recycle formic acid valve **491**. The recovery and recycle vessel **488** is connected to the rare earth metal product vessel **488** via a rare earth metal product conduit **492** having a product valve **493**.

EXPERIMENTS OF THE INVENTION

[0074] The present invention is illustrated by the following examples:

[0075] The NdFeB magnets were obtained from discarded hard disk drives (HDDs). The HDDs were disassembled manually and 2 to 4 magnets were collected from each HDD. Weights of the magnets ranged from about 2.5 g to about 10 g. The NdFeB magnets used for the reactions were pretreated. However, the NdFeB magnets may be used as-removed without any pretreatment. The term "pretreatment" refers here to, but not limited to, demagnetization, roasting, and/or protective coating removal. The magnets were crushed into small pieces using a metal crusher. The brittle magnets are easily breakable into pieces, but any commutating method may be used including grinding, milling, crushing, external pressing, *etc.* The particle sizes varied in a broad range between about 10 nm and about 5 mm. The crushed magnet sample was reacted with a mixture of formic acid and water or an aqueous formic acid solution. In certain embodiments, the particle sizes range between about 100 nm (0.1 μm) to about 5 mm. In other embodiments, the particle sizes range between about 500 nm (0.5 μm) to about 5 mm. In other embodiments, the particle sizes range between about 1 μm to about 5 mm. In other embodiments, the particle sizes range between about 5 μm to about 5 mm. In other embodiments, the particle sizes range between about 10 μm to about 5 mm. In other embodiments, the particle sizes range between about 100 μm to about 5 mm. In other embodiments, the particle sizes range between about 500 μm to about 5 mm.

EXAMPLE 1

[0076] As a first example of the process, a 1:2:2 w/w of magnet materials to formic acid to water reaction mixture was used for the reaction. The reaction was performed at 100°C for 24 h and the product was separated by a filtration method at room temperature. The final product phase of the reaction was a white/pale violet microcrystalline precipitate which was confirmed to be a mixture of rare earth metal formate (**REM**(HCOO)₃) and iron formate dihydrate (Fe(HCOO)₂•2H₂O) phases from the powder X-ray diffraction techniques as shown in **Figure 5**.

[0077] Several methods such as washing with different solvents, magnetic separation and density separation were attempted to remove the impure iron formate phase from the rare earth formate phase. The most successful route was to wash the precipitate with excess amounts of water. As per the PXRD data shown in **Figure 5**, the final product after excess water washing contained only a pure **REM**(HCOO)₃ product, confirming successful recovery of rare earths from NdFeB magnets materials.

[0078] When Fe²⁺ oxidizes to Fe³⁺, it forms nearly insoluble Fe(OH)₃, Fe(O)OH, and/or Fe₂O₃ phases. Thus, for a successful separation of Fe(HCOO)₂•2H₂O, the iron formate phase needs to be fully removed. Any Fe(OH)₃ phase that forms is hard to separate from the **REM**(HCOO)₃ phase, and thus remains as an impurity phase in the final product. **REM**(HCOO)₃ purity will be significantly affected

by $\text{Fe}(\text{OH})_3$ formation, and is a previously known problem associated with the NdFeB magnet recycling techniques.

[0079] One alternative, is to carry out the final filtration step under an inert N_2 atmosphere and use deoxygenated water for the washing steps. This was more successful compared to the regular filtration.

EXAMPLE 2

[0080] In a further example, the amount of formic acid and amount of water and solvent-to-solid ratios in the reaction mixture was systematically varied, with the intention of exploiting the substantial solubility difference between $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$ and $\text{REM}(\text{HCOO})_3$. Excess amounts of water in the reaction mixture lowers the $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$ formation significantly, without affecting the $\text{REM}(\text{HCOO})_3$ formation. When the amount of water increased substantially in the reaction mixture, the amount of $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$ was significantly reduced, or nearly absent from the final solid phase.

[0081] Based on the solubility data of $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$, the required ratio of magnets to water to completely dissolve $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$ was calculated as about 1:30 w/w magnet materials to water at 25°C . Thus, by adding the appropriate amounts of water to the reaction mixture, $\text{Fe}(\text{HCOO}) \cdot 2\text{H}_2\text{O}$ formation can be substantially controlled. With this alteration of the process, the iron level in the final product was reduced between about 0.5% and about 0.8%, and the rare earth purity level improved to 99% or above.

EXAMPLE 3

[0082] The detailed reaction scheme of the optimized process is as follows.

[0083] A ratio of magnet to formic acid was maintained at 1:2 w/w and a ratio of magnets to water was 1:30 w/w. Formic acid was used in a slightly excess amount over the theoretical amount to assist the reaction completion. The reaction temperature was set at 100°C .

[0084] The initial experiments were performed using 10 g of crushed magnets. The samples were mixed with 20 mL of 85% concentrated formic acid and diluted with 300 mL of water. The reactions were performed in a round bottom flask in an oil bath heated to 100°C . A vertically connected Liebig condenser was attached to the flask neck to cool and condense produced vapor. The condenser was used to minimize loss of water and formic acid during the boiling. The open end of the condenser was connected to gas bubbler to monitor hydrogen gas (H_2) evolution during the reaction.

[0085] As the reaction progressed, the magnet pieces dissolved in the solution and a white/greyish precipitate began to form and appear. Initial reactions were performed allowing 24 h reaction time to complete the reaction; subsequent experiments confirmed that within about 6 h of reaction, all of the rare earth metals from the magnet samples were dissolved by the reaction mixture. Throughout

the reaction period, the amount of the solid precipitate in the reaction mixture increased as the portion of dissolvable components of the magnets dissolved.

[0086] Afterward, the mixture was cooled to room temperature, about 25°C and filtered to separate the solid product from the liquid under suction.

[0087] Apart from the precipitate in the reaction mixture, parts of the protective Ni/Cu coating of the magnets were found to have remained unreacted with or undissolved by the formic acid/water mixture. These undissolved parts were easily removed using a magnetic stir bar retriever, but any other type of magnetic separator may be used including permanent or electromagnets or combination thereof. The precipitate was thoroughly washed with water to remove any residual $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ adsorbed in the precipitate. The separation of any residual $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ from the product $\text{REM}(\text{HCOO})_3$ may be achieved by washing the precipitate with excess amounts of water as the two solid materials have substantial different solubility in water. $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ is highly soluble in water, whereas the $\text{REM}(\text{HCOO})_3$ is nearly insoluble in water. Thus, by using an excess amount of water, the residual $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ solid material can be completely removed from the solid product.

[0088] The white/greyish solid precipitate was confirmed as rare earth formate ($\text{REM}(\text{HCOO})_3$). When an inadequate amount of water was used in the reaction, their formate dihydrate ($\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$) phase may be observed in powder X-ray diffraction pattern.

[0068] After the removal of the residual $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ from the reaction mixture, the $\text{REM}(\text{HCOO})_3$ phase was the only solid product remaining from the reaction mixtures. The final solid is dried under vacuum. The method resulted in $\text{REM}(\text{HCOO})_3$ being recovered in high yield of at least 90%.

[0089] As the final step, $\text{REM}(\text{HCOO})_3$ is annealed at 750 °C for 3 h in air to obtain the mixture of rare earth oxides, $\text{REM}_2\text{O}_3/\text{REM}_6\text{O}_{11}$ (REM include Nd, Pr, Dy, Tb) with a recovered yield of at least 90% in a purity of at least 99%. The purity of **REM** formate or oxides herein is measured relative to **NREM** formate or oxides in the relevant product.

[0090] The chemical analysis data of the final rare earth products phases have shown that the methods of this invention are capable of recovering at least 95% recovery efficiency for Nd, at least 95 % recovery efficiency for Pr and at least 90% recovery efficiency for Dy and at least 85 % recovery for efficiency for Tb.

[0091] The chemical analysis data of the final rare earth products phases have shown that the methods of this invention are capable of recovering rare earth formates in greater than 90% purity, for example about 99% purity compared to the non-rare earth formates.

REFERENCES CITED IN THE INVENTION

[0092] The following articles were cited above:

1. U.S. Department of Energy (2011) Critical Materials Strategy.
2. Constantinides, S (2013) The Demand for Rare Earth Materials in Permanent Magnets; Arnold Magnetic Technologies.
3. U.S. Bureau of Mines (1993) Recycling of Neodymium Iron Boron Magnet scrap.
4. Xu X, Chumbley L S and Laabs F S (2000) Liquid metal extraction of Nd from NdFeB magnet scrap. *Journal of Materials Research* 15(11): 2296-2304.
5. Zakotnik M, Devlin E, Harris I R, and Williams A J (2006) Hydrogen Decrepitation and Recycling of NdFeB-type Sintered Magnets. *Journal of Iron and Steel Research, International* 13(1): 289-295.
6. Itoh M, Miura K, and Machida K (2009) Novel rare earth recovery process on Nd-Fe-B magnet scrap by selective chlorination using NH₄Cl. *Journal of Alloys and Compounds* 477: 484-487
7. Samarasekere P, Wang X, Kaveevivitchai W, and Allan J. Jacobson (2015) Reactions of Rare Earth Hydrated Nitrates and Oxides with Formamide: Relevant to Recycling Rare Earth Metals. *Crystal Growth & Design* 15(3):1119-1128
8. Binnemans K, Jones P T, Blanpain B, Van Gerven T, Yang Y, Walton A, and Buchert M (2013) Recycling of rare earths: a critical review. *Journal of Cleaner Production* 51: 1-22 and references therein.
9. Bolotovskii R L, Bolotovskii R L, Bulkin Ap, Krutov G A, Turnov V A, Ul'yanov V A, Anston O, Hiismaki P, Poyry H, Tittla A, Loshmanov A A, and Furmanova N G (1990) Neutron diffraction study of the crystal structure of rareearth and yttrium anhydrous deuterated formates. *Solid State Communications* 76(8):1045-1049.

[0093] All references cited herein are incorporated by reference. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS

We claim:

1. A method for recovering rare earth metals from waste magnets comprising:
contacting a rare earth metal-containing magnet material with a reactant composition including a low molecular weight carboxylic acid and water under reaction conditions sufficient to dissolve or extract and concurrently precipitate rare earth metals from the rare earth metal-containing magnet material forming a rare earth metal precipitate including rare earth metal carboxylates and non-rare earth metal components, and
removing the non-rare earth metal components from the rare earth metal carboxylates with water to form a purified rare earth metal carboxylate product.
2. The method of claim 1, further comprising the step of:
prior to the contacting step, commutating the rare earth metal-containing magnet material to form a particulate rare earth metal-containing magnet material having an average particle size between about 10 nm and about 5 mm.
3. The method of claim 1, wherein the low molecular weight carboxylic acid is formic acid and a rare earth metal-containing magnet material to formic acid to water ratio is between about 1.0:1.0:20 w/w to about 1.0:2.0:50 w/w.
4. The method of claim 3, wherein the rare earth metal-containing magnet material to formic acid to water ratio is between about 1:1.2:20 w/w and about 1:1.8:50 w/w.
5. The method of claim 4, wherein the rare earth metal-containing magnet material to formic acid to water ratio is between about 1.0:1.4:20 w/w and about 1.0:1.5:40 w/w.
6. The method of claim 5, wherein the rare earth metal-containing magnet material to formic acid to water ratio is about 1:1.44:30 w/w.
7. The method of claim 1, wherein the reaction conditions include at least a reaction temperature, a reaction pressure, a reaction time, and a stirring rate.
8. The method of claim 7, wherein:
the reaction temperature is between about 25°C and about 120°C,
the reaction pressure is between about 1 atmosphere and about 5 atmospheres,

the reaction time is at least 24 hours, and
the rate stirring is at least 500 rpm.

9. The method of claim 8, wherein:

the reaction temperature is any discrete temperature in the range between about 25°C and about 120°C,

the reaction pressure is ambient pressure,

the reaction time is any discrete time period in the range between 3 hours and 24 hours, and

the stirring rates is any discrete stirring rate in the range between 100 rpm and 500 rpm.

10. The method of claim 1, wherein:

the rare earth metals are selected from the groups consisting of Lanthanum (La), Cerium (Ce), praseodymium (Pr), neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), Lutetium (Lu), and mixtures or combinations thereof; and

the non-rare earth metals or elements (**NREMs**) are selected from the group consisting of iron (Fe), nickel (Ni), copper (Cu), other transitions metals generally associated with materials that include **REMs**, boron (B), and mixtures or combinations thereof.

11. A system comprising:

a reaction vessel including a rare earth metal containing-magnet material input connect to a rare earth metal containing-magnet material source, a low molecular weight carboxylic acid input connected to a low molecular weight carboxylic acid source, a water input connected to a water source, a waste liquid outlet connected to a waste liquid receiver and a rare earth metal product outlet connected to a rare earth metal product receiver, where an amount of the rare earth metal containing-magnet material, the low molecular weight carboxylic acid and the water are added to the reaction vessel to form a reaction mixture and the reaction mixture is held under reaction conditions sufficient to dissolve or extract the rare earth metals to form rare earth metal carboxylates along with non-rare earth metal carboxylate hydrates that precipitate out of the reaction mixture, and

a separating vessel to separate the precipitate from the liquid and to wash the precipitate with a solvent to remove the non-rare earth metal carboxylate hydrates to form a purified rare earth carboxylate product.

12. The system of claim 11, further comprising:

a commutating unit to fragment the magnet material into a particulate magnet material having an average particle size between about 10 nm and about 5 mm.

13. The system of claim 10, wherein the low molecular weight carboxylic acid is formic acid, the magnet material to formic acid to water ratio is between about 1.0:1.0:20 w/w to about 1.0:2.0:50 w/w.

14. The system of claim 13, wherein the magnet material to formic acid to water ratio is between about 1:1.2:20 w/w and about 1:1.8:50 w/w.

15. The system of claim 14, wherein the magnet material to formic acid to water ratio is between about 1.0:1.4:20 w/w and about 1.0:1.5:40 w/w.

16. The system of claim 15, wherein the magnet material to formic acid to water ratio is between about 1:1.44:30 w/w.

17. The system of claim 10, wherein the reaction conditions include at least a reaction temperature, a reaction pressure, a reaction time, and a stirring rate.

18. The system of claim 17, wherein:
the reaction temperature is between about 25°C and about 120°C,
the reaction pressure is between about 1 atmosphere and about 5 atmospheres,
the reaction time is at least 24 hours, and
the rate stirring is at least 500 rpm.

19. The system of claim 18, wherein:
the reaction temperature is any discrete temperature in the range between about 25°C and about 120°C,
the pressure is ambient pressure,
the reaction time is any discrete time period in the range between 3 hours and 24 hours, and
the stirring rates is any discrete stirring rate in the range between 100 rpm and 500 rpm.

20. The method of claim 1, wherein:
the rare earth metals are selected from the groups consisting of Lanthanum (La), Cerium (Ce), praseodymium (Pr), neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm),

Ytterbium (Yb), Lutetium (Lu), and mixtures or combinations thereof; and

the non-rare earth metals or elements (**NREMs**) are selected from the group consisting of iron (Fe), nickel (Ni), copper (Cu), other transitions metals generally associated with materials that include **REMs**, boron (B), and mixtures or combinations thereof.

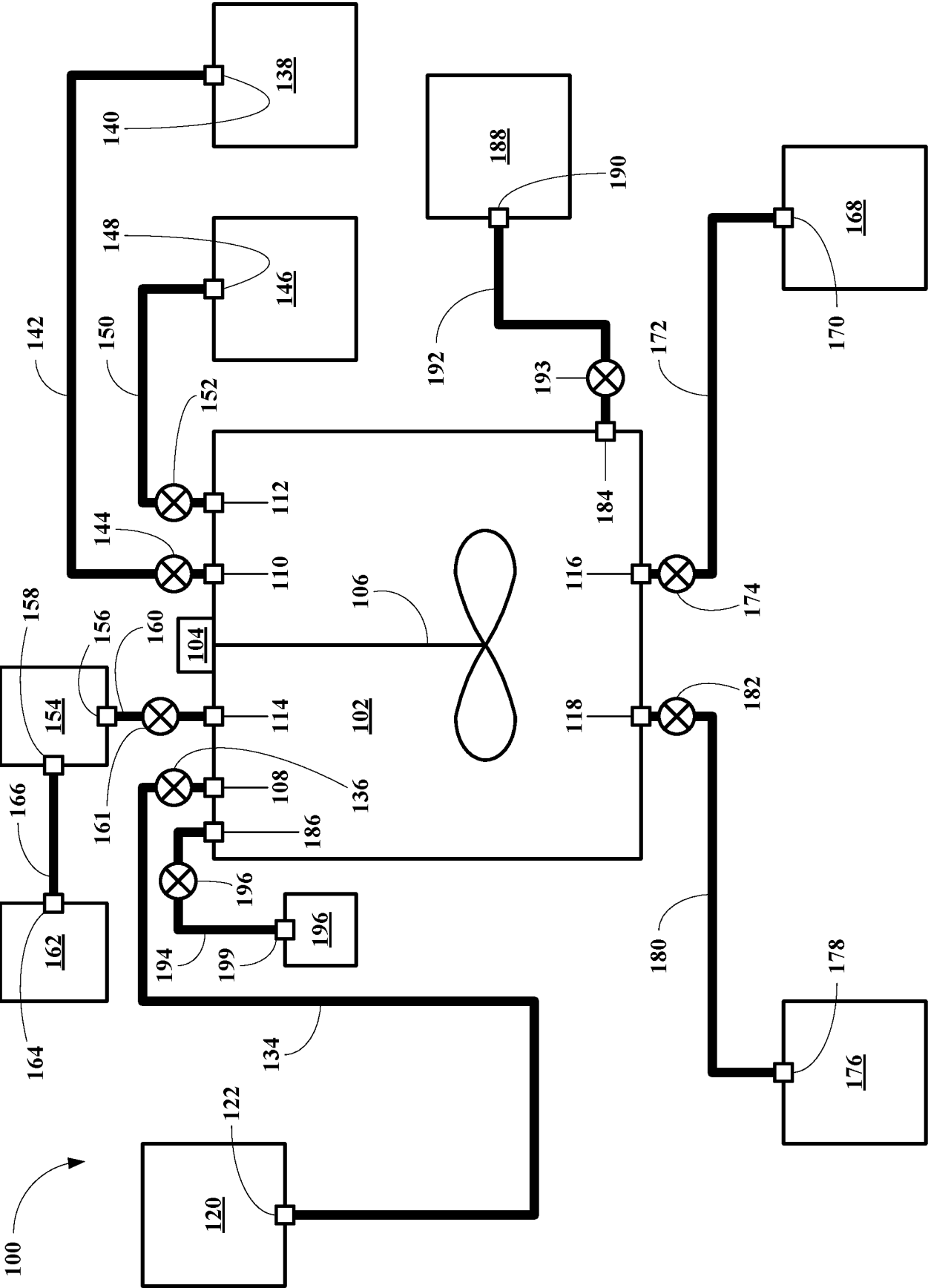


FIG. 1A

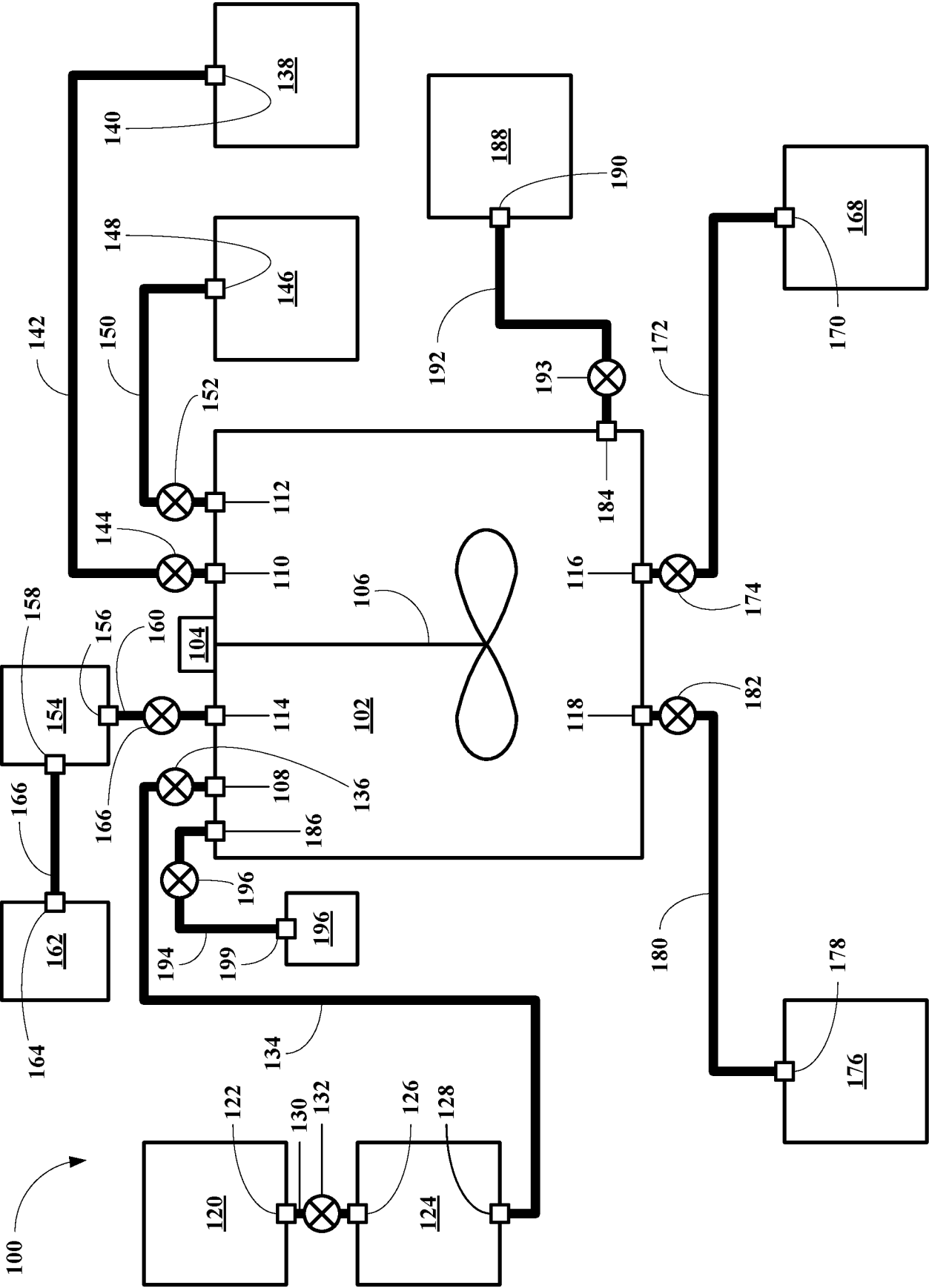


FIG. 1B

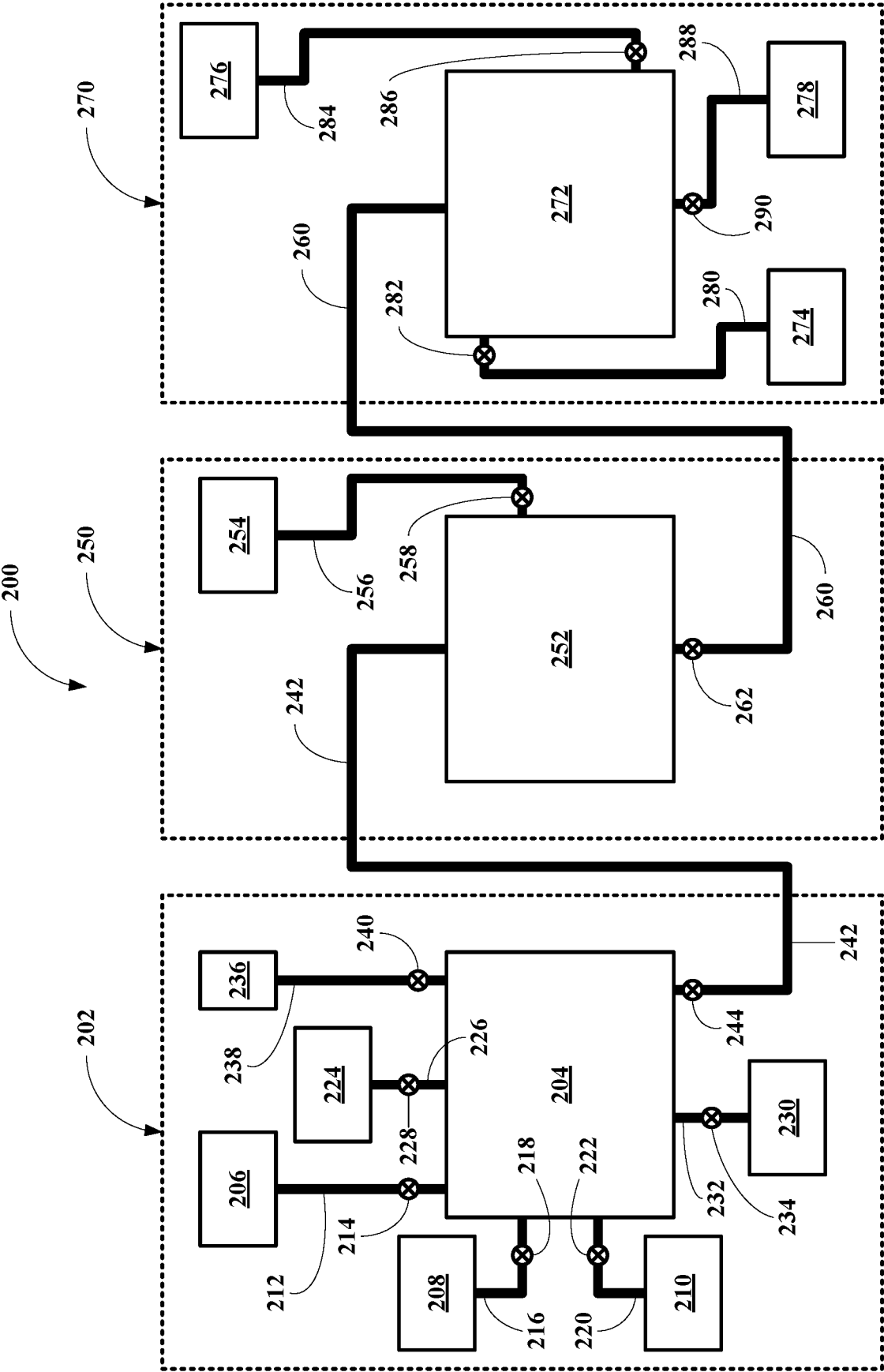


FIG. 2

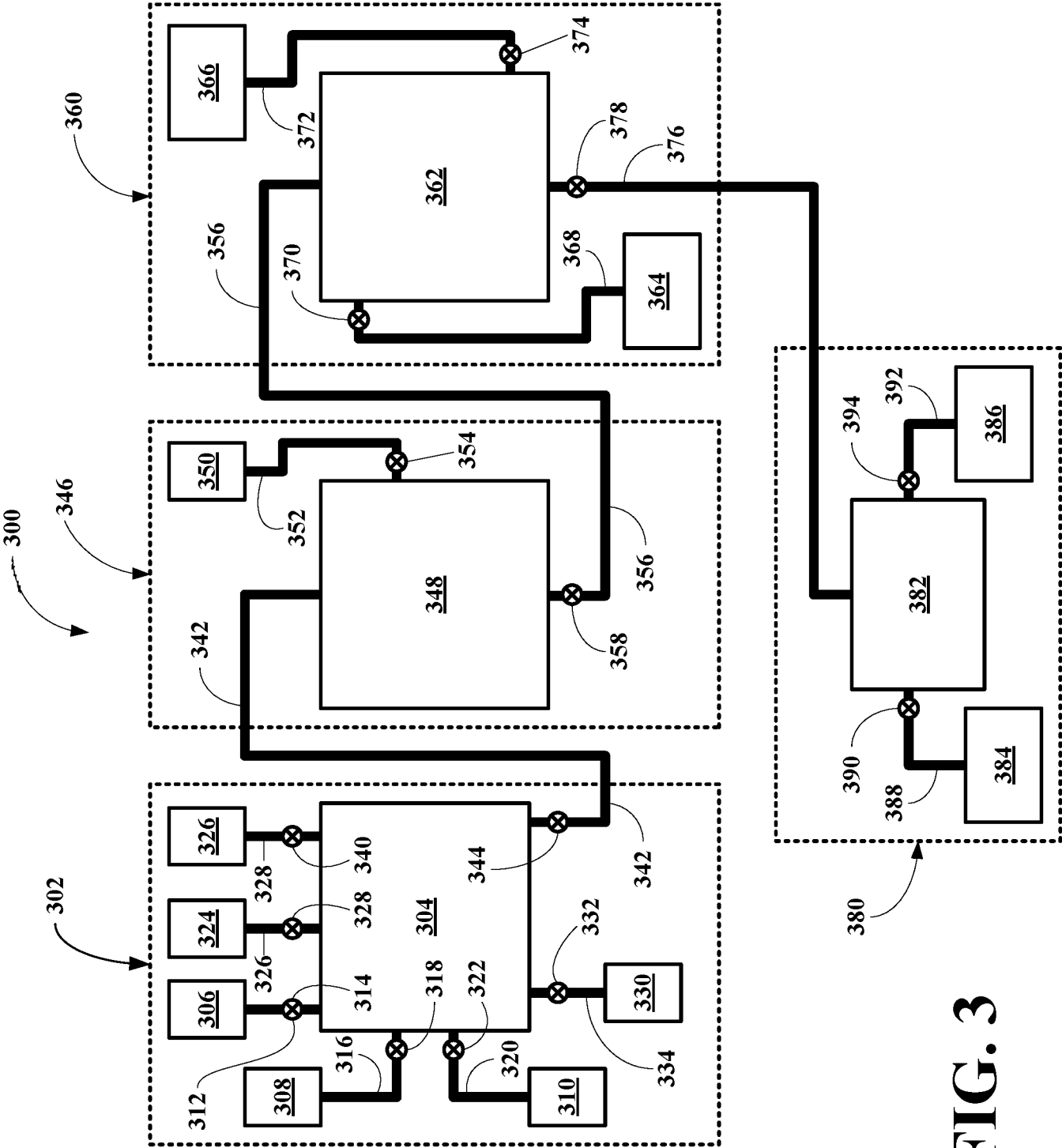


FIG. 3

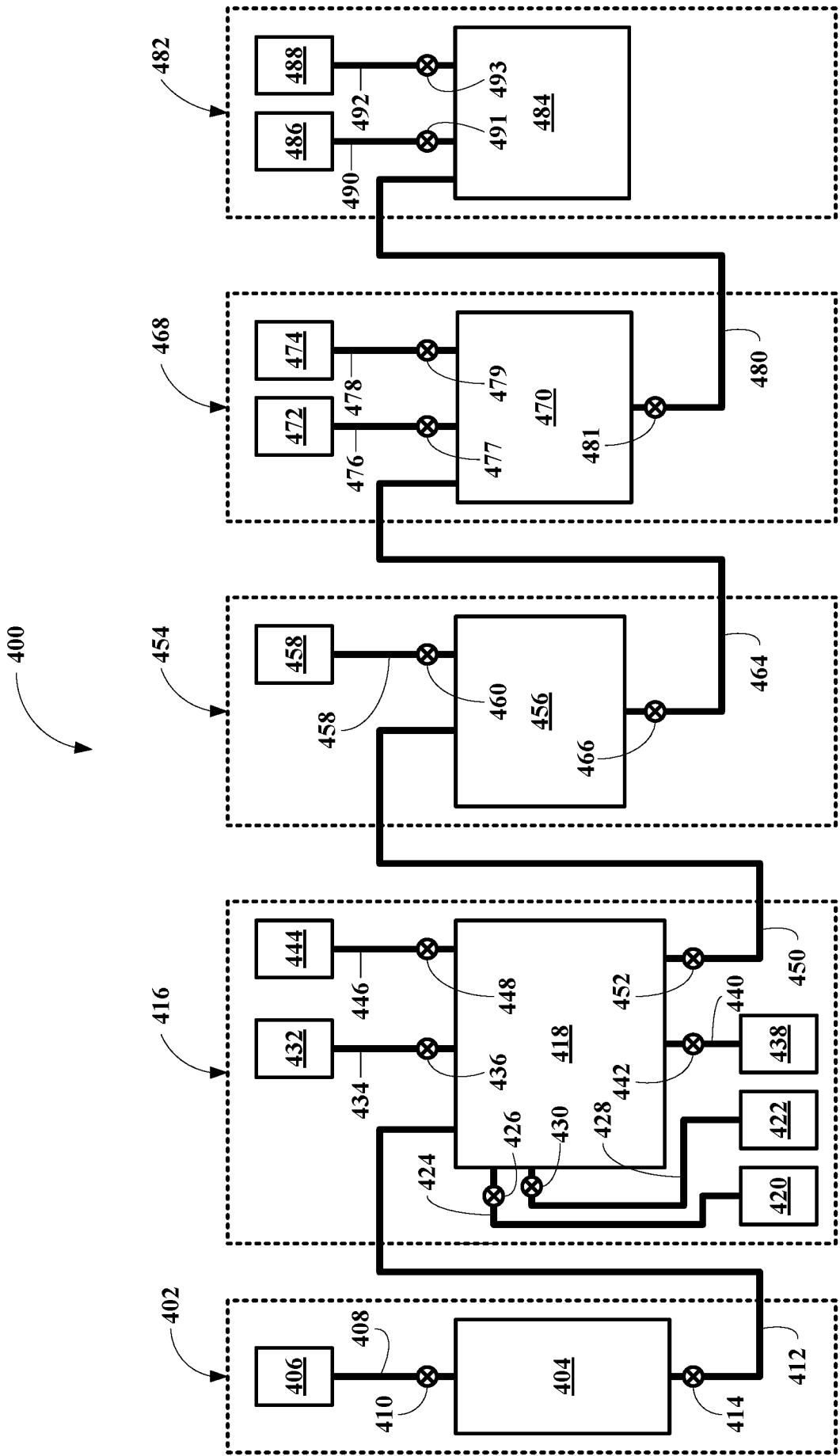
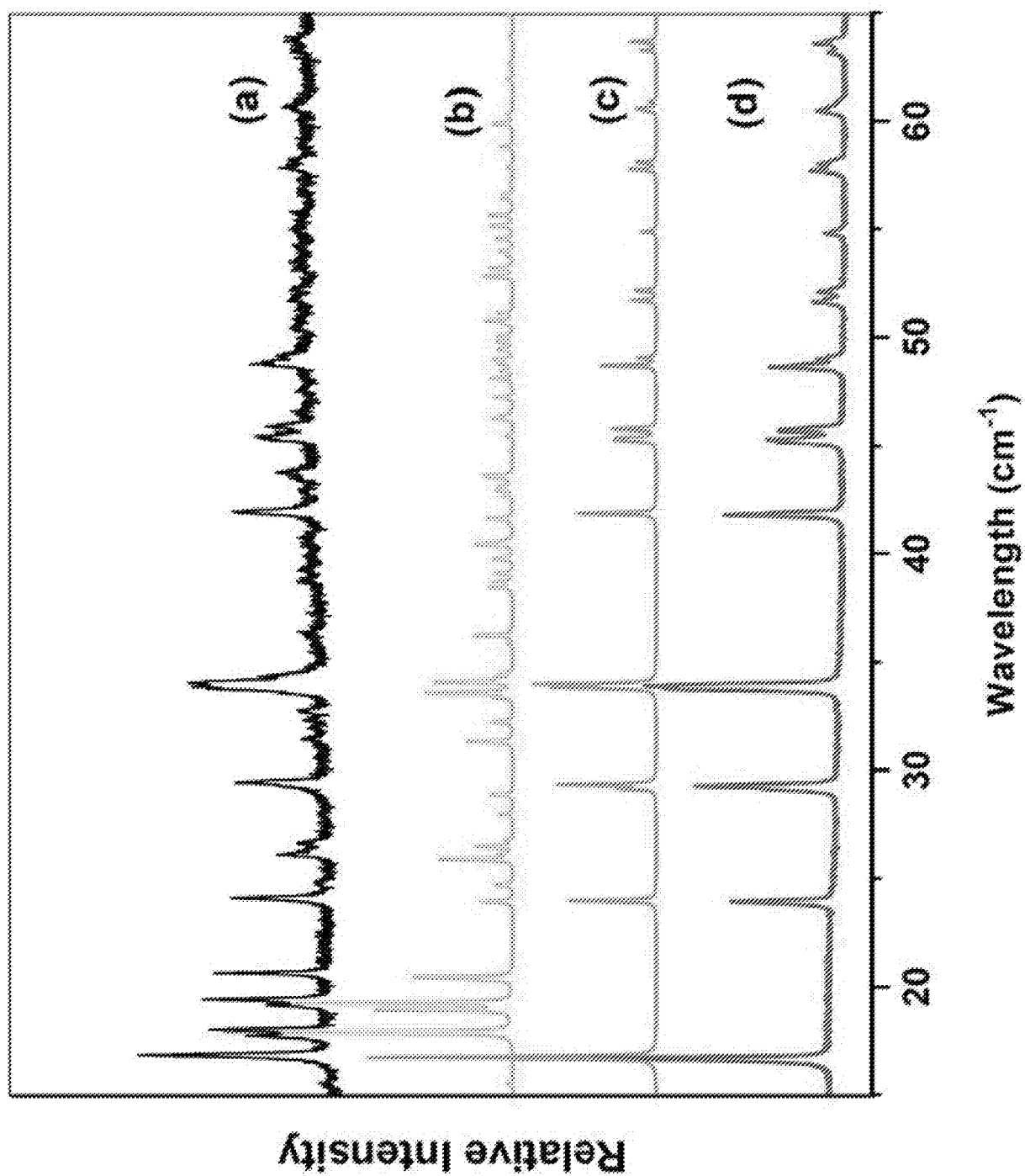


FIG. 4



Wavelength (cm^{-1})

FIG. 5

SEM micrographs and
EDX analysis of rare earth
metal oxide product after
annealing

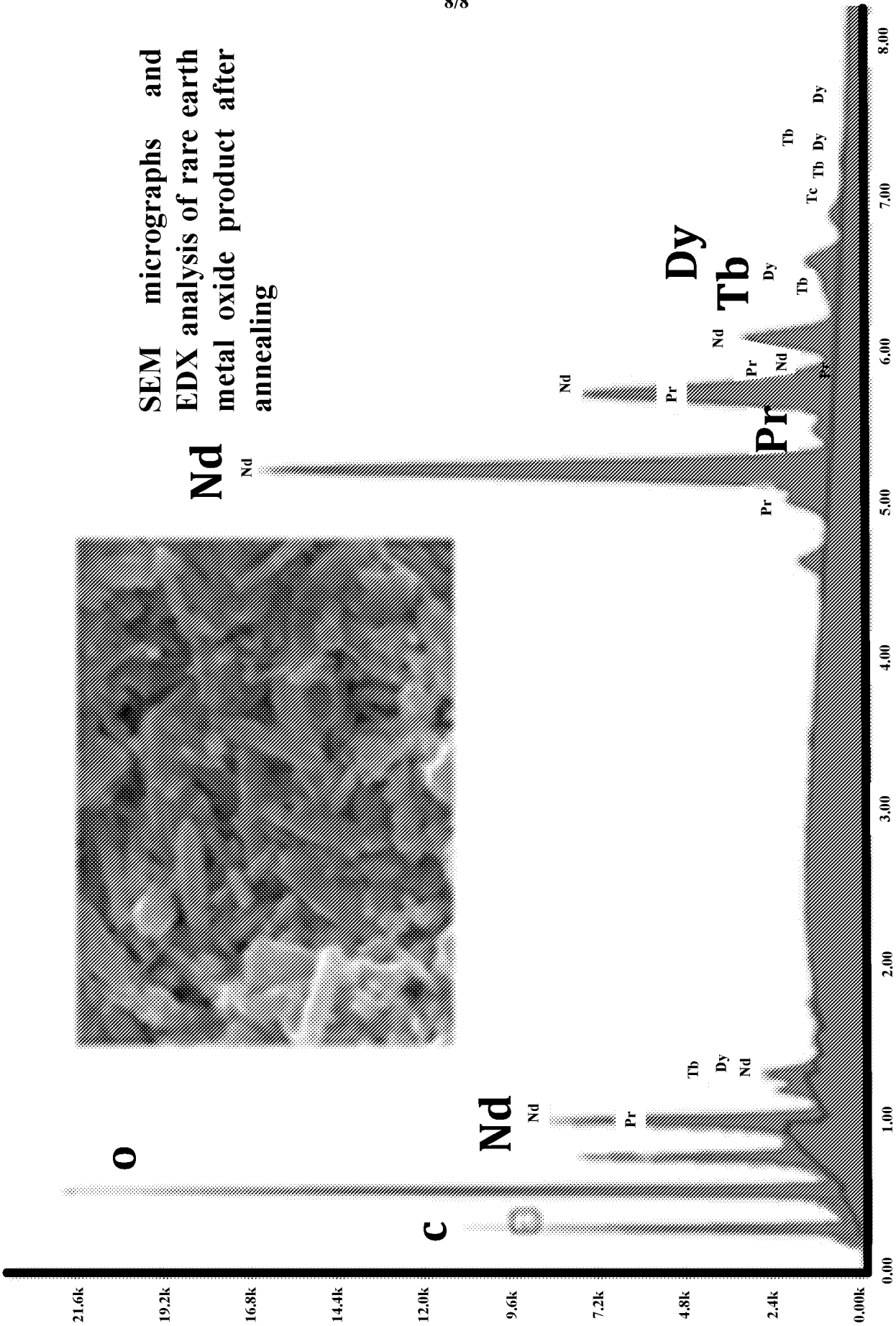


FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/041685**A. CLASSIFICATION OF SUBJECT MATTER****C22B 59/00(2006.01)i, C22B 3/32(2006.01)i, C22B 3/24(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B 59/00; C01F 17/00; C22B 23/00; C01F 7/00; C22B 3/02; C22B 3/32; C22B 3/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: recovery, rare earth metal, carboxylic acid, extraction, separation and purifying

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010-0319491 A1 (SUGAHARA et al.) 23 December 2010	1-9, 11-19
Y	See abstract; paragraphs [0014]-[0018]; and claims 1, 4.	10, 20
Y	US 5362459 A (GREENBERG, BERNARD) 08 November 1994	10, 20
	See abstract; column 6, line 45-column 8, line 65; and claim 1.	
A	US 4265862 A (WHITE et al.) 05 May 1981	1-20
	See abstract; column 3, line 20-column 4, line 9; and claim 1.	
A	US 8936770 B2 (BURBA, III, JOHN L.) 20 January 2015	1-20
	See abstract; and claims 54, 58.	
A	US 8252085 B1 (SMITH et al.) 28 August 2012	1-20
	See abstract; column 3, line 27-column 4, line 16; and claim 1.	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

02 December 2016 (02.12.2016)

Date of mailing of the international search report

02 December 2016 (02.12.2016)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/041685

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US 8936770 B2	20/01/2015	AU 2011-207307 A1 AU 2011-207307 B2 AU 2011-207307 C1 CA 2787515 A1 CN 102939397 A DK 201270462 A EA 024210 B1 EA 201201035 A1 EP 2526213 A1 EP 2526213 A4 JP 2013-528696 A KR 10-2012-0139701 A US 2011-0182786 A1 US 2015-0197826 A1 WO 2011-091231 A1 ZA 201206222 B	06/09/2012 22/05/2014 15/01/2015 28/07/2011 20/02/2013 02/08/2012 31/08/2016 28/02/2013 28/11/2012 21/05/2014 11/07/2013 27/12/2012 28/07/2011 16/07/2015 28/07/2011 29/04/2015
US 8252085 B1	28/08/2012	None	