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(54) **SELECTIVE SULFATION ROASTING OF RARE EARTH MAGNET WASTE**

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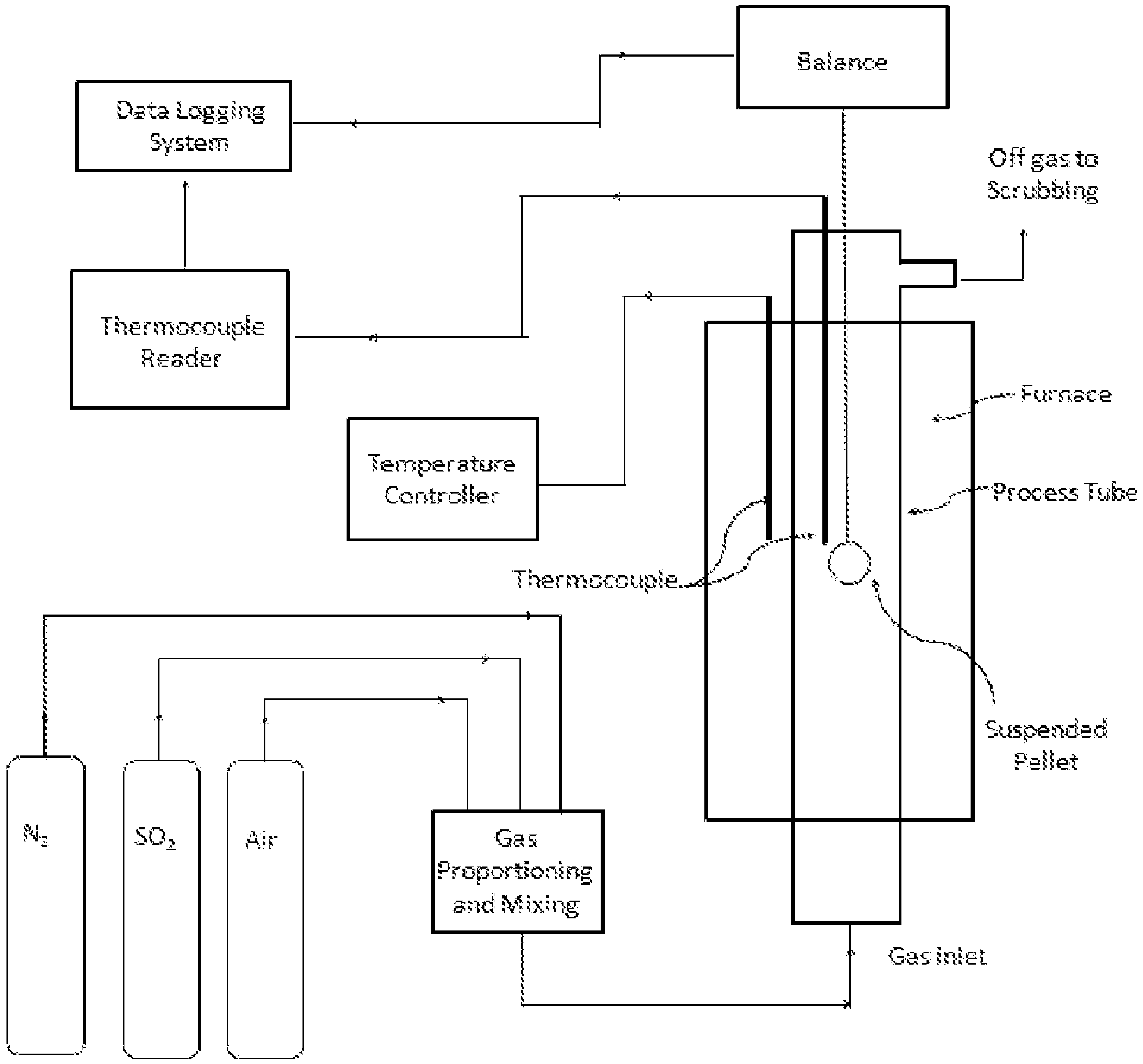
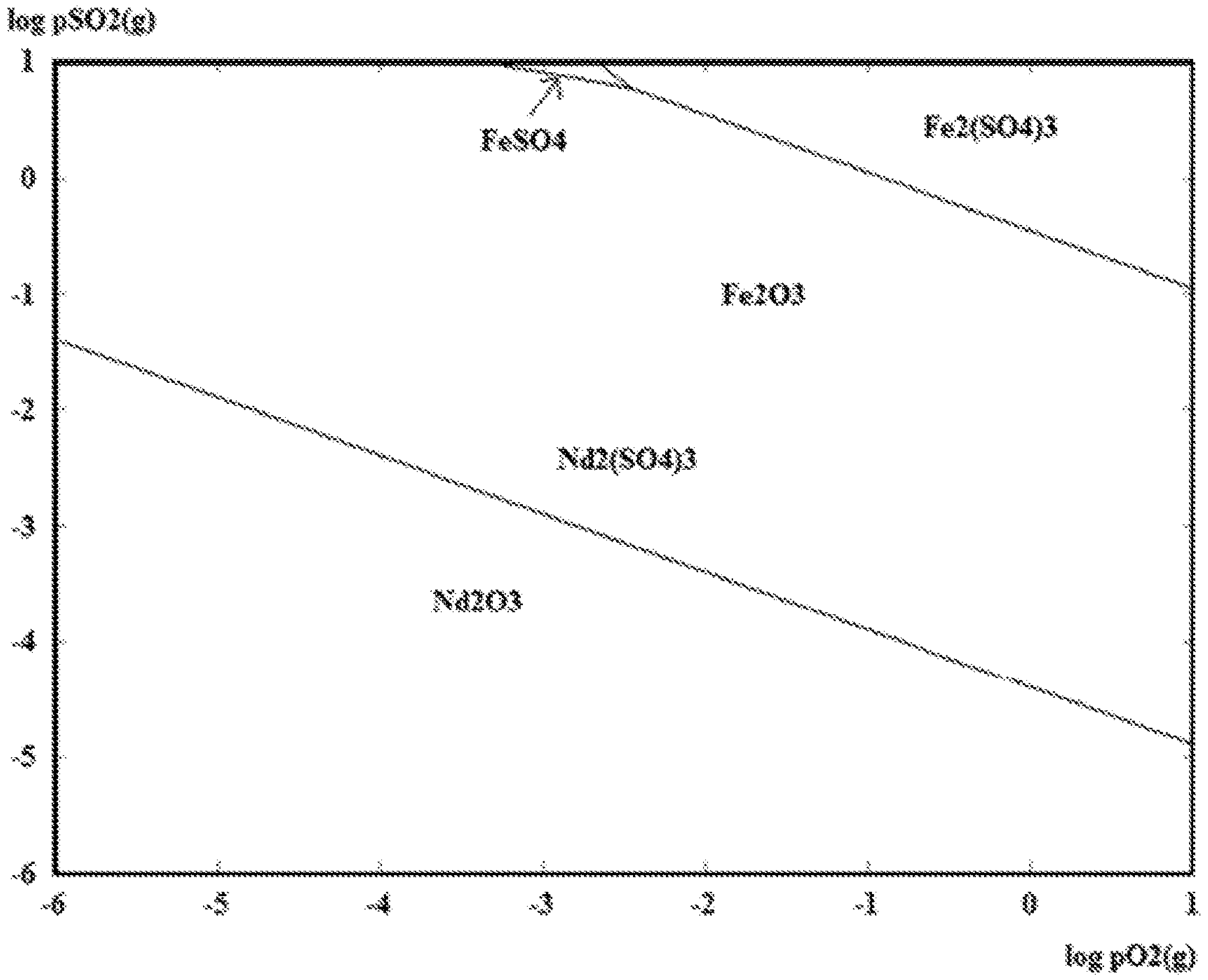
(57) **ABSTRACT**

The present invention relates to a sulfation method which processes a rare earth containing material. The material is roasted and exposed to a sulfur gas, then an aqueous leach to produce an insoluble metal oxide and a soluble rare earth sulfide. The insoluble and soluble material are separated utilizing a solid/liquid separator. Advantageously, the process eliminates the need for additional steps to precipitate the metal oxide in order to separate the metal from the rare earth. A system is also disclosed.

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FeSO4
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-1
0
1
log pO2(g)

FIG. 1

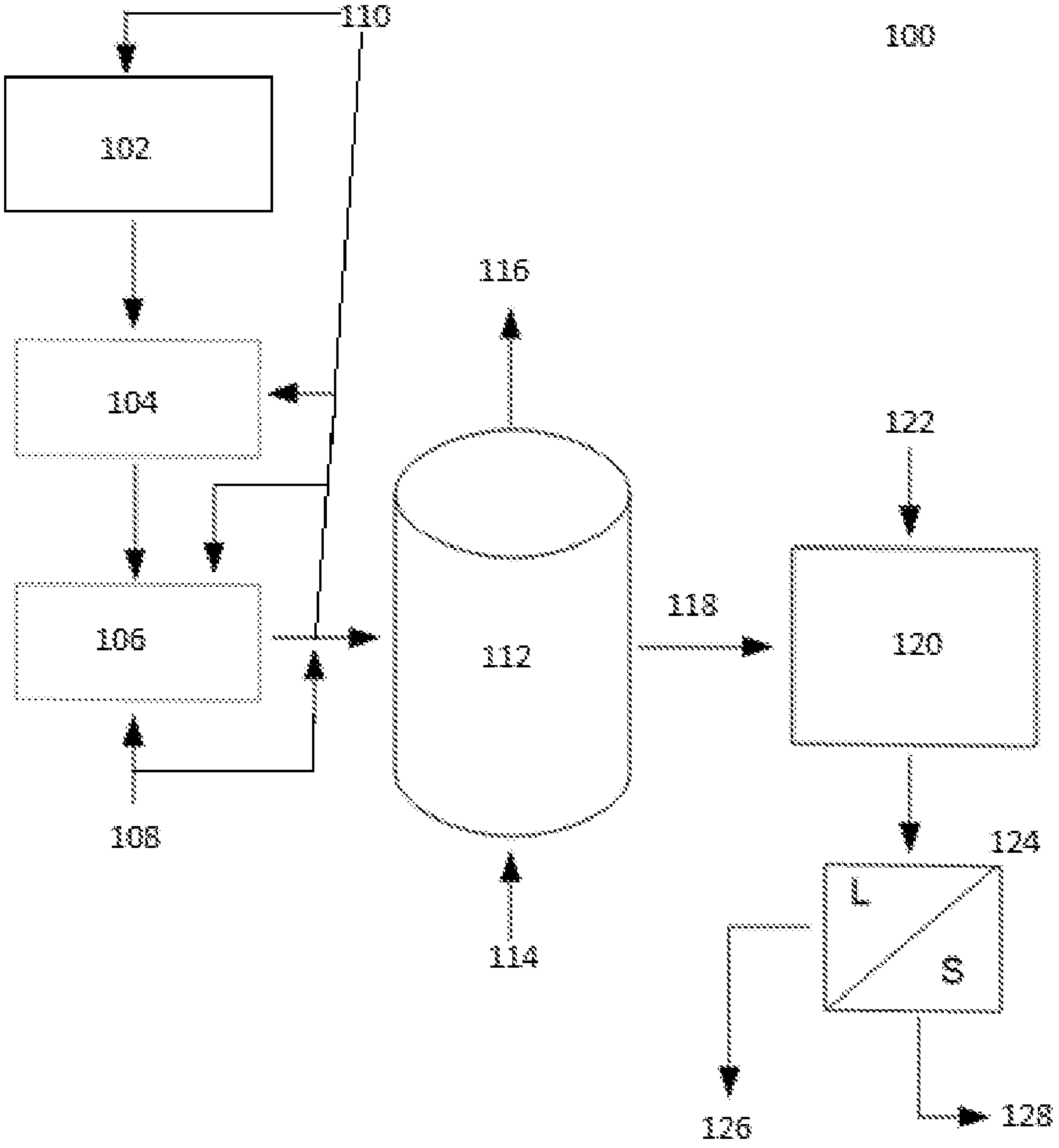
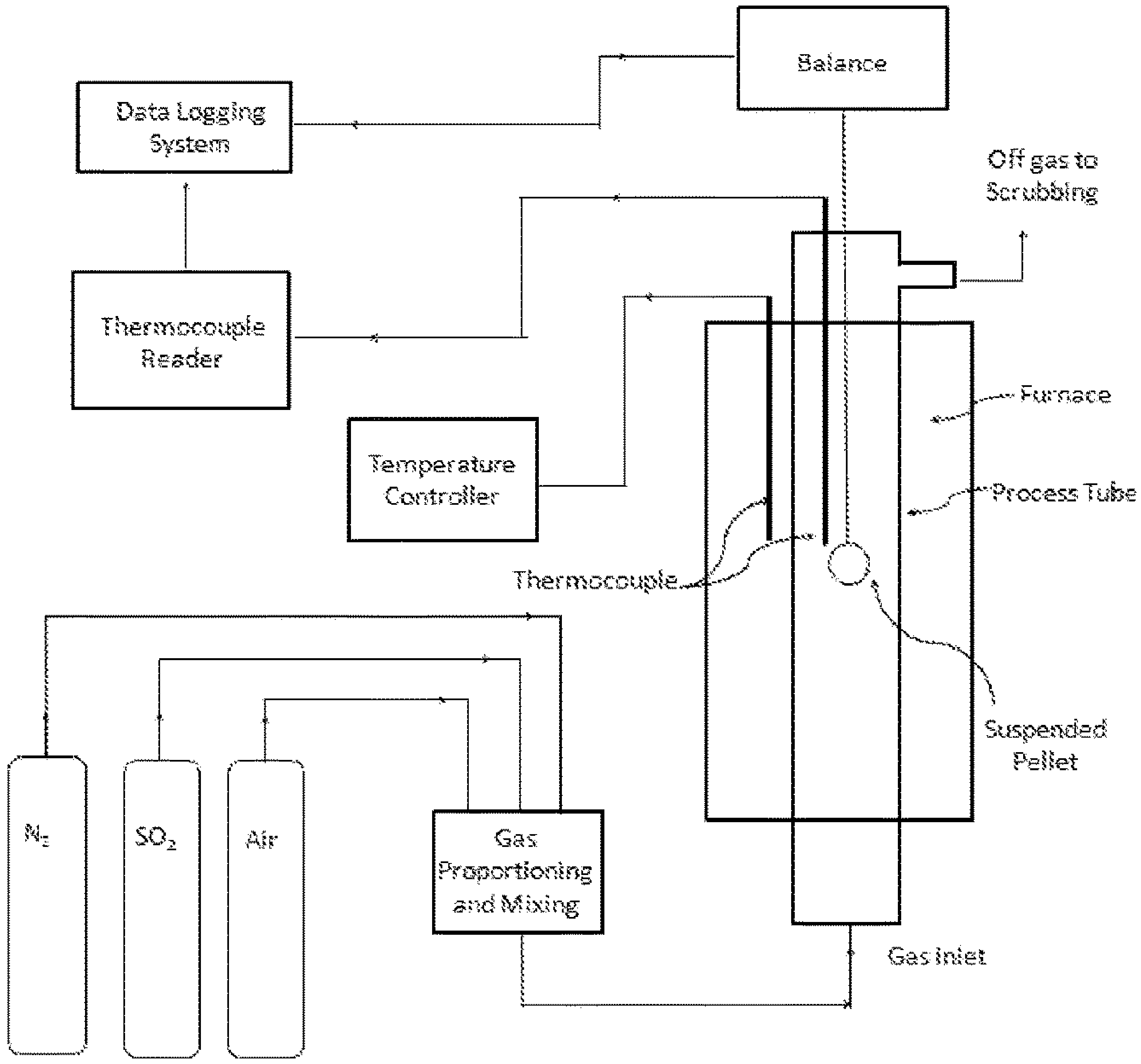


FIG. 2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Thermocouple Reader
Furnace
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Process Tube
Thermocouple
Suspended Pellet
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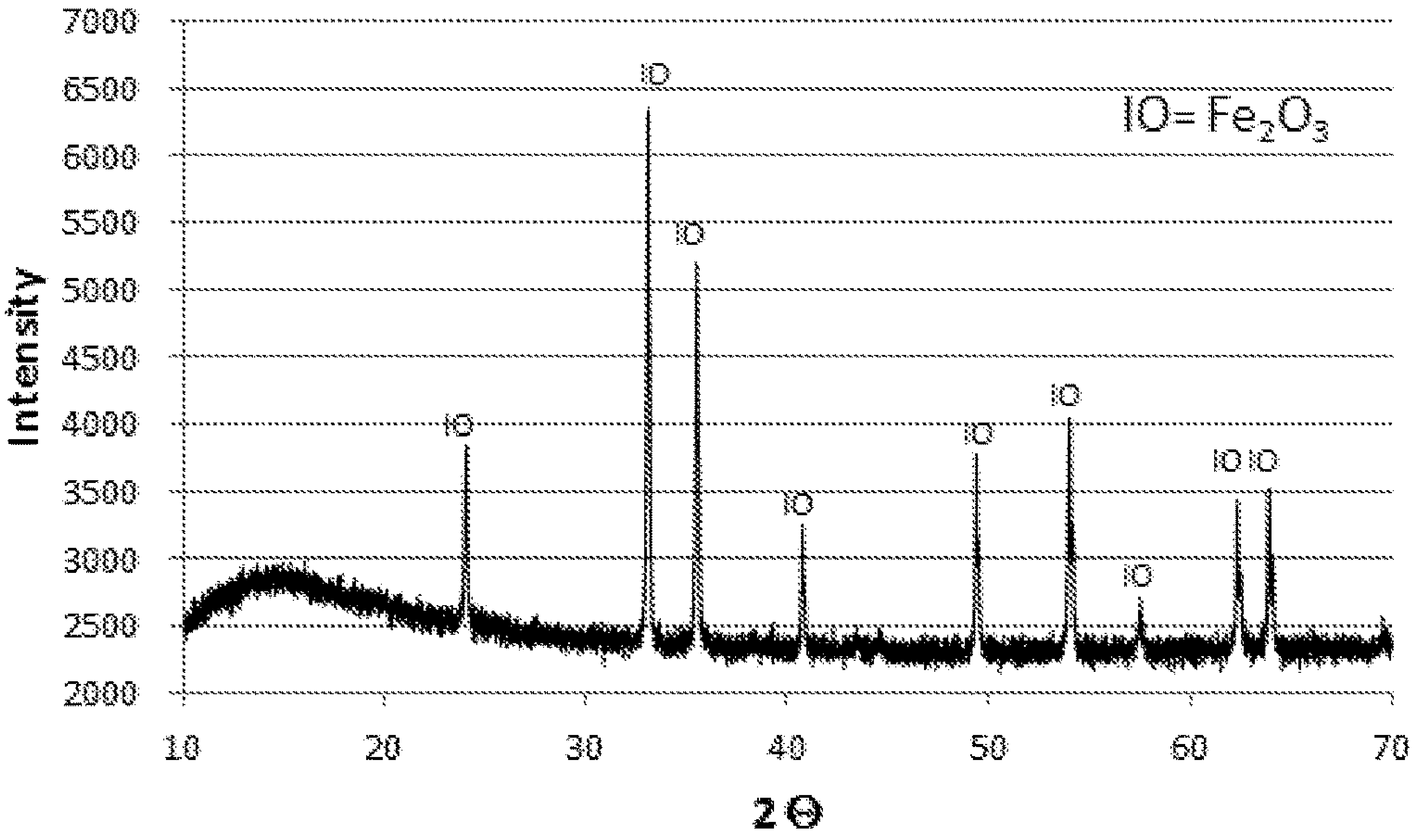
SO_2
Air
Gas Proportioning and Mixing
Gas inlet

FIG. 3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2000
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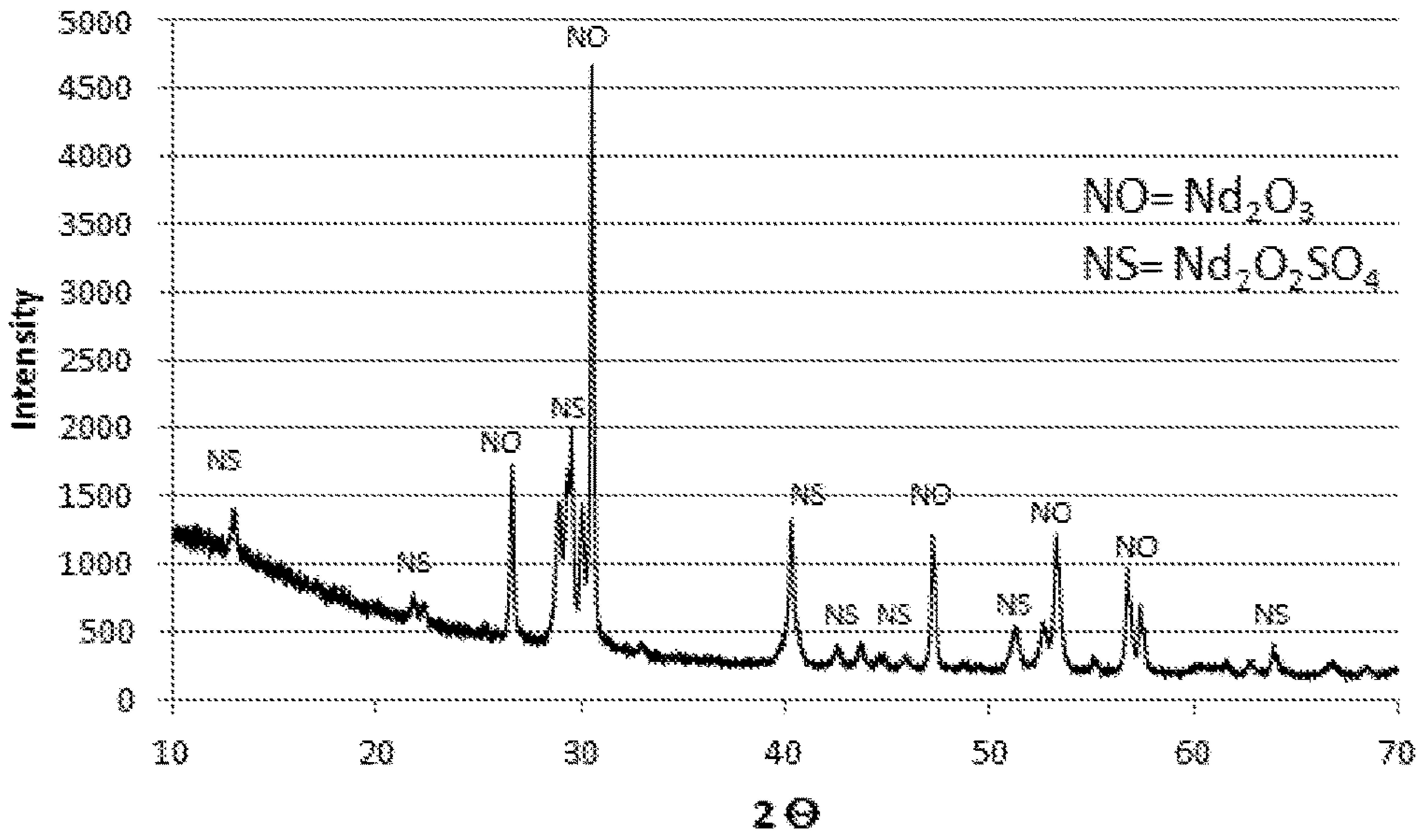
FIG. 4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NO= Nd_2O_3
NS= $Nd_2O_2SO_4$
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NS
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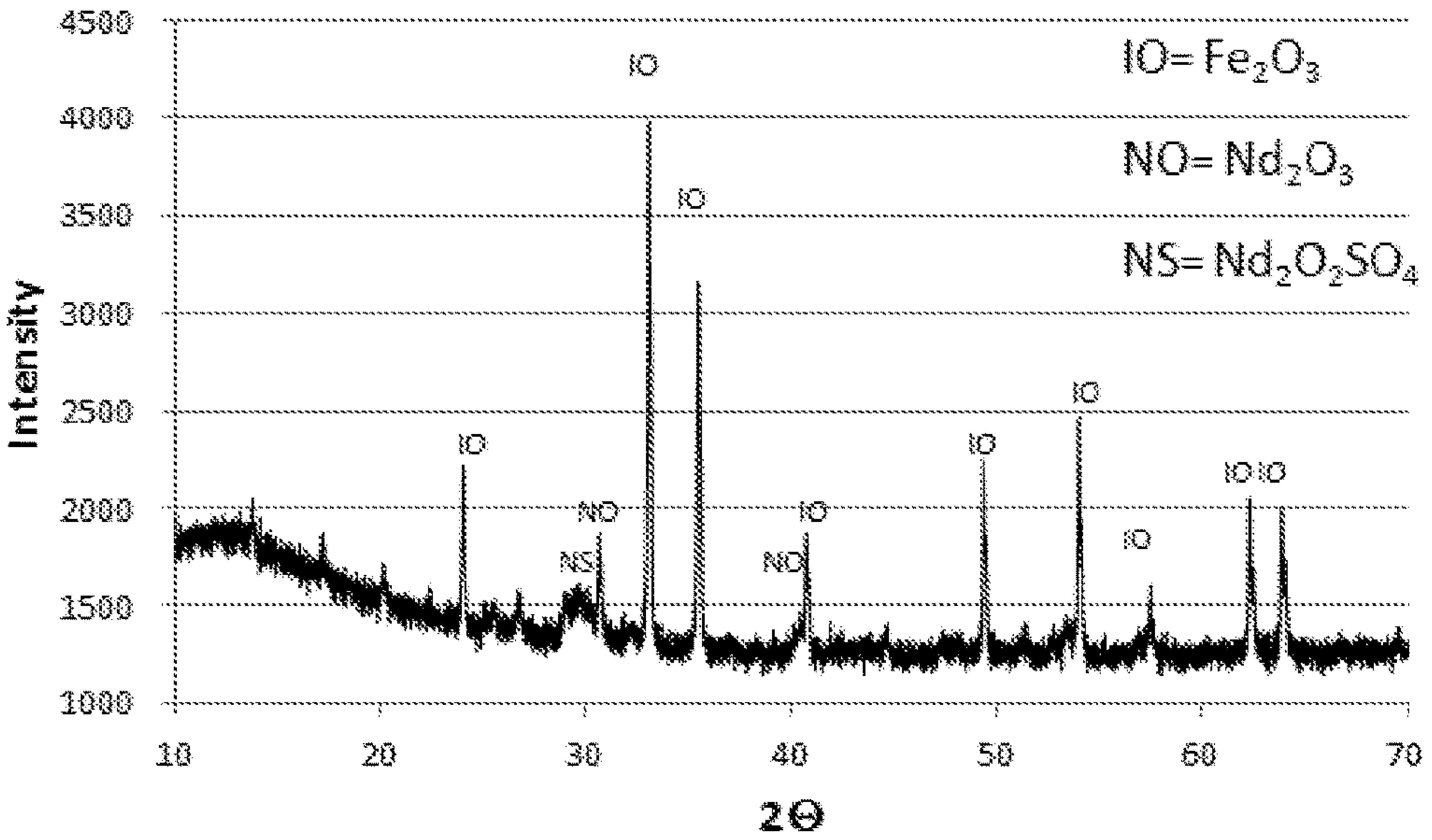
NO
NS

FIG. 5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NO= Nd_2O_3
NS= $Nd_2O_2SO_4$
IO
IO
IO
NO
NS
IO
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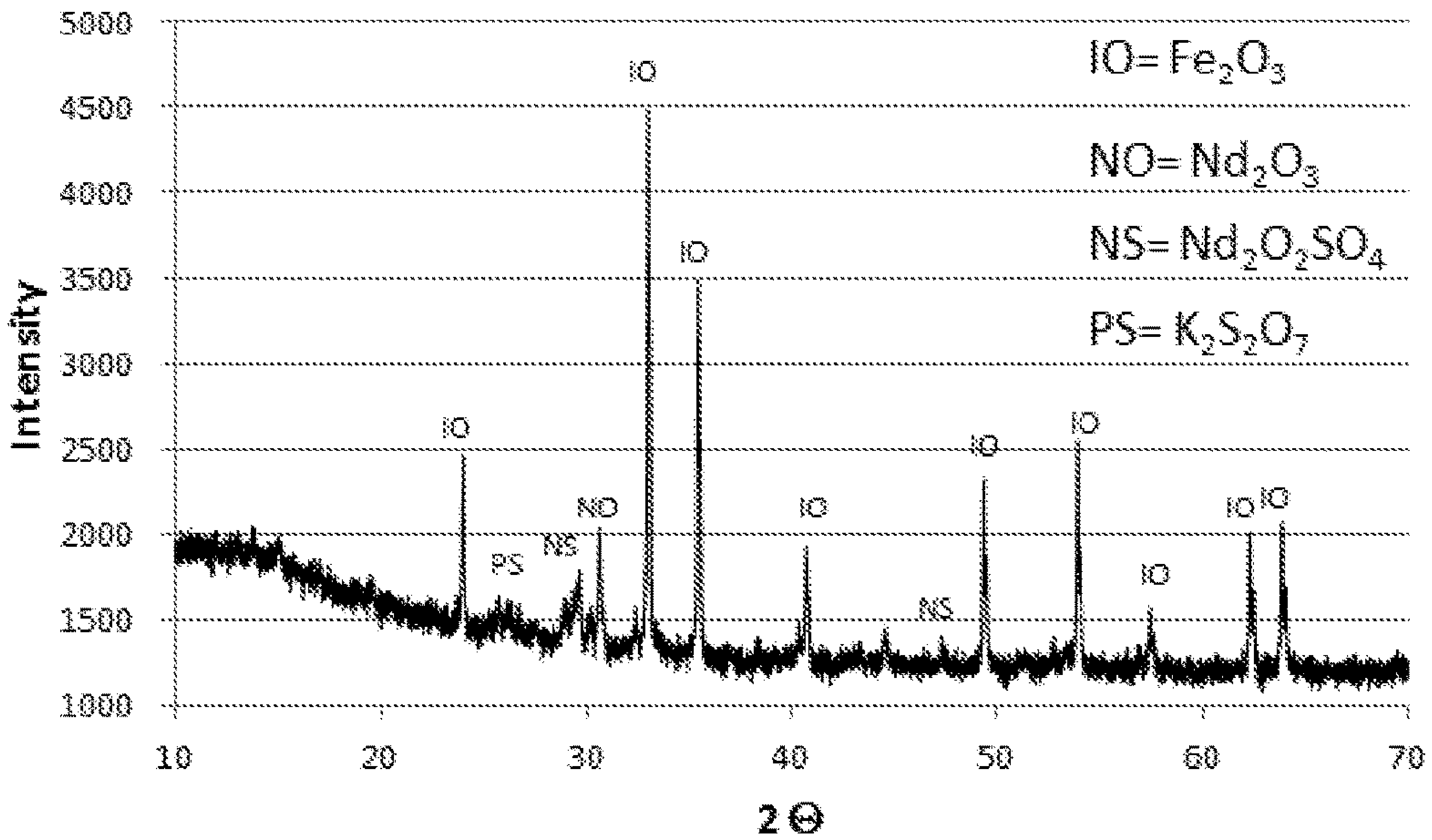
FIG. 6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40
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60
70
2Θ
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IO
NO
NS
PS
IO
NS
IO
IO
IO
IO
IO
IO= Fe_2O_3
NO= Nd_2O_3
NS= $Nd_2O_2SO_4$
PS= $K_2S_2O_7$

FIG. 7

SELECTIVE SULFATION ROASTING OF RARE EARTH MAGNET WASTE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority and benefits under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application Ser. No. 62/461,561 filed on Feb. 21, 2017, which is incorporated herein in its entirety by reference.

GOVERNMENT LICENSE RIGHTS

[0002] This invention was made with government support under grant number 400605 awarded by the Critical Materials Institute (Department of Energy). The Government has certain rights in the invention.

BACKGROUND

[0003] Rare earth magnets are responsible for around one quarter of the world's rare earth metal consumption. Sintered NdFeB type magnets are by far the strongest commercially available variety and are used where size and weight are important factors because a much smaller NdFeB magnet can be used in comparison to more traditional magnetic materials, such as ferrite or alnico. As such, rare earth magnets play an integral role in many high end technologies, such as hybrid and electric vehicles, computer hard drives, and high efficiency wind turbines.

[0004] During the manufacture of sintered rare earth magnets, up to 30% of the starting alloy is lost to machining waste. This waste, known as magnet "swarf" represents a significant waste stream in terms of value. This material cannot be re-used directly as it is contaminated with cutting fluids and grinding media, as well as being partly oxidized during the machining process.

[0005] There is a significant for a more efficient and cost effective method to recover rare earth magnets from scrap waste.

SUMMARY

[0006] Unlike prior art methods, which involve the roasting of magnet waste to oxides, followed by leaching with mineral acids, the present invention can extract rare earths metals, which represent significant value, while leaving the relatively low value base metals, like iron, behind. The resulting rare earth compounds can then be re-introduced into existing production circuits.

[0007] The present invention utilizes selective sulfation roasting, which allows for the selective extraction of rare earth metals from rare earth containing materials, like scrap $Nd_2Fe_{14}B$ or SmCo type magnets. The method of the present invention advantageously makes the high value rare earth metals soluble while converting base metals, like iron or cobalt, which make up most of the magnet's mass, into insoluble oxides. The process of the present invention thereby eliminates the need for separating and precipitating the base metal from solution. The method of the present invention also has the advantage of safely disposing of metalworking fluid contained in rare earth magnet machine waste, a troublesome contaminate from a technical and environmental perspective.

[0008] U. S. Publication No. 2016/0068929 to Taylor et al., which is incorporated by reference in its entirety, discloses a method to separate a rare earth from a base metal using a liquid sulfur material during the roasting step. During the roasting step, the base metal, for example iron, reacts with the liquid sulfur to form iron oxide and sulfur dioxide, and the soluble rare earth sulfide. Advantageously, the present invention utilizes sulfur dioxide rather than producing sulfur dioxide.

[0009] An aspect of the invention is a method to selectively separate at least one rare earth metal from magnetic waste. The method includes roasting the magnetic waste in a sulfur gas environment at a temperature between about 300° C. and about 1000° C. to produce a roasted magnetic waste. The roasted magnetic waste is leached with an aqueous fluid to produce a rare earth liquid containing stream and an insoluble material. The rare earth liquid containing stream comprises less than about 1 wt. % of a total weight of at least one metal of iron, cobalt, aluminum. The insoluble material comprises at least one metal. The rare earth liquid containing stream and the insoluble material are separated.

[0010] An aspect of the invention is a method to recover at least one rare earth metal. The method includes roasting a metal material with a sulfur gas to produce a roasted metal. The metal material comprises at least one rare earth metal, and at least one metal comprising iron. The roasted metal is leached to produce a rare earth containing stream and an insoluble metal. The rare earth containing stream does not comprise the insoluble metal. The rare earth containing stream and the insoluble metal are separated.

[0011] An aspect of the invention is a system to recover at least one rare earth metal. The system includes a furnace for receiving material containing at least one rare earth metal. The furnace is capable of operating at a temperature between about 300° C. and about 1000° C. The system include a sulfur gas inlet, which provides a sulfur gas to the furnace, a leaching tank, which receives a roasted material from the furnace, and a separator, which separates the liquid from the insoluble material. The leaching tank combines water and the roasted material to produce an insoluble material and a liquid, and the liquid includes the rare earth metal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. **1** illustrates a stability diagram composed of superimposed (Nd & Fe)—O_2—SO_2 at about 750° C.;

[0013] FIG. **2** illustrates a method for processing a material of the present invention;

[0014] FIG. **3** illustrates the thermal gravimetric analysis system (TGA) set up utilized in Example 2;

[0015] FIG. **4** illustrates a X-ray diffraction (XRD) pattern of roasted Fe_2O_3 pellet;

[0016] FIG. **5** illustrates a XRD pattern of roasted Nd_2O_3 pellet;

[0017] FIG. **6** illustrates a XRD pattern of roasted Nd_2O_3—Fe_2O_3 pellet; and

[0018] FIG. **7** illustrates a XRD pattern of roasted Nd_2O_3—Fe_2O_3—K_2SO_4 pellet.

DETAILED DESCRIPTION

[0019] Selective sulfation roasting of rare earth containing materials, including magnet swarf, makes possible the selective leaching, with water, of rare earth metals away from base metals. These base metals can be present in the material, such as scrap magnets and machining swarf from the production of $Nd_2Fe_{14}B$ or SmCo type rare earth magnets.

[0020] One aspect of the present invention is a method to selectively separate at least one rare earth metal from magnetic waste. The method includes roasting the magnetic waste in a sulfur gas environment at a temperature between about 300° C. and about 1000° C. to produce a roasted magnetic waste. The roasted magnetic waste is leached with water to produce a rare earth liquid containing stream and an insoluble material. The rare earth liquid containing stream does not include at least one non rare earth metal of iron, cobalt, aluminum, while the insoluble material comprises at least one non rare earth metal. The rare earth liquid containing stream and the insoluble material are then separated.

[0021] The magnetic waste comprises at least one rare earth material, and at least one transition metal. The rare earth material can include neodymium, praseodymium, dysprosium, and combinations thereof, and more typically neodymium. The transition metals can include iron, cobalt, aluminum, and combinations thereof.

[0022] The sulfur gas environment generally comprises a sulfur gas. The sulfur gas environment can include between about 0.01% to about 99% of a sulfur gas, with the remaining amount containing other gases, including oxygen, air and combinations thereof. Inert or incidental gases can be included in the sulfur gas environment without deviating from the present invention. Inert or incidental gases can include nitrogen, argon and combinations thereof. Thus, in some embodiments, the sulfur gas environment can comprise of or consist of air, a sulfur gas and incidental gases. In some embodiments, the sulfur gas environment can include between about 50% and about 80% of a sulfur gas with the remaining gas being air and incidental gases. The sulfur gas can be sulfur dioxide, sulfur trioxide and combinations thereof.

[0023] The material is exposed to the sulfur gas environment at a temperature range of about 300° C. to about 1000° C. In some embodiments, the temperature range can be between about 500° C. and about 800° C., or between about 600° C. and about 800° C. In some embodiments, the temperature can be about 300° C., about 350° C., about 400° C., about 450° C., about 500° C., about 550° C., about 600° C., about 650° C., about 700° C., about 750° C., about 800° C., about 850° C., about 900° C., about 950° C., or about 1000° C. The thermodynamic basis for this reaction can be seen in the stability diagram illustrated in FIG. **1**. As illustrated in FIG. **1**, at about 750° C. there exists a partial pressure O_2 and SO_2, such as log (partial pressure O_2, SO_2)=−0.75, where iron will be stable as an oxide, while rare earths, for example neodymium, will form a rare earth sulfate.

[0024] The material is exposed to the sulfur gas environment at temperature for between about 10 minutes and about 4 hours. In some embodiments, the material can be exposed to the sulfur gas environment at temperature for between about 30 minutes and about 3 hours, or about 2 hours and about 3 hours. In some embodiments, the material can be exposed to the sulfur gas environment at temperature for about 10 minutes, about 20 minutes, about 30 minutes, about 40 minutes, about 50 minutes, about 60 minutes, about 70 minutes, about 80 minutes, about 90 minutes, about 100 minutes, about 110 minutes, about 120 minutes, about 150 minutes, about 180 minutes, about 210 minutes, or about 240 minutes. The material is exposed to the sulfur gas environment at a pressure of between about 10 psi and about 40 psi. The pressure can be between about 20 and about 30 psi, or between about 15 and about 35 psi. In some embodiments, the pressure can be about 10 psi, about 15 psi, about 20 psi, about 25 psi, about 30 psi, about 35 psi, or about 40 psi.

[0025] The insoluble material can be a metal oxide. The metal oxide can be iron oxide, cobalt oxide, aluminum oxide or combinations thereof.

[0026] In some embodiments, a coating can be removed from the material prior to processing. Suitable methods include stripping, blasting, sanding, or combinations thereof. The scrap magnets can be crushed or ground to a powder prior to roasting. The metals can be brittle, thus, the comminution step can be accomplished via traditional mineral processing equipment such as with a jaw crusher, rod mill, ball mill or a combination thereof. The material can either be processed as a powder, a briquette or pellet prior to roasting. Thus, in some embodiments, the metal can be processed into a briquette or pellet using disk pelletizer, briquetting press or combinations thereof. The shape of the briquetted or pelletized metal can be any suitable shape, including but not limited to, spheres, and lumps, or combinations thereof.

[0027] In some embodiments, the material can be mixed with an additive that can volatilize during heating, leaving behind a porous powder/briquette/pellet. The additive can be, but is not limited to, ammonium carbonate, ammonium bicarbonate, cellulose, and combinations thereof. Between about 10 vol. % to about 50 vol. % of the additive can be added to the total amount of the material. An additive, which can be an alkali metal sulfate such as potassium sulfate, can also act as a promoter and increases the conversion of rare earths to sulfates by between about 1% to about 70% compared to when the additive is not used. After the additive is combined with the material, the mixed material can be heated to a temperature between about 50° C. and about 250° C., for between about 30 minutes and about 4 hours to sublimate the mixture. The temperature can be between about 100° C. and about 225° C., or between about 150° C. and about 200° C. In some embodiments, the temperature can be about 50° C., about 100° C., about 150° C., or about 200° C. The mixed material can be at the temperature for between about 1 hour and about 3 hours, or between about 90 minutes and about 120 minutes. In some embodiments, the mixed material can be at the temperature for about 30 minutes, about 60 minutes, about 90 minutes, about 120 minutes, about 150 minutes, about 180 minutes, about 210 minutes, or about 240 minutes. The material can be sintered at a temperature between about 400° C. and about 800° C. for between about 30 minutes and about 10 hours. The sintering temperature can be between about 500° C. and about 700° C., 600° C. and about 700° C. In some embodiments, the sintering temperature can be about 400° C., about 450° C., about 500° C., about 550° C., about 600° C., about 650° C., about 700° C., about 750° C., or about 800° C. The sintering time can be between about 1 hour and about 9 hours, about 2 hours and about 8 hours, about 3 hours and about 7 hours, about 4 hours and about 6 hours, or about 5 hours and about 5.5 hours. In some embodiments, the sintering time can be about 30 minutes, about 1 hour, about 1.5 hours, about 2 hours, about 2.5 hours, about 3 hours, about 3.5 hours, about 4 hours, about 4.5 hours, about 5 hours, about 5.5 hours, about 6 hours, about 6.5 hours, about 7 hours, about 7.5 hours, about 8 hours, about 8.5 hours, about 9 hours, about 9.5 hours or about 10 hours. If the material is in the form of a pellet or briquette, then the material can be turned to form a secondary shape, if desired. The secondary shape can be a pellet, a briquette or a lump, or any other suitable shape, and can be formed at room temperature.

[0028] The off-gasses from the roasting process can be scrubbed in a gas cleaning process to remove any entrapped particles. The sulfur gas can be added to the off-gas and re-introduced in the sulfur gas environment. The particles can be recycled or disposed of as necessary by traditional methods known to those skilled in the art.

[0029] The roasted material can then be sent to the leaching circuit. The rare earth containing stream can comprise at least one rare earth material such as neodymium, yttrium, lanthanum, cerium, dysprosium, terbium, praseodymium, europium, scandium, ytterbium, gadolinium, samarium, lutetium, erbium, thulium, holmium, thorium, and promethium, and combinations thereof. The rare earths are converted to soluble rare earth sulfates. The insoluble material can include transition or base metals, such as iron or cobalt. The base or transition metals forms oxides, which are insoluble. An aqueous material, such as water, can be used to selectively leach the rare earth sulfates. This leaching can take place in a reactor, such as a stirred tank reactor, and can be accomplished at fairly high pulp densities between about 20 grams per liter and about 100 grams per liter. In some embodiments, the pulp density can be between about 30 grams per liter and about 90 grams per liter, about 40 grams per liter and 80 grams per liter, about 50 grams per liter and about 70 grams per liter, about 55 grams per liter and about 65 grams per liter. In some embodiments, the pulp density can be about 30 grams per liter, about 40 grams per liter, about 50 grams per liter, about 60 grams per liter, about 70 grams per liter, about 80 grams per liter, about 90 grams per liter, or about 100 grams per liter. The ratio of the aqueous material to the roasted materials can be between about 1:50 and about 1:10 by weight. The ratio can be between about 1:45 and about 1:15 by weight, or between about 1:30 and about 1:20 by weight. In some embodiments, the ratio can be about 1:50, about 1:40, about 1:30, about 1:20 or about 1:10 by weight. The leaching can occur at a temperature between about 10° C. and about 50° C., for between about 5 minutes and about 2 hours, at a pressure of between about 10 psi and about 20 psi. In some embodiments, the leaching temperature can be between about 20° C. and about 40° C., or between about 30° C. and about 40° C. In some embodiments, the leaching temperature can be about 10° C., about 20° C., about 30° C., about 40° C., or about 50° C. The leaching time at temperature can be between about 30 minutes and about 1.5 hours, or between about 45 minutes and about 75 minutes. In some embodiments, the leaching time can be about 5 minutes, about 10 minutes, 15 minutes, about 20 minutes, about 25 minutes, about 30 minutes, about 35 minutes, about 40 minutes, about 45 minutes, about 50 minutes, about 60 minutes, about 70 minutes, about 80 minutes, about 90 minutes, about 100 minutes, about 110 minutes, or about 120 minutes. The leaching pressure can be between about 15 psi and about 20 psi. In some embodiments, the leaching pressure can be 10 psi, about 15 psi, or about 20 psi. Advantageously, because the transition metals are insoluble while the rare earth metals are soluble following the leaching, the liquid does not need to be processed to remove the transition metals as the liquid stream does not contain soluble transition metals (i.e. contains between about 0 and about 1% of a transition metal sulfate). Thus, unlike prior art methods, the present invention does not require additional steps to precipitate the transition metals from the liquid stream. After leaching, the insoluble solid residue can be separated from the leach liquor using a solid liquid separation step. The washed solids, containing the transition metal oxides, can be sent to tailing disposal, or if produced at a high enough purity, sold as a powdered oxide product. The liquid stream comprising the rare earth can be processed by oxalic acid precipitation to form rare earth oxides. In some embodiments, the liquid stream can include less than about 1 wt. % of an insoluble metal. In some embodiments, the liquid stream can include less than about 0.9 wt. % of an insoluble metal, less than about 0.8 wt. % of an insoluble metal, less than about 0.7 wt. % of an insoluble metal, less than about 0.6 wt. % of an insoluble metal, less than about 0.5 wt. % of an insoluble metal, less than about 0.4 wt. % of an insoluble metal, less than about 0.3 wt. % of an insoluble metal, less than about 0.2 wt. % of an insoluble metal, less than about 0.1 wt. % of an insoluble metal, or about 0 wt. % of an insoluble metal.

[0030] An aspect of the present invention is a method to recover at least one rare earth metal. The method includes roasting a metal material with a sulfur gas to produce a roasted metal. The metal material comprises at least one rare earth metal, and at least one non rare earth metal comprising iron, cobalt, aluminum. The roasted metal is leached to produce a rare earth containing stream and an insoluble metal. The rare earth containing stream does not comprise more than about 1% of the insoluble metal. The rare earth containing stream and the insoluble metal are then separated.

[0031] The metallic material comprises at least one rare earth material, and at least one transition metal. The rare earth material can include neodymium, praseodymium, dysprosium, and combinations thereof, and more typically neodymium. The transition metals can include iron, cobalt, aluminum, and combinations thereof.

[0032] The sulfur gas generally comprises a sulfur gas. The sulfur gas can include between about 0.01% to about 99% of a sulfur gas, with the remaining amount containing other gases, including oxygen, air and combinations thereof. Inert or incidental gases can be included in the sulfur gas without deviating from the present invention. Inert or incidental gases can include nitrogen, argon and combinations thereof. Thus, in some embodiments, the sulfur gas can comprise of or consist of air, a sulfur gas and incidental gases. In some embodiments, the sulfur gas can include between about 50% and about 80% of a sulfur gas with the remaining gas being air and incidental gases. The sulfur gas can be sulfur dioxide, sulfur trioxide and combinations thereof.

[0033] The material is exposed to the sulfur gas at a temperature range of about 300° C. to about 1000° C. In some embodiments, the temperature range can be between about 500° C. and about 800° C., or between about 600° C. and about 800° C. In some embodiments, the temperature can be about 300° C., about 350° C., about 400° C., about 450° C., about 500° C., about 550° C., about 600° C., about 650° C., about 700° C., about 750° C., about 800° C., about 850° C., about 900° C., about 950° C., or about 1000° C. The thermodynamic basis for this reaction can be seen in the stability diagram illustrated in FIG. **1**. As illustrated in FIG. **1**, at about 750° C. there exists a partial pressure O_2 and SO_2, such as log (partial pressure O_2, SO_2)=−0.75, where iron will be stable as an oxide, while rare earths, for example neodymium, will form a rare earth sulfate.

[0034] The material is exposed to the sulfur gas at temperature for between about 10 minutes and about 4 hours. In some embodiments, the material can be exposed to the sulfur gas at temperature for between about 30 minutes and about 3 hours, or about 2 hours and about 3 hours. In some embodiments, the material can be exposed to the sulfur gas at temperature for about 10 minutes, about 20 minutes, about 30 minutes, about 40 minutes, about 50 minutes, about 60 minutes, about 70 minutes, about 80 minutes, about 90 minutes, about 100 minutes, about 110 minutes, about 120 minutes, about 150 minutes, about 180 minutes, about 210 minutes, or about 240 minutes. The material is exposed to the sulfur gas at a pressure of between about 10 psi and about 40 psi. The pressure can be between about 20 and about 30 psi, or between about 15 and about 35 psi. In some embodiments, the pressure can be about 10 psi, about 15 psi, about 20 psi, about 25 psi, about 30 psi, about 35 psi, or about 40 psi.

[0035] The insoluble material can be a metal oxide. The metal oxide can be iron oxide, cobalt oxide, aluminum oxide or combinations thereof.

[0036] In some embodiments, a coating can be removed from the material prior to processing. Suitable methods include stripping, blasting, sanding, or combinations thereof. The scrap magnets can be crushed or ground to a powder prior to roasting. The metals can be brittle, thus, the comminution step can be accomplished via traditional mineral processing equipment such as with a jaw crusher, rod mill, ball mill or a combination thereof. The material can either be processed as a powder, a briquette or pellet prior to roasting. Thus, in some embodiments, the metal can be processed into a briquette or pellet using disk pelletizer, briquetting press or combinations thereof. The shape of the briquetted or pelletized metal can be any suitable shape, including but not limited to, spheres, and lumps, or combinations thereof.

[0037] In some embodiments, the material can be mixed with an additive that can volatilize during heating, leaving behind a porous powder/briquette/pellet. The additive can be, but is not limited to, ammonium carbonate, ammonium bicarbonate, cellulose, and combinations thereof. Between about 10 vol. % to about 50 vol. % of the additive can be added to the total amount of the material. An additive, which can be an alkali metal sulfate such as potassium sulfate, can also act as a promoter and increases the conversion of rare earths to sulfates by between about 1% to about 70% compared to when the additive is not used. After the additive is combined with the material, the mixed material can be heated to a temperature between about 50° C. and about 250° C., for between about 30 minutes and about 4 hours to sublimate the mixture. The temperature can be between about 100° C. and about 225° C., or between about 150° C. and about 200° C. In some embodiments, the temperature can be about 50° C., about 100° C., about 150° C., or about 200° C. The mixed material can be at the temperature for between about 1 hour and about 3 hours, or between about 90 minutes and about 120 minutes. In some embodiments, the mixed material can be at the temperature for about 30 minutes, about 60 minutes, about 90 minutes, about 120 minutes, about 150 minutes, about 180 minutes, about 210 minutes, or about 240 minutes. The material can be sintered at a temperature between about 400° C. and about 800° C. for between about 30 minutes and about 10 hours. The sintering temperature can be between about 500° C. and about 700° C., 600° C. and about 700° C. In some embodiments, the sintering temperature can be about 400° C., about 450° C., about 500° C., about 550° C., about 600° C., about 650° C., about 700° C., about 750° C., or about 800° C. The sintering time can be between about 1 hour and about 9 hours, about 2 hours and about 8 hours, about 3 hours and about 7 hours, about 4 hours and about 6 hours, or about 5 hours and about 5.5 hours. In some embodiments, the sintering time can be about 30 minutes, about 1 hour, about 1.5 hours, about 2 hours, about 2.5 hours, about 3 hours, about 3.5 hours, about 4 hours, about 4.5 hours, about 5 hours, about 5.5 hours, about 6 hours, about 6.5 hours, about 7 hours, about 7.5 hours, about 8 hours, about 8.5 hours, about 9 hours, about 9.5 hours or about 10 hours. If the material is in the form of a pellet or briquette, then the material can be turned to form a secondary shape, if desired. The secondary shape can be a pellet, a briquette or a lump, or any other suitable shape, and can be formed at room temperature.

[0038] The off-gasses from the roasting process can be scrubbed in a gas cleaning process to remove any entrapped particles. The sulfur gas can be added to the off-gas and re-introduced in the sulfur gas. The particles can be recycled or disposed of as necessary by traditional methods known to those skilled in the art.

[0039] The roasted material can then be sent to the leaching circuit. The rare earth containing stream can comprise at least one rare earth material such as neodymium, yttrium, lanthanum, cerium, dysprosium, terbium, praseodymium, europium, scandium, ytterbium, gadolinium, samarium, lutetium, erbium, thulium, holmium, thorium, and promethium, and combinations thereof. The rare earths are converted to soluble rare earth sulfates. The insoluble material can include transition or base metals, such as iron or cobalt. The base or transition metals forms oxides, which are insoluble. An aqueous material, such as water, can be used to selectively leach the rare earth sulfates. This leaching can take place in a reactor, such as a stirred tank reactor, and can be accomplished at fairly high pulp densities between about 20 grams per liter and about 100 grams per liter. In some embodiments, the pulp density can be between about 30 grams per liter and about 90 grams per liter, about 40 grams per liter and 80 grams per liter, about 50 grams per liter and about 70 grams per liter, about 55 grams per liter and about 65 grams per liter. In some embodiments, the pulp density can be about 30 grams per liter, about 40 grams per liter, about 50 grams per liter, about 60 grams per liter, about 70 grams per liter, about 80 grams per liter, about 90 grams per liter, or about 100 grams per liter. The ratio of the aqueous material to the roasted materials can be between about 1:50 and about 1:10 by weight. The ratio can be between about 1:45 and about 1:15 by weight, or between about 1:30 and about 1:20 by weight. In some embodiments, the ratio can be about 1:50, about 1:40, about 1:30, about 1:20 or about 1:10 by weight. The leaching can occur at a temperature between about 10° C. and about 50° C., for between about 5 minutes and about 2 hours, at a pressure of between about 10 psi and about 20 psi. In some embodiments, the leaching temperature can be between about 20° C. and about 40° C., or between about 30° C. and about 40° C. In some embodiments, the leaching temperature can be about 10° C., about

20° C., about 30° C., about 40° C., or about 50° C. The leaching time at temperature can be between about 30 minutes and about 1.5 hours, or between about 45 minutes and about 75 minutes. In some embodiments, the leaching time can be about 5 minutes, about 10 minutes, 15 minutes, about 20 minutes, about 25 minutes, about 30 minutes, about 35 minutes, about 40 minutes, about 45 minutes, about 50 minutes, about 60 minutes, about 70 minutes, about 80 minutes, about 90 minutes, about 100 minutes, about 110 minutes, or about 120 minutes. The leaching pressure can be between about 15 psi and about 20 psi. In some embodiments, the leaching pressure can be 10 psi, about 15 psi, or about 20 psi. Advantageously, because the transition metals are insoluble while the rare earth metals are soluble following the leaching, the liquid does not need to be processed to remove the transition metals as the liquid stream does not contain soluble transition metals (i.e. contains between about 0 and about 1% of a transition metal sulfate). Thus, unlike prior art methods, the present invention does not require additional steps to precipitate the transition metals from the liquid stream. After leaching, the insoluble solid residue can be separated from the leach liquor using a solid liquid separation step. The washed solids, containing the transition metal oxides, can be sent to tailing disposal, or if produced at a high enough purity, sold as a powdered oxide product. The liquid stream comprising the rare earth can be processed by oxalic acid precipitation to form rare earth oxides. In some embodiments, the liquid stream can include less than about 1 wt. % of an insoluble metal. In some embodiments, the liquid stream can include less than about 0.9 wt. % of an insoluble metal, less than about 0.8 wt. % of an insoluble metal, less than about 0.7 wt. % of an insoluble metal, less than about 0.6 wt. % of an insoluble metal, less than about 0.5 wt. % of an insoluble metal, less than about 0.4 wt. % of an insoluble metal, less than about 0.3 wt. % of an insoluble metal, less than about 0.2 wt. % of an insoluble metal, less than about 0.1 wt. % of an insoluble metal, or about 0 wt. % of an insoluble metal.

[0040] Another aspect of the present invention is a system/apparatus to recover at least one rare earth metal. The system can include, but is not limited to, a furnace for receiving material containing at least one rare earth metal. The furnace is capable of operating at a temperature between about 300° C. and about 1000° C. In some embodiments, the furnace can operate at a temperature between about 600° C. and about 1000° C., between about 700° C. and about 1000° C., between about 800° C. and about 1000° C., or between about 900° C. and about 1000° C. A sulfur gas inlet is provided to introduce a sulfur gas to the furnace. A leaching tank receives a roasted material from the furnace, and water and the roasted material are combined in the leaching tank to produce an insoluble material and a liquid, wherein the liquid comprises the at least one rare earth metal. A separator separates the liquid from the insoluble material.

[0041] In some embodiments, the system can further include a comminutor to comminute the material. The system can include a stripper to remove a coating from the material prior to processing. The system can further include a briquette or a pelletizer.

[0042] Different reactors can be used based on needs. For example, the reactor can depend upon the received material. If the material is a powder, then the furnace can be a reactor such as a fluidized bed furnace. If the material is a pellet or a briquette, the furnace can be a rotary kiln, a rotary hearth, or a similar furnace. The leaching tank can be a stirred tank reactor.

[0043] FIG. **2** illustrates a process or method **100** of the present invention. As depicted, a feed stream **108** is provided. If coated, material can be decoated in a decoater **102**. The material can be comminuted using a grinder/crusher **104** before being fed into a pelletizer or briquetter **106**. An additive **108** can be combined with the material in the pelletizer/briquetter **106** or with the feed material **110**. The material **110** (which can be pre-processed using any of the previous steps individually, or in combination) is provided to a furnace **112** with a sulfur gas **114** (which can be combined with other gases such as air or oxygen). Off-gas **116** from the furnace **112** can be cleaned and recycled. The roasted material **118** is provided for leaching **120** where an aqueous material **122** (for example water) is provided for leaching **120**. The slurry is separated in a separator **124**. After separation, the leach stream can be washed and can separate the soluble rare earth metals from insoluble metal oxides. The liquid stream **126** includes rare earths, while the solids are metal oxides **128**.

EXAMPLES

Example 1

[0044] An analog of magnet waste was formed by the creation of a pellet made of iron oxide and neodymium oxide mixed at a 1:7 molar volume, as that found in the $Nd_2Fe_{14}B$ magnet compound. The oxides were mixed with 20 vol % ammonium bicarbonate and pressed into a ½" pellet, which was then sintered, the ammonium bicarbonate sublimating and giving the pellet porosity.

[0045] The pellet was roasted at 750° C. under an atmosphere of 0.3 atm SO_2 and 0.7 atm air for 1 hour. The pellet was then cooled, removed from the furnace, and crushed to −50 mesh. The crushed pellet was then leached in water at a ratio of approximately 7.5 grams of sample per liter of water. The sample was then filtered and washed. It was found at these conditions, 63.9% of the contained neodymium was found to dissolve, while only 0.24% of the iron was dissolved.

Example 2

[0046] Several compositions of porous pellets were prepared. Reagent grade components were utilized, all of which were sieved to −74 μm and +53 μm. In the samples containing Nd_2O_3 and Fe_2O_3, a 1:7 mol Fe:Nd ratio was used, corresponding to the $Nd_2Fe_{14}B$ phase utilized in NdFeB type magnets. Where potassium sulfate was added, a 0.1 mol per mol oxides ratio was used. Each pellet composition was mixed with ammonium bicarbonate so that this fraction took up 1/7 of the total volume. These components were pressed into 20 mm cylindrical die. These pellets were heated at 100° C. for one hour, sublimating the contained ammonium bicarbonate, leaving behind a porous structure, and then sintered at 600° C. for 6 hrs. They were then turned to rough spheres by rotating the pellet in a 12.7 mm hole drilled in 4.8 mm steel plate.

[0047] Pellets were loaded in the a thermal gravimetric analysis system (TGA), as illustrated in FIG. **3**, and heated to 750° C. under a flow of Na gas. When the desired temperature was reached, a flow of SO_2 and air was introduced into the furnace which provides an atmosphere which corresponded to a −log (P_{O2},P_{SO2}) of 0.76. This temperature lies within a region which iron is stable as an oxide, while neodymium is stable as a sulfate (see FIG. **1**). The pellet was reacted for 1 hour after which the furnace was flushed with N_2 and allowed to cool. The resulting pellet weighed was crushed to −295 μm for analysis by X-ray diffraction (XRD) to determine the phases present in the sample.

[0048] The weight change of each pellet after sulfation roasting can be seen in Table 1.

TABLE 1

Change in weight of sample after roasting

Sample	% Weight Change
Fe_2O_3	−0.37
Nd_2O_3	12.27
Nd_2O_3—Fe_2O_3	7.03
Nd_2O_3—Fe2O3—K_2SO_4	7.96

[0049] The XRD pattern of the iron oxide pellet is illustrated in FIG. **4**, a XRD pattern of the neodymium oxide pellet is illustrated in FIG. **5**, and XRD pattern of the iron oxide and neodymium oxide pellet is illustrated in FIG. **6**, and a XRD pattern of the iron oxide and neodymium oxide pellet that included potassium sulfate is illustrated in FIG. **7**.

[0050] As seen in the XRD pattern in FIG. **4**, the pellet of iron oxide appears to not have reacted at the experimental conditions used. This pattern is in agreement with the Kellog diagram in FIG. **1**, which shows that Fe_2O_3 is the thermodynamically stable phase at 750° C. and −log(PO_2, PSO_2) =0.76.

[0051] The samples containing neodymium oxide were shown to be reactive, as seen in Table 1, as they all exhibited a weight gain. Looking at the XRD patterns, however, it appears that in place of the sulfate species expected, a neodymium oxy-sulfate phase is dominant. It may be that this phase is an intermediate which forms in between the oxide and sulfate, and simply more reaction time is necessary. This experiment demonstrates with XRD analysis, iron oxide does not seem to react at the conditions used, as predicted by the thermodynamic stability diagram. However, neodymium was found to form an oxy-sulfate species.

[0052] Ranges have been discussed and used within the forgoing description. One skilled in the art would understand that any sub-range within the stated range would be suitable, as would any number within the broad range, without deviating from the invention.

[0053] The foregoing description of the present invention has been presented for purposes of illustration and description. Furthermore, the description is not intended to limit the invention to the form disclosed herein. Consequently, variations and modifications commensurate with the above teachings, and the skill or knowledge of the relevant art, are within the scope of the present invention. The embodiment described hereinabove is further intended to explain the best mode known for practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with various modifications required by the particular applications or uses of the present invention. It is intended that the appended claims be construed to include alternative embodiments to the extent permitted by the prior art.

1. A method to selectively separate at least one rare earth metal from magnetic waste, comprising:

roasting the magnetic waste in a sulfur gas environment at a temperature between about 300° C. and about 1000° C. to produce a roasted magnetic waste;

leaching the roasted magnetic waste with an aqueous fluid to produce a rare earth liquid containing stream and an insoluble material, wherein the rare earth liquid containing stream comprises less than about 1 wt. % of a total weight of at least one metal, and wherein the insoluble material comprises the at least one metal of iron, cobalt, aluminum; and

separating the rare earth liquid containing stream and the insoluble material.

2. The method of claim **1**, wherein the sulfur gas environment comprises air and sulfur dioxide.

3. The method of claim **1**, wherein a ratio of the aqueous fluid to the roasted magnetic waste is between about 1:50 and about 1:10.

4. The method of claim **1**, wherein the roasted magnetic waste comprises a metal oxide and an at least one stable rare earth sulfate.

5. The method of claim **1**, wherein temperature is between about 600° C. and about 800° C.

6. The method of claim **1**, wherein the at least one metal is an iron, a cobalt, aluminum and combinations thereof.

7. The method of claim **2**, wherein the sulfur dioxide is recycled.

8. The method of claim **1**, wherein a metal sulfide is not formed following the roasting of the magnetic waste.

9. The method of claim **1**, further comprising comminuting the magnetic waste prior to the roasting step.

10. The method of claim **1**, further comprising removing a coating from the magnetic waste prior to the roasting step.

11. The method of claim **9**, further comprising processing the comminuted magnetic waste to form a pellet or a briquette.

12. The method of claim **1**, further comprising combining the magnetic waste and an additive prior to the roasting step.

13. The method of claim **12**, wherein the magnetic waste further comprises between about 10 wt. % and about 50 wt. % of the additive.

14. The method of claim **12**, wherein the additive is an alkali metal sulfate, an ammonium carbonate, an ammonium bicarbonate, a cellulose, and combinations thereof.

15. The method of claim **14**, wherein the additive is the alkali metal sulfate comprising potassium sulfate.

16. The method of claim **1**, further comprising substantially purifying the at least one rare earth containing stream by oxalic acid precipitation to form a purified rare earth metal, wherein the purified rare earth metal comprises at least 90% of the at least one rare earth.

17. A method to recover at least one rare earth metal, comprising:

roasting a metal material with a sulfur gas to produce a roasted metal, wherein the metal material comprises at least one rare earth metal, and at least one metal comprising iron;

leaching the roasted metal to produce a rare earth containing stream and an insoluble metal, wherein the rare earth containing stream does not comprise the insoluble metal; and

separating the rare earth containing stream and the insoluble metal.

18. A system to recover at least one rare earth metal, comprising:

a furnace for receiving material containing the at least one rare earth metal, wherein the furnace is capable of operating at a temperature between about 300° C. and about 1000° C.;

a sulfur gas inlet, wherein the sulfur gas inlet provides a sulfur gas to the furnace;

a leaching tank, wherein the leaching tank receives a roasted material from the furnace, and wherein the leaching tank combines water and the roasted material to produce an insoluble material and a liquid, wherein the liquid comprises the at least one rare earth metal; and

a separator, wherein the separator separates the liquid from the insoluble material.

19. The system of claim **18**, wherein the furnace is selected from the group comprises at least one of a rotary kiln, a rotary hearth, and a fluidized bed.

20. The system of claim **18**, wherein the leaching tank is a stirred tank reactor.

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