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Neumann et al.(10) **Pub. No.: US 2015/0143954 A1**(43) **Pub. Date: May 28, 2015**(54) **SYSTEM AND METHOD FOR SELECTIVELY
REMOVING METALS FROM INDUSTRIAL
WASTE****Related U.S. Application Data**

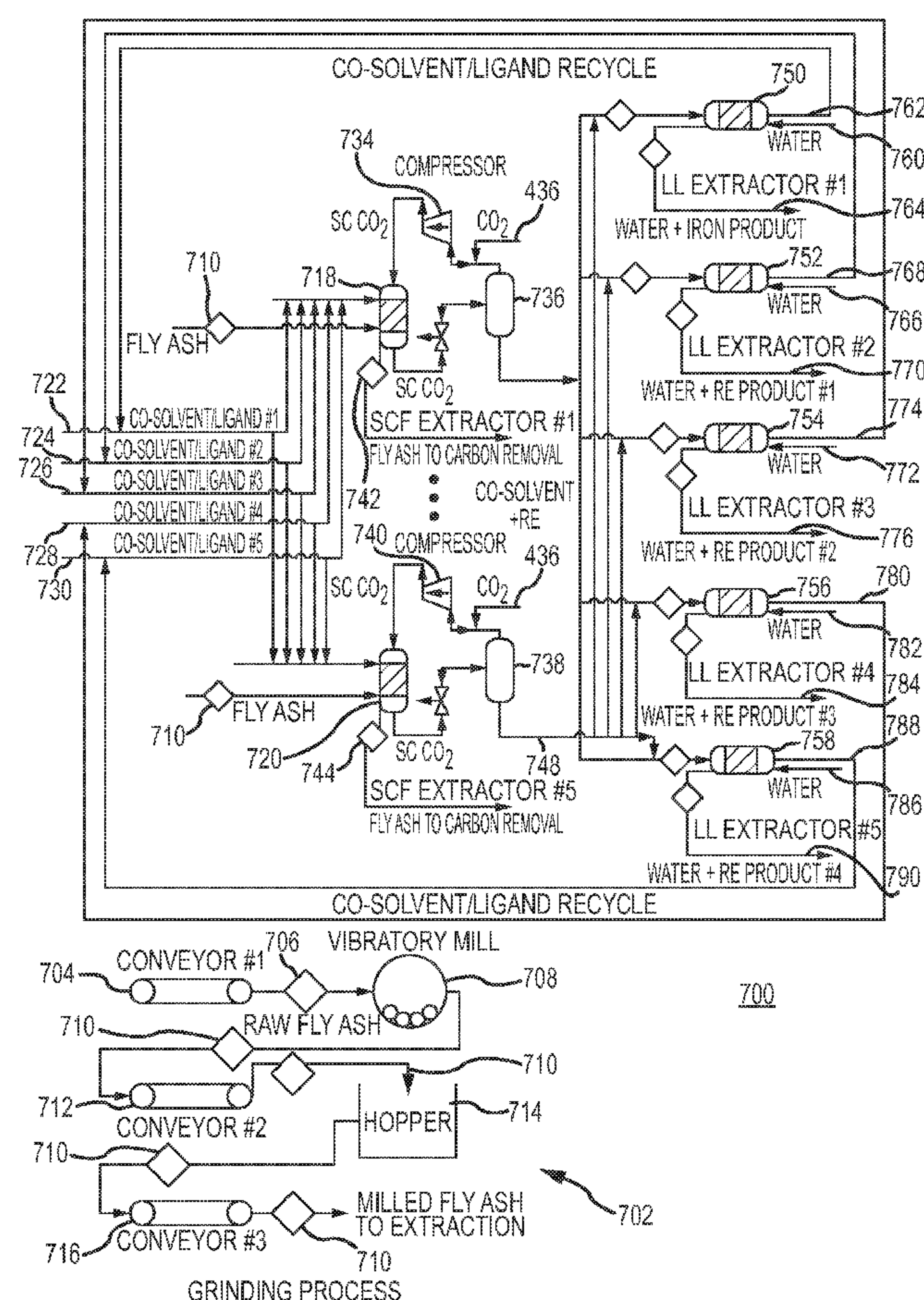
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(71) Applicant: **Neumann Systems Group, Inc.,**
Colorado Spring, CO (US)**Publication Classification**(72) Inventors: **Kurt David Neumann**, Colorado Springs, CO (US); **Claire MacLeod Ohman**, Colorado Springs, CO (US); **Eric John Klein**, Castle Rock, CO (US); **Jason Kenneth Brasseur**, Colorado Springs, CO (US)(51) **Int. Cl.**
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CPC **C22B 7/001** (2013.01); **C22B 59/00** (2013.01)(21) Appl. No.: **14/402,097**(22) PCT Filed: **May 28, 2013**(86) PCT No.: **PCT/US2013/042819**

§ 371 (c)(1),

(2) Date: **Nov. 18, 2014**(57) **ABSTRACT**

The invention generally relates to a system and method for selectively removing metals from a metal containing substance, and more particularly to a method and system for selectively extracting metals from fly ash with one or more of an acidic extraction process, basic extraction process, and supercritical carbon dioxide (scCO₂) and a co-solvent extraction process. Moreover, bi-products from an industrial process, e.g., coal fired plant, may be utilized in the extraction processes.



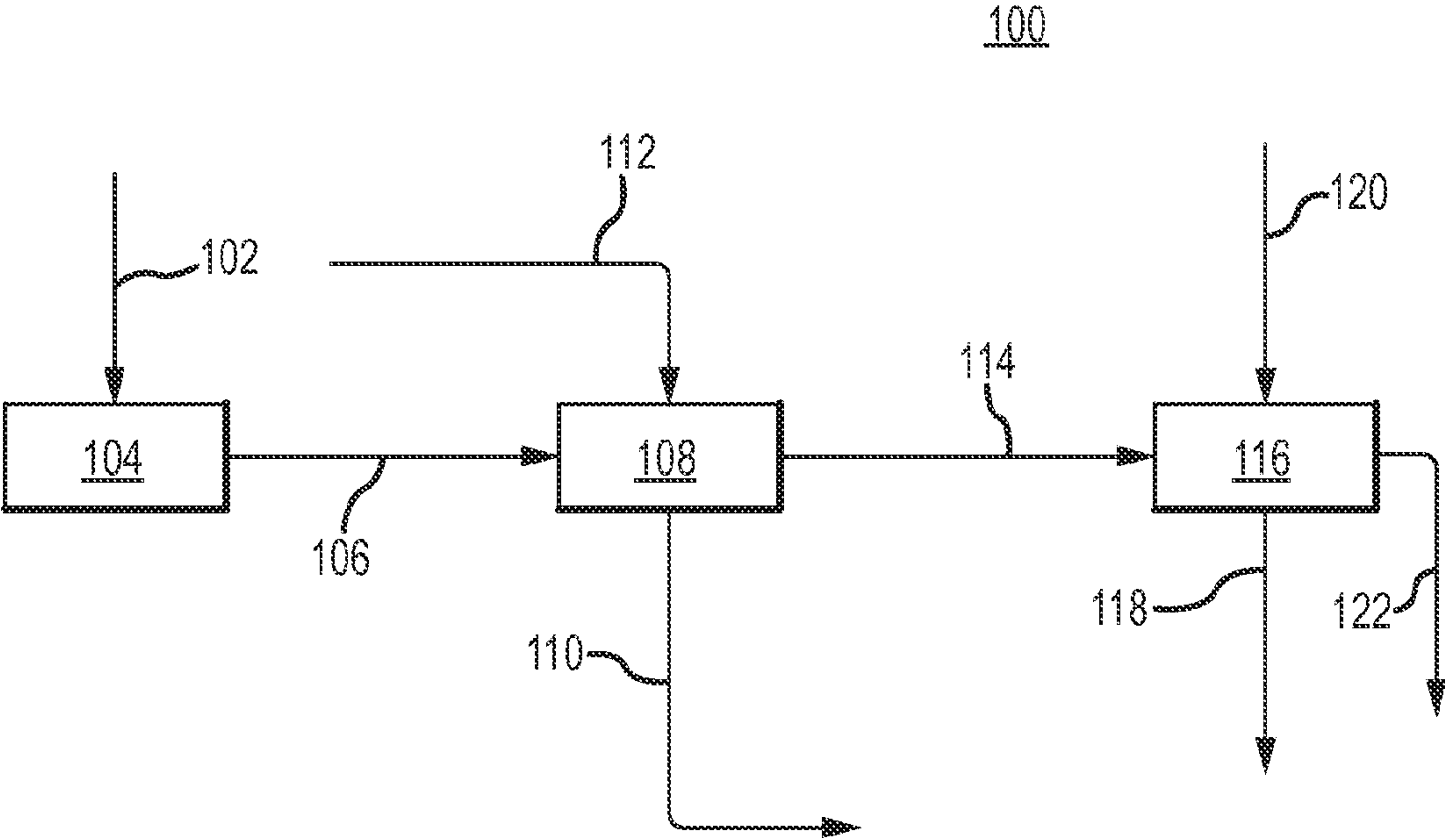


FIG.1

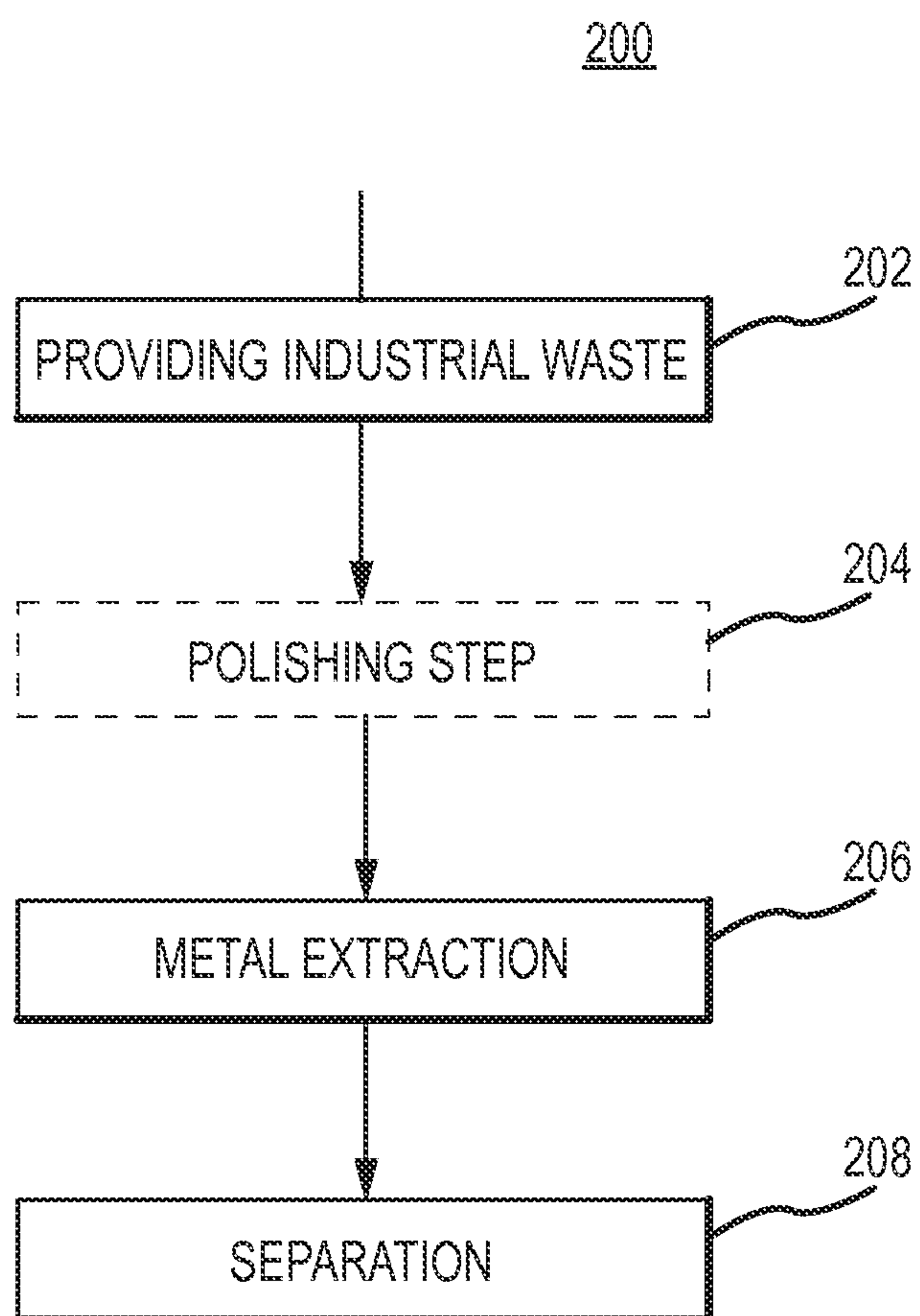


FIG.2

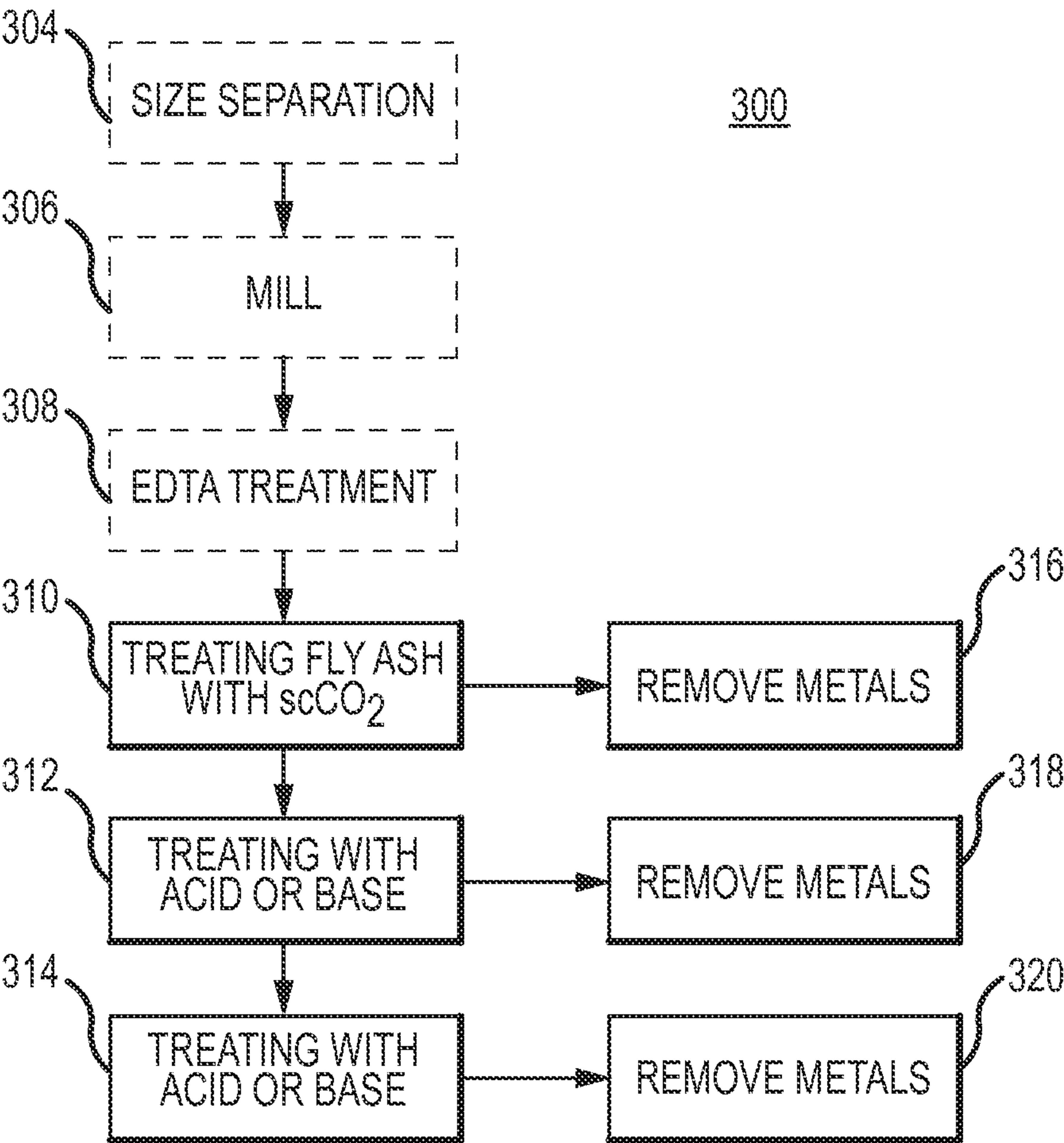


FIG.3

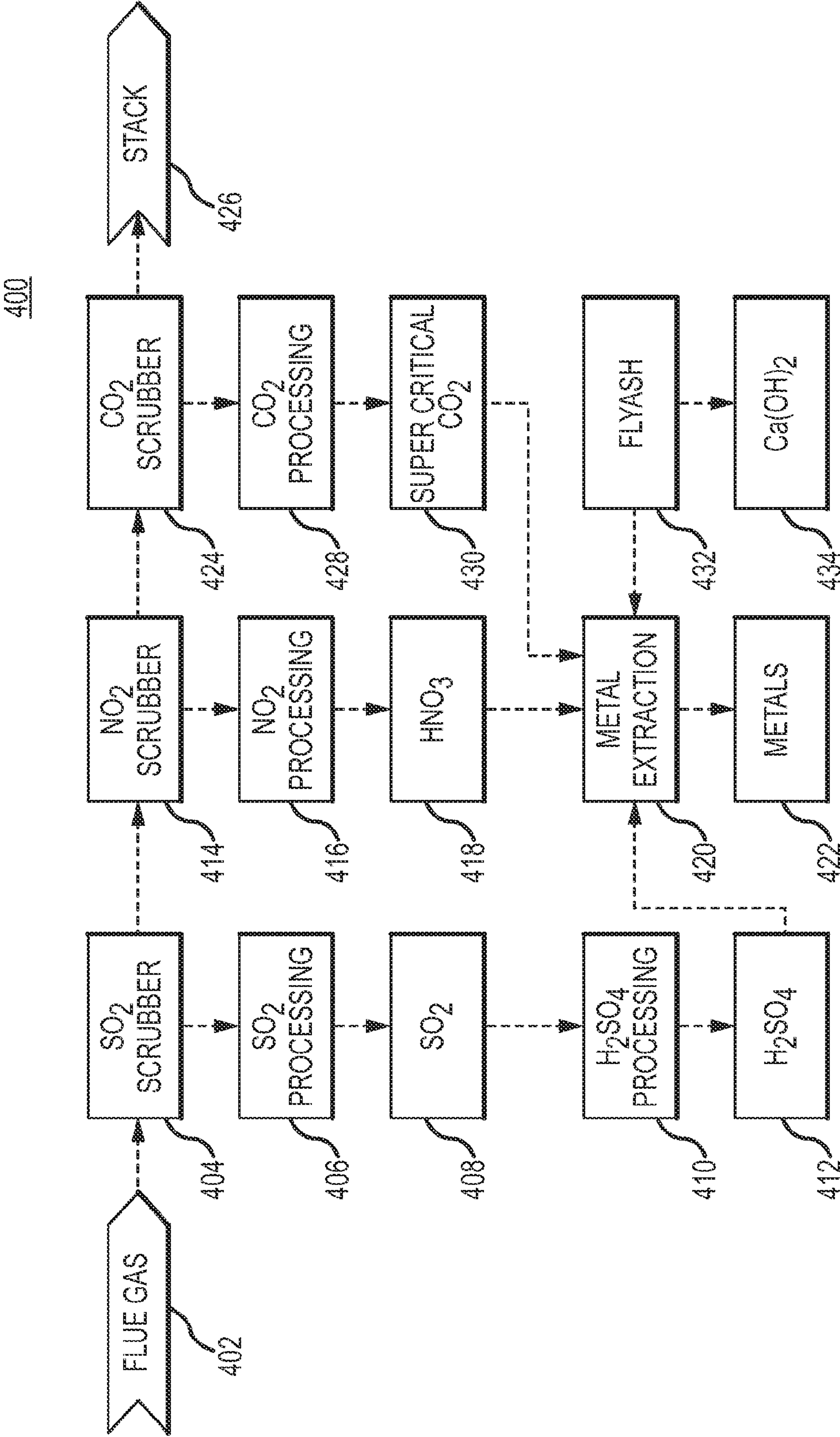


FIG.4

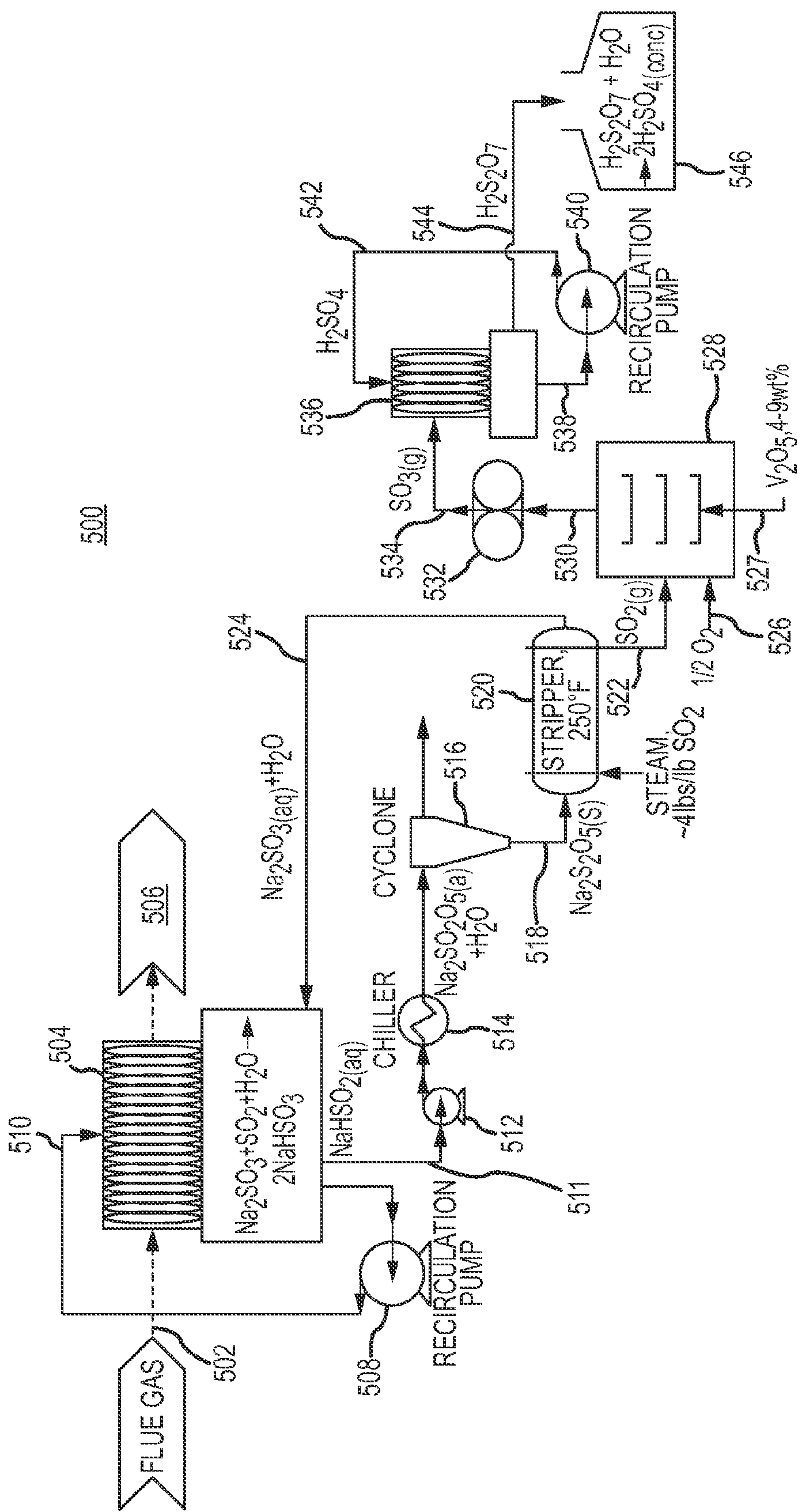


FIG.5

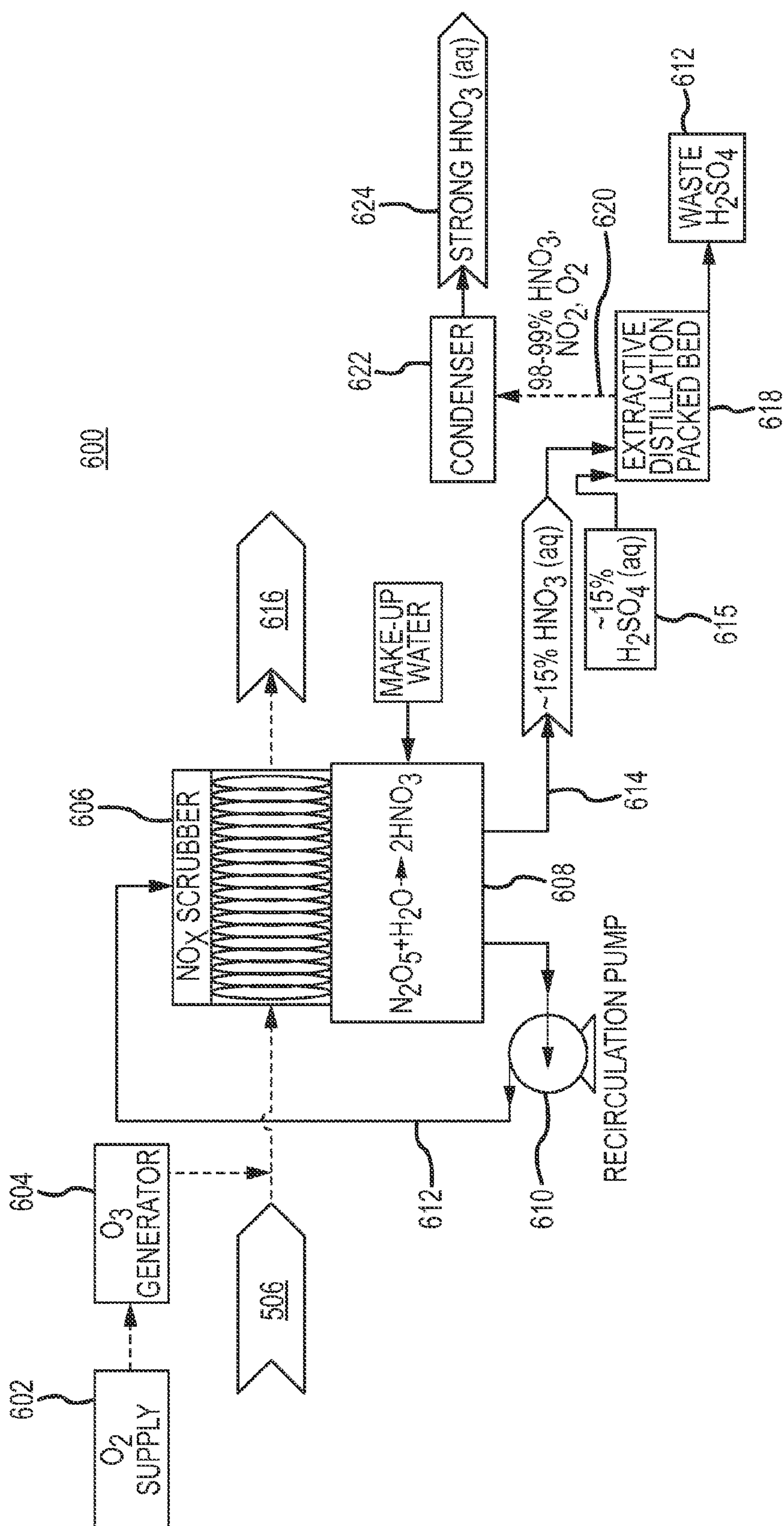
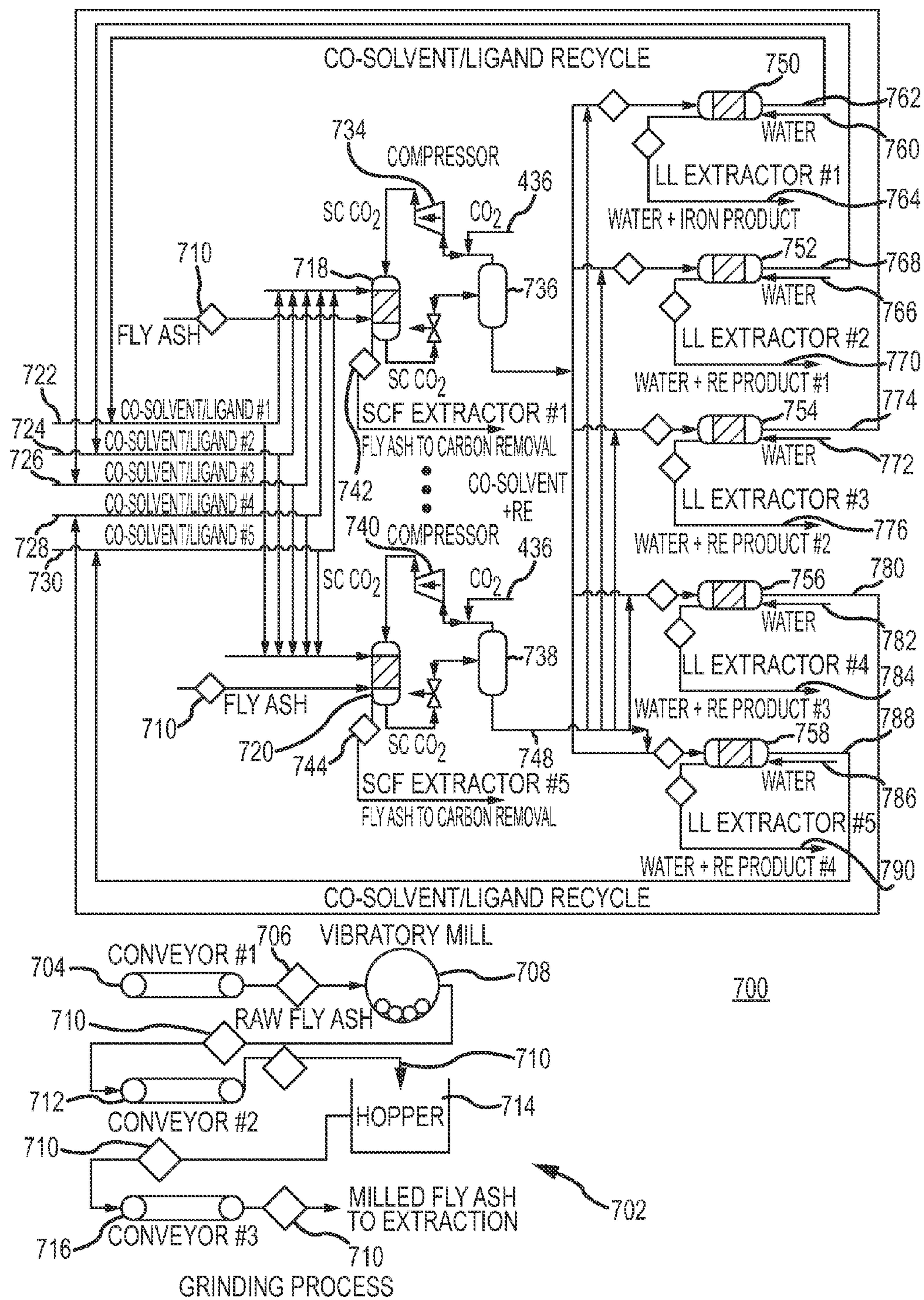


FIG.6



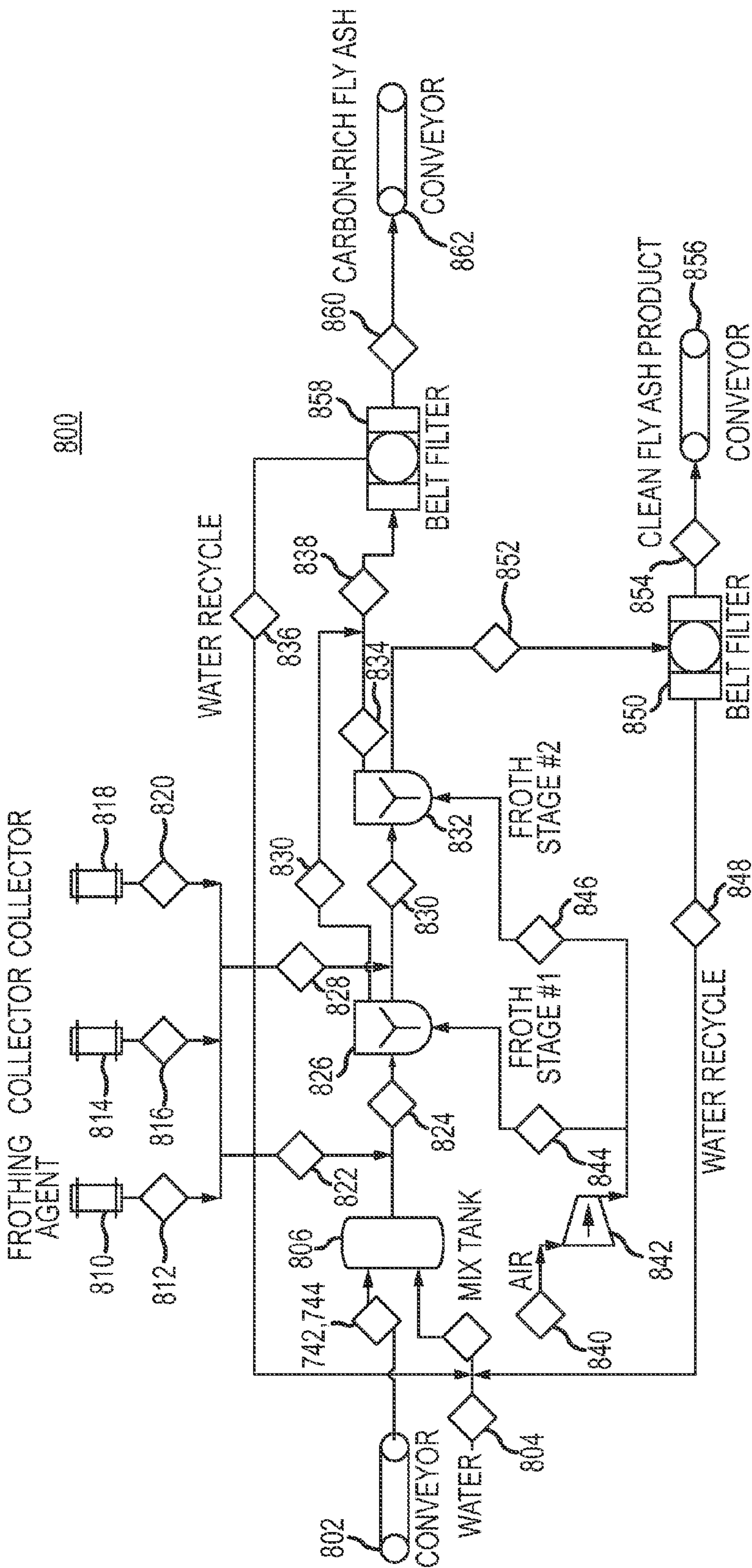
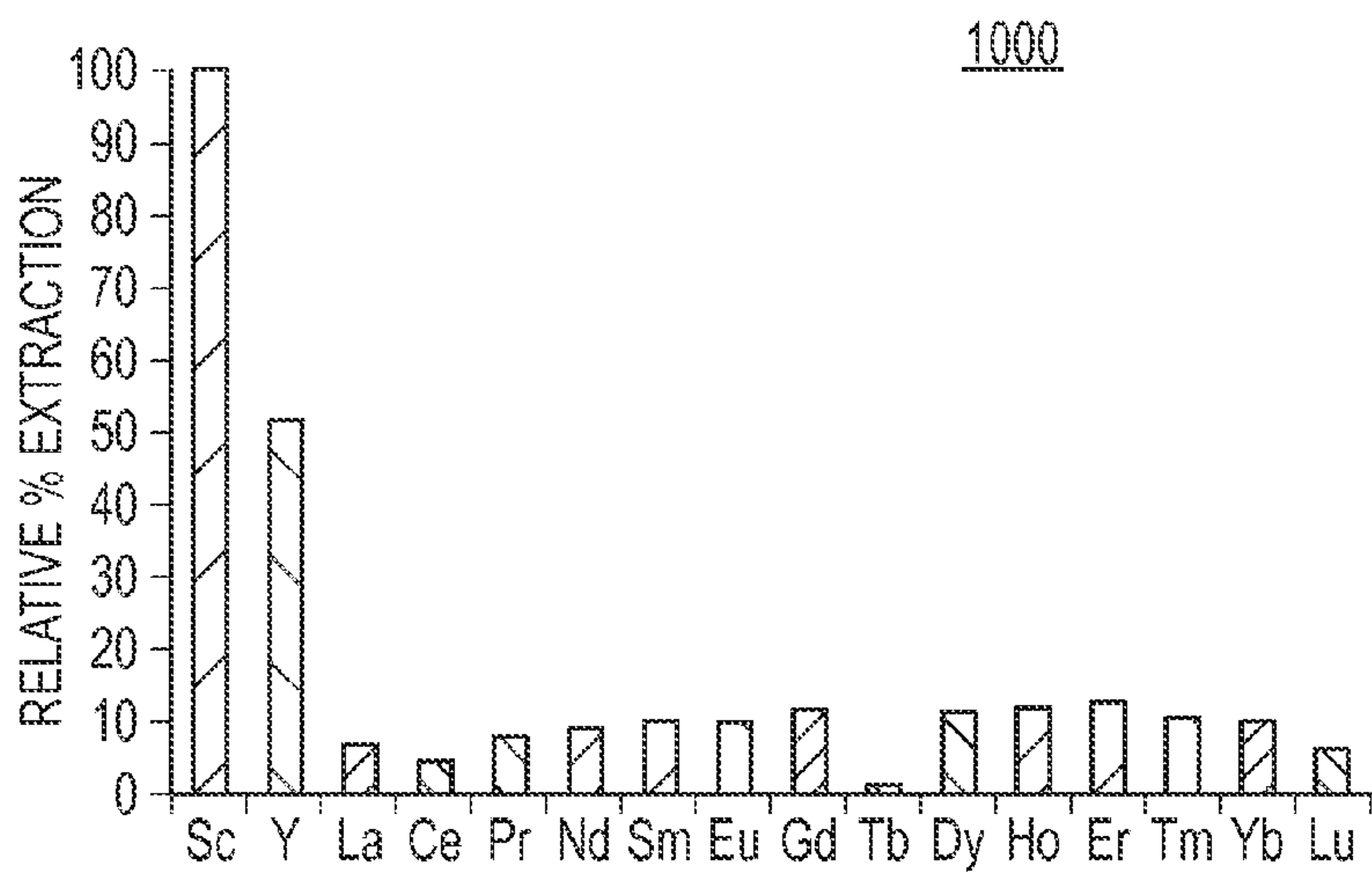
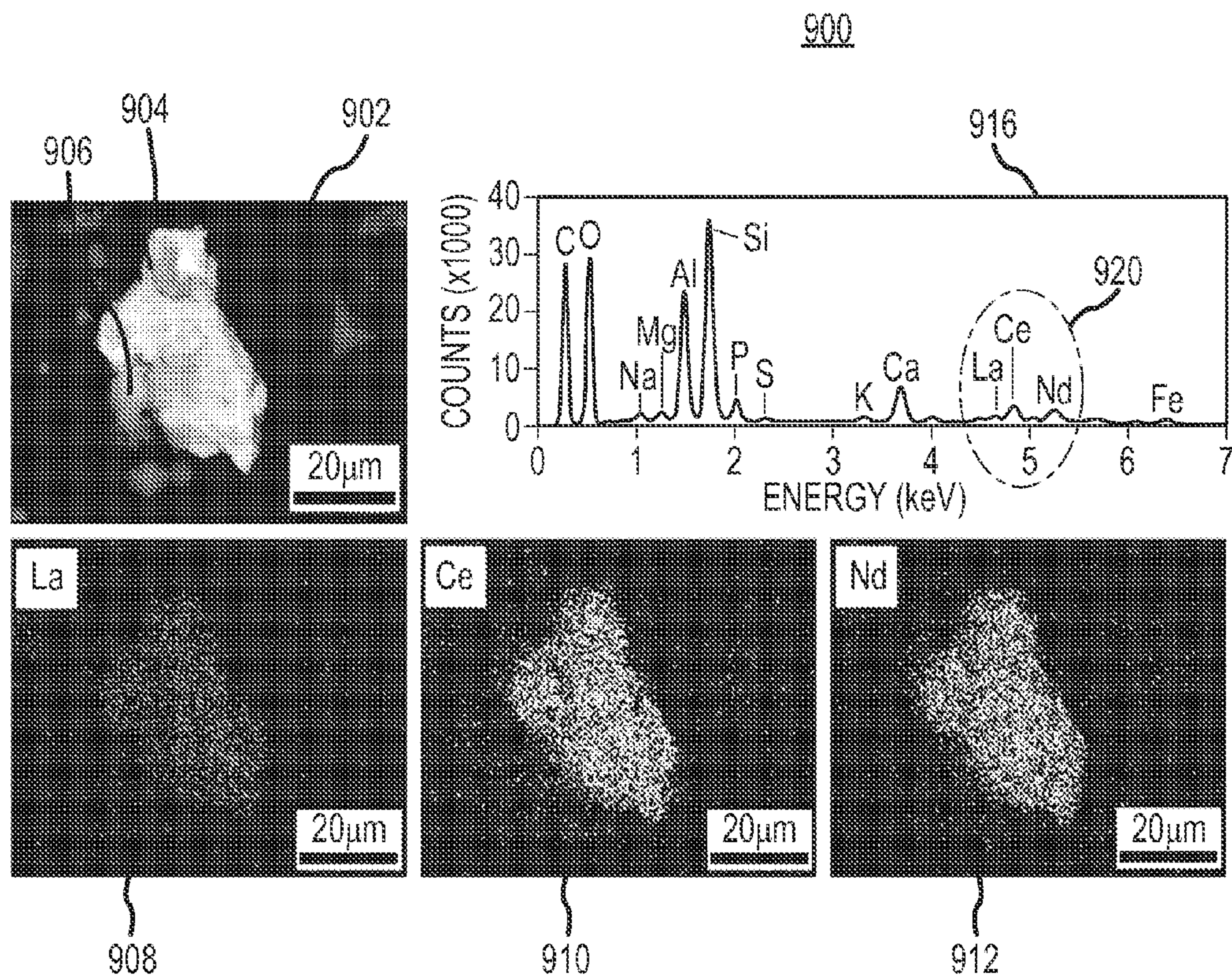


FIG.8



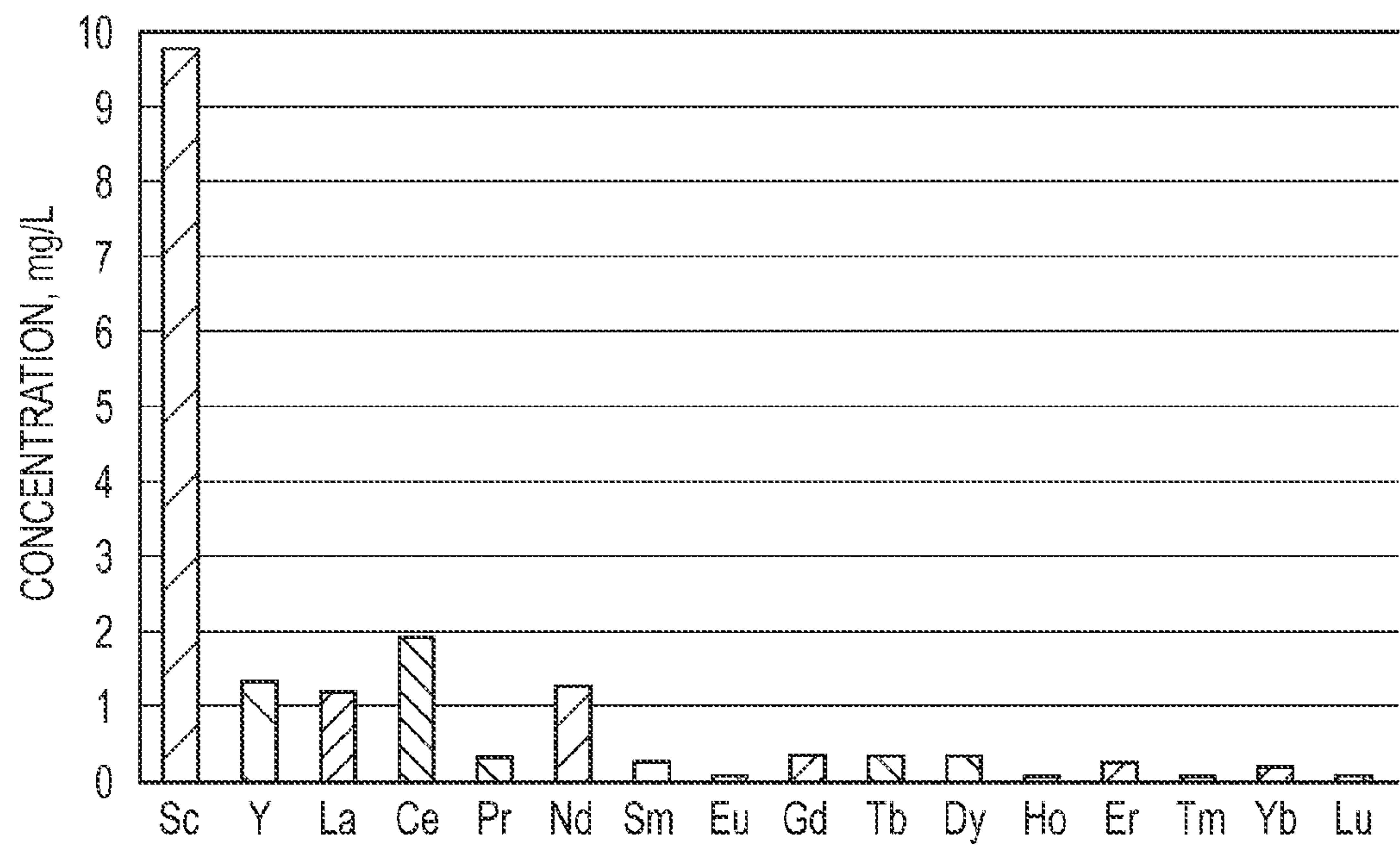


FIG.10B

SYSTEM AND METHOD FOR SELECTIVELY REMOVING METALS FROM INDUSTRIAL WASTE

[0001] This application claims the benefits under 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 61/652,036 filed May 25, 2012, and U.S. Provisional Patent Application No. 61/652,080 filed May 25, 2012, each of the above-identified applications being fully incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention generally relates to a system and method for removing metals from any source of metal containing material, and more particularly to a method and system for selectively extracting metals from industrial waste with supercritical carbon dioxide (scCO_2) and a chelating agent (ligand).

[0004] 2. Discussion of the Related Art

[0005] Rare earth metals (REM) and other strategic metals are critically important in Renewable Energy and Aerospace systems manufacturing. In December 2010, the Department of Energy (DOE) released a study entitled "Critical Materials Strategy." In this study several key metals were highlighted due to their importance in clean energies such as wind turbines, electric vehicles, photovoltaic cells and fluorescent lighting. From this study the DOE identified the following metals: yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), terbium (Tb), dysprosium (Dy), indium (In), gallium (Ga), tellurium (Te), cobalt (Co), and lithium (Li). Nine of these elements are rare-earth elements among other metals.

[0006] There has been a significant increase in the global demand for metals including rare earth metals. In recent years, the cost of rare earth metals increased 300-700% due to this increase in global demand. To meet current and future needs for metals, a priority on obtaining alternate sources of these metals and methods is required.

SUMMARY OF THE INVENTION

[0007] Accordingly, the invention is directed to a system and method for selectively removing or extracting metals from a metal containing material that substantially obviates one or more of the problems due to limitations and disadvantages of the related art.

[0008] An advantage of the invention is to provide an alternative source for obtaining toxic and potentially hazardous metals, rare earth metals, and other transition metals from materials such as contaminated soil, industrial waste, and/or fly ash.

[0009] Another advantage of the invention is to provide an economically viable process that extracts metals and other minerals from fly ash while eliminating the hazardous waste content.

[0010] Yet another advantage of the invention is to provide a process and system that is configured to selectively remove metals from material containing metals, e.g., fly ash.

[0011] Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure

particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0012] To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described, one embodiment of the invention is directed towards a method of selectively extracting metals from industrial waste. The method includes providing the industrial waste in an extraction unit, e.g., supercritical fluid (SCF) extraction columns and selectively extracting a predetermined one or more metals with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a chelating agent (ligand). The extraction unit may be operated in static mode and dynamic mode at various temperatures and pressures.

[0013] In another aspect of the present invention is directed towards selectively removing or extracting one or more metals from fly ash. The method includes providing the fly ash to an extraction unit and selectively extracting various predetermined metals in series in one or more extraction unit. The method includes extracting a first metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a first chelating agent (ligand), extracting a second metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a second chelating agent (ligand), extracting a third metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a third chelating agent (ligand), extracting a fourth metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a fourth chelating agent (ligand), extracting a fifth metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a fifth chelating agent (ligand), and extracting a sixth metal with the extraction unit by processing with supercritical carbon dioxide (scCO_2) and a sixth chelating agent (ligand). In addition, additional metal extractions with additional chelating agents may be utilized. In a preferred embodiment, the first, second, third, fourth, fifth, and sixth metals and chelating agents are distinct or different metals and co-solvents, respectively. Moreover, in addition to or alternatively, metals may be selectively extracted with one or more co-solvents by adjusting the temperature and pressure so that the solubility of the metal containing complex changes, favoring one complex over others.

[0014] Still yet another aspect of the present invention is directed towards a method of removing metals from industrial waste. The method includes providing industrial waste from a fossil fuel-fired system to the first extraction unit. In this embodiment, by-products of an industrial process, e.g., coal fired power plant, may be used. For example, removing SO_x from a flue gas of the fossil fuel-fired system and processing the SO_x to form sulfuric acid (H_2SO_4), removing NO_x from the flue gas of the fossil fuel-fired system and processing the NO_x to form nitric acid (HNO_3), and removing CO_2 from the flue gas of the fossil fuel-fired system and processing the CO_2 to form supercritical carbon dioxide (scCO_2). Extracting one or more metals in the extraction unit or units with one or more of the nitric acid (HNO_3) and the sulfuric acid (H_2SO_4) and selectively extracting one or more metals from the industrial waste with the supercritical carbon dioxide (scCO_2).

[0015] Yet still another aspect of the invention is directed towards a system for selectively removing one or more metals from industrial waste including a plurality of metals including an extraction unit configured to selectively extract one or more metals from the industrial waste comprising the plurality of metals. The extraction unit includes a first input in

communication with the extraction unit configured to receive super critical CO₂ (scCO₂), a second input in communication with the extraction unit configured to receive a co-solvent, a third input in communication with the extraction unit configured to receive the industrial waste, a first output in communication with the extraction unit configured to output the selectively removed one or more metals, and a second output of the extraction unit configured to output the industrial waste.

[0016] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

[0018] In the drawings:

[0019] FIG. 1 illustrates an exemplary system for removing metals from industrial waste according to an embodiment of the invention;

[0020] FIG. 2 illustrates an exemplary process for removing metals from industrial waste according to another embodiment of the invention;

[0021] FIG. 3 illustrates an exemplary metal extraction process for removing metals from industrial waste according to another embodiment of the invention;

[0022] FIG. 4 illustrates an exemplary system and process for removing metals from fly ash utilizing several by-products of the coal combustion process according to another embodiment of the invention;

[0023] FIG. 5 illustrates an exemplary SO_x system and process for utilizing by-products of a coal combustion process of FIG. 4 according to another embodiment of the invention;

[0024] FIG. 6 illustrates an exemplary NO_x system and process for utilizing by-products of a coal combustion process of FIG. 4 according to another embodiment of the invention;

[0025] FIG. 7 illustrates a metal extraction system and process according to another embodiment of the invention;

[0026] FIG. 8 illustrates a carbon removal system and process according to another embodiment of the invention;

[0027] FIG. 9A illustrates some properties of fly ash from a coal-fired plant according to an example of the invention;

[0028] FIG. 10A illustrates a percent extraction graph of elements selectively extracted according to an example of the invention; and

[0029] FIG. 10B illustrates concentration graph of elements selectively extracted according an example of the invention.

DETAILED DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

[0030] An embodiment of the invention generally relates to a system and method for selectively removing metals from any metal containing substance, e.g., soil, industrial waste, fly ash the like. The system and method may be configured to extract a metal from the material with supercritical carbon

dioxide (scCO₂) and a chelating agent (ligand) to selectively remove one or more metals from the industrial waste.

[0031] One embodiment of the invention is directed towards a method of selectively extracting metals from industrial waste. The method includes providing the industrial waste in an extraction unit, e.g., supercritical fluid (SCF) extraction columns and selectively extracting a predetermined one or more metals with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a chelating agent (ligand). The extraction unit may be operated in static mode or dynamic mode at various temperatures and pressures.

[0032] Another embodiment of the invention is directed towards selectively removing or extracting one or more metals from fly ash. The method includes providing the fly ash to an extraction unit and selectively extracting various predetermined metals in series in one or more extraction unit. The method includes extracting a first metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a first chelating agent (ligand), extracting a second metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a second chelating agent (ligand), extracting a third metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a third chelating agent (ligand), extracting a fourth metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a fourth chelating agent (ligand), extracting a fifth metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a fifth chelating agent (ligand), and extracting a sixth metal with the extraction unit by processing with supercritical carbon dioxide (scCO₂) and a sixth chelating agent (ligand). In addition, additional metal extractions with additional chelating agents may utilized. In one embodiment, the first, second, third, fourth, fifth, and sixth metals and chelating agents are distinct or different metals and co-solvents, respectively. Moreover, in addition to or alternatively, metals may be selectively extracted with one or more co-solvents by adjusting the temperature and pressure so that the solubility of the metal containing complex changes, favoring one complex over others.

[0033] Yet another embodiment is directed towards a method of removing metals from industrial waste. The method includes providing industrial waste from a fossil fuel-fired system to first extraction unit. Removing SO_x from a flue gas of the fossil fuel-fired system and processing the NO_x to form sulfuric acid (H₂SO₄), removing NO_x from the flue gas of the fossil fuel-fired system and processing the NO_x to form nitric acid (HNO₃), and removing CO₂ from the flue gas of the fossil fuel-fired system and processing the CO₂ to form supercritical carbon dioxide (scCO₂). Extracting one or more metals in the extraction unit or units with one or more of the nitric acid (HNO₃) and the sulfuric acid (H₂SO₄) and selectively extracting one or more metals from the industrial waste with the supercritical carbon dioxide (scCO₂).

[0034] Still yet another embodiment is directed towards a system for selectively removing one or more metals from industrial waste including a plurality of metals including an extraction unit configured to selectively extract one or more metals from the industrial waste comprising the plurality of metals. The extraction unit includes a first input in communication with the extraction unit configured to receive supercritical CO₂ (scCO₂), a second input in communication with the extraction unit configured to receive a co-solvent, a third input in communication with the extraction unit configured to

receive the industrial waste, a first output in communication with the extraction unit configured to output the selectively removed one or more metals, and a second output of the extraction unit configured to output the industrial waste.

[0035] In another embodiment the type (acidic, basic, and/or scCO_2) and order of the extraction processes may be optimized for commercial and environment purposes. For example, selective extraction of fly ash or other industrial waste may be optimized to only focus on the selective extraction with supercritical CO_2 (scCO_2) of scandium due to its high commercial value. Alternatively or in addition to, the process may be optimized to remove heavy metals in the fly ash or other industrial waste for environmental reasons. The toxic and potentially hazardous metals may include Cr, Hg, As, Ba, Sr, V and combinations of the same.

[0036] The alternative source material may include any material, e.g., industrial waste, that has one or metals that is a desired metal to be extracted. The desired metals to be extracted include one or more of a transition metal, lanthanides and actinides. In addition, the metals may also be classified as industrial metals and rare earth metals. Industrial metals include at least cobalt, columbium/niobium, gallium, indium, manganese and tungsten. Rare earth metals include at least dysprosium, europium, neodymium, praseodymium, samarium, terbium, yttrium, and scandium.

[0037] In a preferred embodiment, the industrial waste or alternative source for obtaining metals including rare-earths and other strategic metals is fly ash. Fly ash is a composite

mixture of silica, alumina, iron oxides, and calcium-bearing minerals. Trace elements comprise 0.1-2.0% of the mixture and can include mercury, chromium, and titanium, among others. Two classes of fly ash are Class F and Class C. One difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical composition of the fly ash is largely influenced by the chemical content of the coal burned. Class F fly ash contains less than 20% lime (CaO) while Class C fly ash contains greater than 20% lime. In one embodiment, either Class F or Class C fly ash can be used. In another embodiment, fly ash collected downstream of a pollution control facility can be used.

[0038] The material containing metal may be any material containing a desired metal to be extracted, e.g., industrial waste, soil, rock, fly ash, combinations of the same and the like.

[0039] While there is limited availability of data on the strategic metal content of fly ash, including the rare earth metals, it is clear that significant potential exists to begin to meet some of the growing demand for metals. Typical metal content for western coal fly ash and the economic value that can be derived per ton of the fly ash is shown in Table 1. See Gladney, et al., 1982 Compilation of Elemental Concentration Data for NBS Biological, Geological, and Environmental Standard Reference Materials. National Bureau of Standards: 1984; Metal Pages available at <http://www.metal-pages.com>; Metal Prices available at <http://www.metalprices.com/>, all of which are hereby incorporated by reference as if fully set forth herein.

TABLE 1

Comparison of the rare earth element output for various mines.					
DOE Strategic Metals	Fly Ash		2010 World		Application
	mg/kg	Est. Value \$/Ton	Est. Fly Ash Production Tons (US)	Wide Metal Production (Tons)	
Lithium	120	\$ 8.00	8,400	134,600	batteries
Cobalt	40	\$ 1.41	2,800	75,900	magnets
Gallium	41	\$ 36.90	2,870	207	semiconductors
Indium	0.27	\$ 0.20	19	1,345	semiconductors
Tellurium	2.3	\$0.81	161	500	semiconductors, solar panels
<u>Light Rare Earths</u>					
Lanthanum	80	\$ 13.20	5,600	33,887	hybrid engines, metal alloys
Cerium	148	\$ 24.86	10,360	49,935	auto catalyst, petroleum refining, metal alloys
Praseodymium	25	\$ 7.00	1,750	6,292	magnets
Neodymium	61	\$ 25.01	4,270	21,307	auto catalyst, petroleum refining, laptop hard drives, headphones, hybrid engines
Samarium	13	\$ 2.34	910	2,666	magnets
Europium	2.6	\$ 17.55	182	592	red color for television and computer screens
Gadolinium	11.7	\$2.61	819	2,257	magnets
<u>Heavy Rare Earths</u>					
Terbium	2	\$ 10.20	140	252	phosphors, permanent magnets
Dysprosium	10.2	\$34.68	714	1,377	permanent magnets, hybrid engines
Holmium	2	\$ 2.40	140		glass coloring, lasers
Erbium	11	\$ 10.00	770		phosphors
Thulium	1.3	\$ 10.40	91		medical x-rays units, lasers
Ytterbium	6	\$ 3.00	420		lasers, stell alloys
Lutetium	1	\$ 10.00	70		catalysts in petroleum
Yttrium †	66	\$13.53	4,620	8,750	phosphors, lasers
<u>Other Variable Materials</u>					
Iridium	6	\$202.55	420		corrosion resistant material
Germanium	24	\$ 40.00	1,750		semiconductors
Platinum	0.4	\$ 22.51	28		precious metal, corrosion resistant material, medical and laboratory applications
Ruthenium	0.5	\$ 3.88	3518		electrical contacts, catalysis, solar applications

TABLE 1-continued

Comparison of the rare earth element output for various mines.					
DOE Strategic Metals	Fly Ash		2010 World		Application
	mg/kg	Est. Value \$/Ton	Est. Fly Ash Production Tons (US)	Wide Metal Production (Tons)	
Scandium	26.7	\$534.00	1,869		aerospace industry components
Iron	~6%				approximately 95% of world-wide metal production
CaO	~20%	\$ 31.00			concrete, FGD systems
		\$1,079			per ton

† While Yttrium is technically a transition metal it exhibits properties similar to a heavy rare earth.

[0040] The metals in Table 1 are differentiated by Department of Defense (DOE) as strategic metals, light rare earth metals, heavy rare earth metals, and other valuable materials. Based on this data, the potential exists for extracting metals worth over \$1000 from each ton of fly ash. The Appalachia America Energy Research Center claims that they can recover metals worth approximately \$500 from each ton of fly ash, at a processing cost near \$200/ton of fly ash. See Coal Fly Ash Remediation available at <http://www.aaerc.org/technologies/coal-fly-ash-remediation/>, all of which are hereby incorporated by reference as if fully set forth herein. Currently about 70 million tons of fly ash is generated per year in the United States, making the extraction of rare earths from the material a viable industry. See Coal Combustion Product (CCP) Production and Use Survey Report, American Coal Ash Association (ACCA), available at http://www.acaa-usa.org/associations/8003/files/2009_Production_and_Use_Survey_Revised_100511.pdf, all of which are hereby incorporated by reference as if fully set forth herein.

[0041] Further incentive for processing fly ash to recover metals lies in proposed changes in EPA regulations that would cover fly ash under the Resource Conservation and Recovery Act (RCRA). See Smith, et al., White House, EPA at Odds Over Coal-Waste Rules, *The Wall Street Journal*, Jan. 9, 2010, (2010), p A6, which is hereby incorporated by reference as if fully set forth herein. Fly ash is currently exempt from RCRA regulation, but in 2010 the EPA proposed changes to classify it as a special waste under subtitle C of RCRA. See Hazardous and Solid Waste Management System: Identification and Listing of Special Wastes, Disposal of Coal Combustion Residuals from Electric Utilities. Environmental Protection Agency (EPA): Federal Register, 2010, Vol. 75, pp 35128-35264, which is hereby incorporated by reference as if fully set forth herein. Processing the fly ash to remove the metals that would leach out into water systems would be extremely beneficial for fly ash disposal and the ecosystem as well as meet the proposed new RCRA regulations for fly ash. See Bhattacharyya, et al., Solubility and Fractionation of Different Metals in Fly Ash of Powder River Basin Coal, *Water, Air, & Soil Pollution*, 2011, 220 (1), pp. 327-337, which is hereby incorporated by reference as if fully set forth herein.

[0042] Moreover, removal of these metals from fly ash could potentially have a positive impact on the environment due to a reduced amount of metals being released into the water system and the transformation of a waste product into a saleable product. Geological sources of rare earth metals usually form in pockets of light rare earths (lanthanum-gadolinium) or heavy rare earths (terbium-lutetium) but not both, due to the size of the rare earths and their ability to fit into

pockets of the minerals that are being formed. Fly ash contains significant amounts of both the light and heavy rare earths. See Long, et al., The Principal Rare Earth Elements Deposits of the United States—A Summary of Domestic Deposits and a Global Perspective. United States Geological Survey (USGS): Virginia, 2010, which is hereby incorporated by reference as if fully set forth herein. Based on current and future supplies, the DOE identified key strategic and rare-earth metals and assessed the supply risk and importance to clean energy. Coal burning power plants in the United States and Europe generate about 70 million of tons of fly ash per year which contains numerous hazardous materials. See Coal Combustion Product (CCP) Production and Use Survey Report, American Coal Ash Association (ACCA), available at http://www.acaa-usa.org/associations/8003/files/2009_Production_and_Use_Survey_Revised_100511.pdf; Production and Utilization of CCPs in 2008 in Europe, European Coal Combustion Products Association (ECOBA), available at <http://www.ecoba.com/ecobaccpprod.html>, all of which are hereby incorporated by reference as if fully set forth herein.

[0043] While there have been some beneficial uses for fly ash in the past such as concrete filler, much of it is deposited in landfills. Fly ash contains substantial amounts of metals. In addition, strategic metals are also part of the green technology industry because they improve energy efficiency in magnets, batteries, and computers.

[0044] One embodiment of the invention is directed towards a system to remove SO_x and NO_x from the flue gas of a coal fired plant and convert these pollutants to a concentrated acidic form. The system is optionally also configured to efficiently remove CO₂ from flue gas and compress it to its supercritical phase for use as a solvent, extract CaO from fly ash and convert it to a concentrated base, and employ these concentrated acids, bases and solvents to extract strategic metals from fly ash by adapting conventional extractive metallurgy techniques. In one embodiment, the system for removing or scrubbing SO_x, NO_x, and CO₂ is described in one or more of U.S. Patent Application Publication No. 2010-0092368 and U.S. Pat. Nos. 7,379,487; 7,866,638; 8,113,491; and 8,398,059, all of which are hereby incorporated by reference as if fully set forth herein.

[0045] The remediated fly ash can then be safely incorporated into other products or put into a landfill, the CO₂ can be recycled and used for enhanced oil recovery or sequestered, and the strategic metals sold on the market.

[0046] In one embodiment, gas-liquid contactor technology can be utilized to remove SO_x, NO_x and/or CO₂ and is used as part of the system for extracting metals from industrial waste including fly ash. The gas-liquid contactor may

include any existing technology including the gas-liquid contactor technology described in U.S. Patent Application Publication No. 2010-0092368 and U.S. Pat. Nos. 7,379,487; 7,866,638; 8,113,491; and 8,398,059, all of which are hereby incorporated by reference as if fully set forth herein.

[0047] Reference will now be made in detail to an embodiment of the present invention, example of which is illustrated in the accompanying drawings.

[0048] FIG. 1 illustrates an exemplary system for removing metals from industrial waste according to an embodiment of the invention.

[0049] Referring to FIG. 1, the system is generally depicted as reference 100. The system includes a first unit 104 for sizing, processing, grinding and/or milling solid waste into a preferred size. The preferred particle size or average particle size may be 30 microns or less, more preferred 20 microns or less and most preferred 15 microns or less. The second unit 108 is for processing the solid waste to remove metals. The third unit 116 is an optional unit for carbon removal from the output from the second unit 108. The term unit is used herein to mean one or more processing system and is not limited to only one unit or system. The more than one system or unit may be any conventional system or unit as known in the art, e.g., mill, grinder, vibratory mill, gas-liquid contactor, batch reactor, continuous stir tank reactor, other reactor, combinations of the same and the like.

[0050] In this embodiment, the solid waste 102 is fly ash. The first unit 104 may be a vibratory mill to grind the fly ash 102 to increase the surface area, thereby increasing the efficiency of the metal extraction in the second unit 108. The sized fly ash has particles of about 15 microns or less in a preferred embodiment. This sized fly ash is an input 106 to the second unit 108. In this embodiment, sized fly ash 106 is contacted with supercritical carbon dioxide (scCO_2) and ligand-containing co-solvents to extract metals including at least strategic and rare earth metals. Input 112 may include one or more inputs including at least one of, scCO_2 , and/or co-solvent/ligand.

[0051] In one embodiment, assuming an 80% loading factor and a fly ash density of 1.5 g/ml, a 100L supercritical fluid (SCF) extraction column is cable of processing 265 lbs of fly ash per run may be used. The amount of processing of fly ash with the system is scalable and may be increased or decreased by scaling the reactor size. Moreover, the metal extraction in unit 108 may optimized by using different co-solvents/ligands, pressures and/or temperatures in different runs. In one embodiment, two to six consecutive extraction processes per load of fly ash may be utilized. The process conditions and co-solvents (ligands) to extract the metals are optimized as known in the art based on the solubility of the desired metal. More specifically, extraction with scCO_2 has distinct advantages over aqueous acid/base extractions, e.g., it has been observed that scCO_2 diffuses like a gas through solid but dissolves substances like a liquid. As the temperature and pressure are adjusted, slight changes in density allow for very precise separation between substances as they are extracted from the solid. Thereby, the ability to selectively separate mixtures of natural products or metal-ligand complexes by temperature and pressure manipulation has been observed.

[0052] In embodiments of the invention, co-solvents generally called metal chelating agents or ligands are utilized in the selective metal extraction processes. In one embodiment, these may include organic ligands such as acetylacetone, fluorinated organic ligands such as hexafluoroacetylac-

etone, a variety of phosphine oxides and combinations of the same. In a preferred embodiment, a ligand is used or chosen for extraction with a supercritical fluid (SCF) extraction column and process based on solubility in scCO_2 as known in the art. Moreover, the presence of long aliphatic chains in the co-solvent is one way of promoting solubility while another method is the substitution of hydrogen with fluorine in the co-solvent, therefore, co-solvents with these properties may also be used.

[0053] In a preferred embodiment, the chelating agents may include one or more of acetylacetone, hexafluoroacetylacetone, fluorinated crown ether, Bis(2,4,4-trimethylpentyl) phosphinic acid, tributylphosphate, thenoyltrifluoroacetylacetone, lithium bis(trifluoroethyl)dithiocarbamate and combinations of the same. Moreover, acids and bases may also be part of the co-solvent, e.g., nitric acid and methanol may be part of the co-solvent, thereby in one embodiment the co-solvent may be thenoyltrifluoroacetylacetone and methanol, and the co-solvent may be thenoyltrifluoroacetylacetone, methanol and nitric acid.

[0054] Next, in unit 116 is an optional carbon removal unit for processing carbon removal may be conducted. The input 114 includes carbon rich fly ash and input 120 includes one or more inputs water, air and an organic collector. The output 118 includes a carbon rich froth and output 122 includes fly ash with carbon removed. This process is optional as it is dependent on the solid waste that is being processed. In a preferred embodiment, when using fly ash as the solid waste a carbon removal process is conducted to remove carbon from fly ash to increase the post processing price of fly ash. In one embodiment, a froth flotation process is used to remove the carbon. Froth flotation is known in the art for separating carbon from fly ash as described in literature. See Coal Fly Ash Remediation, available at <http://www.aaerc.org/technologies/coal-fly-ash-remediation>, 2011; Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors—Section 8.7: Nitric Acid. Emission Factor and Inventory Group (EFIG). 5th ed.; U.S. Environmental Protection Agency: Triangle Park, N.C., 1995; Vol. I.; and U.S. Pat. No. 7,866,638, each of which is herein incorporated by reference as if fully set forth herein.

[0055] FIG. 2 illustrates an exemplary process for removing metals from industrial waste according to another embodiment of the invention. FIG. 3 illustrates an exemplary metal extraction process for removing elements that are high in concentration, including calcium and sodium, from industrial waste according to another embodiment of the invention.

[0056] Referring to FIGS. 2-3, the process is generally depicted with reference to number 200. The process includes providing the industrial waste 202, an optional polishing step 204, metal extraction 206 and separation 208. The industrial waste is described herein and in a preferred embodiment is fly ash as described herein. The polishing step 204 is used to make the processing of the industrial waste or fly ash more efficient by removing calcium from the fly ash. The polishing step 204 may include at least one or more of milling the fly ash 306 or metal containing substance to size to a size of about 20 microns or less, size separation step 304 to further size or separate the metal containing substance into preferred treatment groups configured to optimize the metal extraction, ethylenediaminetetraacetic acid (EDTA) treatment 308 to reduce calcium in the fly ash and combinations of the same. More specifically, milling the fly ash 306 is conducted to size the fly ash to a size of about 15 microns or less in a preferred

embodiment. The ethylenediaminetetraacetic acid (EDTA) treatment **308** is conducted to reduce a concentration of calcium in the fly ash or metal containing substance as known in the art.

[0057] In step **310**, the fly ash is treated with scCO_2 to selectively extract predetermined metals. The metals are extracted in step **316** by processes described herein. Additional sequential processing may be accomplished with acid and/or bases to further remove metals in steps **312** and **318**. These steps may be repeated various times in steps **314** and **320** to remove remaining metals.

[0058] FIG. 4 illustrates an exemplary system and process for removing metals from fly ash utilizing several by-products of the coal combustion process according to another embodiment of the invention.

[0059] Referring to FIG. 4, an exemplary system and process are generally depicted as reference number **400**. In this

embodiment, several unwanted by-products of fossil-fuel combustion process are utilized, including SO_2 , NO_x , CO_2 and fly ash. These by-products are also used to reclaim metals, e.g., valuable rare-earth and strategic metals from the fly ash. Moreover, the order of removing SO_2 , NO_x , CO_2 may be different than shown, e.g., the order may be NO_x removal, SO_2 removal and then CO_2 removal or any combination of the foregoing. Moreover, any technique as known in the art for removing SO_2 , NO_x , and CO_2 may be utilized in the invention. There are a number of benefits with this approach including reducing dependence on non-preferred sources of rare-earth and other strategic metals and reducing the amount of pollutants from coal-burning power plants resulting in “clean coal” with natural gas like emissions as shown in Table 2. See Tobin, et al., Natural Gas 1998: Issues and Trends. National Energy Information Center: Energy Information Administration: Office of Oil and Gas (1998), which is hereby incorporated by reference.

TABLE 2

Emissions from various types of fossil fuels. Fossil Fuel Emission Levels Pounds per Billion BTU of Energy Input					
Pollutant	Natural Gas	Oil	Coal	Clean Coal (Gas-Like)	
Carbon Dioxide	117,000	164,000	208,000	104,000	50% Capture
Carbon Monoxide	40	33	208	208	
Nitrogen Oxides	92	448	457	46	90% Capture
Sulfur Dioxides	1	1,122	2,591	78	97% Capture
Particulates	7	84	2,744	82	97% Capture
Mercury	0.000	0.007	0.016	0.003	80% Capture

[0060] In one embodiment, when a metal extraction system is utilized in a coal burning power plant system one aspect of the emission control system includes a SO_x emission control system for sulfur removal. In one embodiment, the coal used will be a low sulfur coal, however, other coal types can be used. The resulting flue gas has a flow rate between 1000 and 3000 SCFM/MW or higher and a composition which includes 300 ppm SO_x , with typical oxygen concentrations of 5%. The CO_2 in the flue gas is typically around 12%, and the NO_x is 200 ppm.

[0061] This selective removal of flue gas constituents is possible because of the extremely low transfer of NO (primary NO_x component, >95%, in non-selective catalytic reduction flue gas) into the aqueous sorbent used to scrub SO_x . The acid produced from the waste streams of both the SO_x and NO_x removal systems can be used in fly ash acid treatment for metal extraction. Referring to FIG. 4, the metal extraction system **400** leverages several of the key reagents, which can be extracted from flue gas from a fossil-fuel electric generation system. Hydrated lime can be extracted from the fly ash to use for alkaline processes, while the acidic processes will use sulfuric acid and nitric acid produced from SO_2 and NO_x emissions, respectively. In addition, supercritical CO_2 can be used as a solvent in the reclamation process to extract the metals directly from the fly ash. Kersch, et al., Supercritical Fluid Extraction of Heavy Metals from Fly Ash, *Industrial & Engineering Chemistry Research*, 2003, 43 (1), p. 190-196, which is hereby incorporated by reference. In addition, the supercritical CO_2 can be recycled and used in enhanced oil recovery (EOR) or be sequestered.

[0062] Referring again to FIG. 4, the flue gas impurities SO_x and NO_x will be absorbed and then extracted as acid while CO_2 will be absorbed and then concentrated and pressurized to a supercritical fluid. Flue gas **402** from coal fired power plant is one input in the system. The SO_x is absorbed with a scrubber **404** with process steps **406** to produce SO_2 **408**. Further processing in step **410** to produce sulfuric acid **412**. The sulfuric acid **412** is utilized in a metal extraction process **420** to produce extract desired metals **422** from the fly ash **432**.

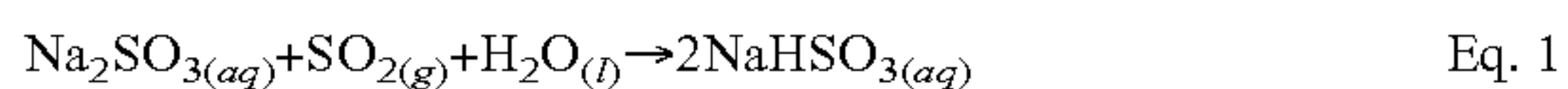
[0063] A slipstream of flue gas containing NO_x is absorbed with a scrubber **414** with process steps **416** to remove NO_x . Further processing is conducted to produce nitric acid **418**. The nitric acid **418** is utilized in a metal extraction process **420** to extract desired metals **422** from the fly ash **432**. A slipstream of flue gas containing CO_2 is absorbed with a scrubber **424** with process steps **428** to remove CO_2 . Further processing **430** is conducted to produce supercritical CO_2 . The scCO_2 is utilized in a metal extraction process **420** to produce extract desired metals **422** from the fly ash **432**. Moreover, the fly ash may be processed to remove calcium hydroxide as known in the art.

[0064] In step **404**, a gas liquid contactor or other system is utilized to remove SO_x from flue gas as known in the art, e.g., scrubber. In step **414**, a gas liquid contactor or other system is used to remove NO_x from the flue gas as known in the art. In step **424**, a gas liquid contactor or other system is used to remove CO_2 from the flue gas.

[0065] In one embodiment, the SO_x , NO_x , and CO_2 are removed as described in one or more of U.S. Patent Application Publication No. 2010-0092368 and U.S. Pat. Nos. 7,379,

487; 7,866,638; 8,113,491; and 8,398,059, all of which are hereby incorporated by reference as if fully set forth herein.

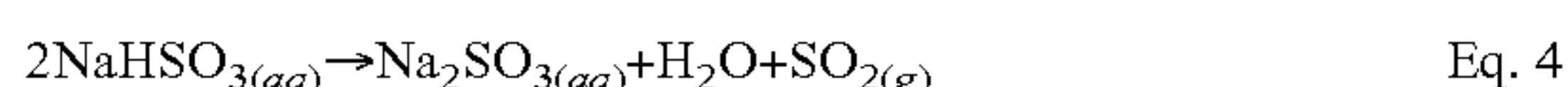
[0066] SO₂ capture 404 and sulfuric acid production may be conducted with a dual alkali process. In an alternate process 406, SO₂ can be captured and regenerated in concentrated form where it can be used as feed stock for sulfuric acid preparation. A common process for providing a purified SO₂ product from flue gas desulfurization is the Wellman-Lord Process, also known as the alkali metal sulfite-bisulfite process. See Kohl, et al., *Gas Purification*, 5th ed.; Gulf Publishing Company An Imprint of Elsevier: Houston, Tex. (1997). The process may be carried out using potassium as the alkali; however, sodium is more recently used as a lower-cost option. In one embodiment, in step 404, SO₂ in flue gas is captured using a water sorbent containing sodium sulfate according to Equation 1.



[0067] Sodium bisulfite is soluble in the solution at the nominal capture temperature. A slip-stream of the sorbent is sent for processing where it is cooled, e.g., to 4° C., to form insoluble sodium pyrosulfite according to Equation 2.



[0068] Solids can be removed from the solution using a hydrocyclone or other solid removing system. The solids-containing slurry from the cyclone underflow is sent to a stripper where it is heated to about 121° C. to redissolve the pyrosulfite to bisulfite. The bisulfite decomposes at this temperature, releases SO₂, and regenerates sodium sulfite which is sent back to the capture system. The overall stripper process is shown in Equations 3 and 4.

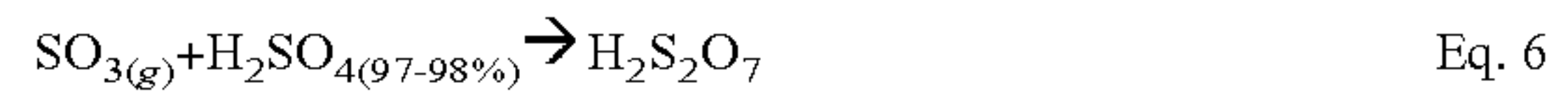


[0069] Potential side products for the above reactions include thiosulfate and sulfite, which are inactive and do not regenerate in the stripper to form SO₂ gas and sulfite. These are typically removed via fractional freeze-crystallization processes. This is more problematic in systems that burn low sulfur coal as the ratio of O₂ in the flue gas relative to the SO₂ is much higher and promotes oxidation of more of the sulfite to sulfate that can't be used for SO₂ regeneration. Inhibitors such as thiosulfate or ethylenediaminetetraacetic acid (EDTA) may be used to minimize oxidized sulfur species.

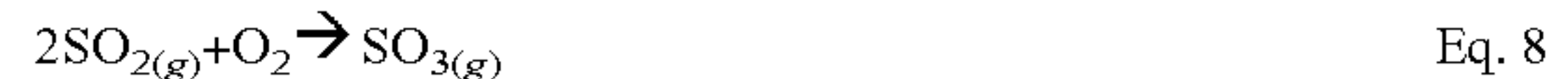
[0070] The SO₂, shown as 408 in FIG. 4, is formed ultimately from Equation 4 and can be reduced to elemental sulfur, shipped/sold as liquid SO₂, or used in sulfuric acid production. After a clean SO₂ feedstock is produced, there are two methods for producing sulfuric acid processing in step 410 including a contact process and wet sulfuric acid process. In both processes 410, the first step is to oxidize SO₂ gas to SO₃ using a catalyst, e.g., vanadium pentoxide (V₂O₅) catalyst. In the contact process the SO₃ is contacted with about 97-98% sulfuric acid to produce oleum (fuming sulfuric acid), which is then reacted with water to produce concentrated sulfuric acid. In the wet sulfuric acid process the SO₃ is reacted in the gas phase with water to produce sulfuric acid, which is then condensed. The two sulfuric acid processes 410

are summarized below in Equations 5-9 to produce H₂SO₄ illustrated as reference number 412.

[0071] Contact Process:



[0072] Wet Sulfuric Acid Process:



[0073] A proposed process flow diagram employing a gas-liquid contactor for SO₂ capture and sulfuric acid production through the contacting process is shown in FIG. 5. This process demonstrates how flue gas can be scrubbed to remove SO₂ and that SO₂ can then be used as a feedstock to produce sulfuric acid which then can be used for metal extraction from fly ash.

[0074] FIG. 5 illustrates an exemplary SO_x system and process for utilizing by-products of a coal combustion process of FIG. 4 according to another embodiment of the invention.

[0075] Referring to FIG. 5, a system 500 is configured to generate acid from the flue gas of a fossil-fuel fired plant. The system 500 includes a flue gas input 502 to a gas liquid contactor 504 and an output of flue gas 506 is sent to a processing unit such as NO_x or CO₂ removal system as described herein. In one embodiment, the gas liquid contactor 504 is configured to use a water sorbent containing sodium sulfite to capture SO₂ according to Equation 1. A recirculation pump 508 is utilized for recycling some of the sorbent via input 510. An output 511 of the gas liquid contactor 504 containing sodium bisulfite, NaHSO₃(aq), is transported via a pump 512 to a chiller 514 to cool the sodium bisulfite to desired temperature. In a preferred embodiment, the sodium bisulfite is soluble in the solution at the nominal capture temperature. This chiller 514 cools the sodium bisulfite to about 4° C. in order to form insoluble sodium pyrosulfite, Na₂S₂O₅(s), according to Equation 2.

[0076] Next the Na₂S₂O₅(s) is sent to a cyclone 516 to remove solids from the solution. The solids-containing slurry from the cyclone underflow output 518 is sent to a stripper 520 where it is heated to about 121° C. to redissolve the pyrosulfite to bisulfite. The bisulfite decomposes at this temperature and releases SO₂ as an output 522 and regenerates sodium sulfite which is sent back to the capture system via stream 524.

[0077] Next a processing system for producing H₂SO₄, sulfuric acid, is shown. An oxidizer 528 is utilized to oxidize SO₂ gas 522 to SO₃ using a catalyst 527, e.g., vanadium pentoxide (V₂O₅) catalyst. The SO₃ outputs 530 to a blower unit 532 to provide oxygen and input 534 into a gas liquid contactor 536 from output 538 and providing it to the gas liquid contactor unit 536. The gas liquid contactor 536 has a recirculation pump 540 for recycling the sulfuric acid. The gas liquid contactor 536 is configured to output H₂S₂O₇ via output stream 544 by Equation 6. This is sent to a reactor 546 for performing Equation 7 to produce sulfuric acid.

[0078] FIG. 6 illustrates an exemplary NO_x system and process for utilizing by-products of the coal combustion process of FIG. 4 according to another embodiment of the invention.

[0079] Referring to FIG. 6, the system is generally depicted as reference number 600. Nitric Oxide (NO) is effectively

non-soluble, and NO_2 has a moderate mass transfer rate into typical sorbents. The system **600** may be configured to effectively capture NO_x from flue gas by first oxidizing NO to NO_2 and NO_3 using ozone (O_3) by supplying O_2 from an O_2 supply **602** to an ozone generator **604**. A slip stream **616** may be sent to another unit or to the atmosphere. A gas liquid contactor **606** can be configured with the inputs and presence of ozone to form N_2O_5 , which has a high mass transfer rate, into an aqueous solution. The reaction of NO with O_3 to form the highly soluble N_2O_5 product is dependent on residence time, mixing ratio and reaction temperatures.

[0080] Once in solution, the N_2O_5 disassociates into NO_2/NO_3 , both of which form nitric acid in the presence of water. The waste stream is HNO_3 , nitric acid. Separating the SO_x/NO_x capture processes would allow for the utilization of the waste streams to produce sulfuric and nitric acid, respectively. Nitric acid (HNO_3) is the product of absorbing the oxidized NO_x species (N_2O_5) in a gas-liquid contactor that utilizes water for the uptake medium (sorbent).

[0081] There are significant benefits of using the NO_x from flue gas to produce HNO_3 by way of comparison to normal industrial production of HNO_3 which uses NH_3 . The mass generation of nitric acid (HNO_3) at a production facility involves first catalytically converting NH_3 into NO via Equation 10.



Next, reducing the temperature to about $50\text{-}100^\circ\text{C}$., and increasing the pressure to about 2-8 atm. the NO is converted to NO_2 in the presence of excess oxygen via Equation 11.



This oxidation takes place in a gas liquid contactor where it is followed by the uptake of NO_2 to form nitric acid with Equation 12.



The staging of the absorber and the residence time of the gas through the absorber sets the nitric acid concentration in a range of about 30-70%. The gas stream that is processed after the catalytic conversion generally has about 9-11% NO in the flow, and thus electricity is required to compress this flow to facilitate oxidation and absorption and is worth the cost of generating HNO_3 at a production facility.

[0082] In contrast, flue gas from a coal fired power plant has typical NO concentrations on the order of about 200 ppm at flow rates ranging from about 300,000 scfm to greater than 1,000,000 scfm. The parasitic power required to compress this flow, for such a relatively small amount of HNO_3 per unit volume, makes this technique for nitric acid unrealistic and expensive. Additionally, with such low concentrations of NO in the flue gas the concentration of the liquid from the scrubber would be limited to 15-20% by the vapor pressure of HNO_3 . Above this concentration the vapor pressure of HNO_3 would be on the order of the initial NO concentration in the flue gas.

[0083] Referring now to FIG. 6, a more cost effective approach to producing nitric acid from the NO present in flue gas **506** is to inject ozone **604** into the gas flow at a mixing ratio of approximately 1.5 O_3/NO . It has been shown that oxidizing the flue gas with ozone is an effective way to convert the insoluble NO to other, more soluble NO_x constituents, such as NO_2 , NO_3 , N_2O_4 and N_2O_5 . See Ellison, Chemical Process Design Alternatives to Gain Simultaneous NOx removal in Scrubbers, In POWER-GEN International, Las

Vegas, Nev., 2003; Solutions, Low Temperature Oxidation System Demonstration at RSR Quemetco, Inc. California Air Resources Board Innovative Clean Air Technology Murray Hill, N.J., 2001, all of which are hereby incorporated by reference as if fully set forth herein.

[0084] The final product in these oxidation reactions depends on the amount of ozone added to the flow in relation to NO, the temperature of the flue gas, and the mixing time allowed. There are no adverse effects of adding ozone to flue gas on the other acid gasses present in the flow. The gas-phase reaction rate constants used for conversion are shown below. See Atkinson, et al., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I—gas phase reactions of O(x), HO(x), NO(x) and SO(x) species, Atmos. Chem. Phys. 2004, 4, pp. 1461-1738; Tsang, et al., Chemical Kinetic Data-Base for Propellant Combustion. 1. Reactions Involving NO, NO_2 , HNO, HNO_2 , HCN and N_2O , *Journal of Physical and Chemical Reference Data*, 1991, 20 (4), 609-663; Baulch, et al., Evaluated kinetic data for combustion modeling: Supplement II., *Journal of Physical and Chemical Reference Data*, 2005, 34 (3), pp. 757-1397, all of which are hereby incorporated by reference as if fully set forth herein.

[0085] These rate constants show that the addition of ozone is selective in targeting NO because the reaction with NO is so much faster than the other competing reactions, resulting in a high utilization with respect to NO_x removal.



[0086] $k = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecule}/\text{sec}$ at 298K



[0087] $k = 3.5 \times 10^{-17} \text{ cm}^3/\text{molecule}/\text{sec}$ at 298K



[0088] $k < 1.1 \times 10^{-21} \text{ cm}^3/\text{molecule}/\text{sec}$ at 298K



[0089] $k = 2.2 \times 10^{-22} \text{ cm}^3/\text{molecule}/\text{sec}$ at 298K

[0090] Once sufficient oxidation has taken place the flue gas then passes through a gas liquid contactor **606** to form the higher oxidized species N_2O_5 . This species has mass transfer rates on the order of about 10-20 cm/s, which is equivalent to the mass transfer of SO_2 . The sorbent used for the NO_x scrubber **606** is simply de-ionized water, which must be staged to maximize the concentration of the nitrates in the waste stream. The N_2O_5 , once in solution, reacts and decomposes through Equation 17. See Schutze, Determination of phase transfer parameters for the uptake of HNO_3 , N_2O_5 and O_3 on single aqueous drops, Phys. Chem. Chem. Phys., 2002, 4 (1), pp. 60-67.



[0091] As was mentioned above, the maximum concentration from the flue gas would be about 15-20%. However, the concentration could then be increased using a distillative distillation, which requires a dehydrating agent (typically 1:1 mixing ratio of sulfuric acid with the nitric acid) if necessary. See Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors—Section 8.7: Nitric Acid. Emission Factor and Inventory Group (EFIG). 5th ed., U.S. Environmental Protection Agency: Triangle Park, N.C., 1995, Vol. I which is hereby incorporated by reference as if fully set forth herein.

[0092] Referring again to FIG. 6, ozone **604** is generated and injected into a slipstream of flue gas **506** to oxidize the NO to the more soluble N_2O_5 . The flue gas then passes through a multistage scrubber **606** where N_2O_5 is absorbed

into water. As the flue gas has N_2O_5 removed, it is contacted with leaner solvent to maintain the driving force for removal. A catch tank **608** and recirculation pump **610** for each stage continuously provides fluid to the scrubber **606** via stream **612**. The rich solvent from the absorber may have about 15-20% w/w nitric acid in water. This stream **614** will then undergo a distillative distillation with in an extractive distillation packed bed **618** where sulfuric acid 10-20% w/w **615** will be mixed with the nitric acid stream **614**. The nitric acid **620** will be released as gas and passed through a condenser **622** to condense out the acid and achieve a concentration of 95-99% of strong HNO_3 . There is also a waste stream **612** of sulfuric acid. In addition, another slip stream **616** of flue gas is sent to a system configured to remove CO_2 .

[0093] In one embodiment, the system **600** is staged such that the inlet flue gas, richest in N_2O_5 , will be contacted with the richest sorbent to increase the concentration of the nitric acid outlet. Subsequently, the following stages with decreasing sorbent loading of NO_x will be contacted with flue gas that has already been subjected to previous stages and has reduced NO_x concentrations. Next, the CO_2 is captured from the flue gas slip stream **616** with systems as known in the art. In one embodiment, the CO_2 capture is described with reference to one or more of U.S. Patent Application Publication No. 2010-0092368 and U.S. Pat. Nos. 7,379,487; 7,866,638; 8,113,491; and 8,398,059, all of which are hereby incorporated by reference as if fully set forth herein.

[0094] In one embodiment, by implementing the capture and regeneration of the SO_2 at a coal plant, the more hazardous sulfuric acid production operations can be removed from the power generation operations and centralized for supporting SO_2 regeneration from many power generation units. Even though the intent of the proposed project is to use the sulfuric acid for metal leaching from fly ash, the sulfuric acid is a highly marketable product in and of itself with more than 200 million tons/year consumed globally, and a sharp market increase in recent years. Producer Price Index Industry—325180 Other Basic Inorganic Chemical Manufacturing—Sulfuric Acid. Labor, D.o., Ed. Bureau of Labor Statistics available at <http://www.bls.gov/data/>, 2011; Boyd, Sulfuric acid market seeks balance, <http://www.icis.com/Articles/2010/09/06/9390780/sulfuric-acid-market-seeks-balance.html>, both of which are incorporated by reference as if fully set forth herein.

[0095] FIG. 7 illustrates a metal extraction system and process according to another embodiment of the invention.

[0096] The use of supercritical CO_2 is attractive for the selective extraction of metals from solid material due to it being a relatively cheap solvent, environmentally benign in nature, and its low viscosity and high diffusivity, which allows it to penetrate the fly ash particles easily. Furthermore, the solubility of metal complexes in supercritical CO_2 can be easily tuned by just changing the pressure and temperature, which allows a wide variety of extraction choices in a single solvent that is easily recycled and can be used elsewhere such as EOR or sequestration. The system is generally depicted as reference number **700**.

[0097] The system **700** is configured to use sequential extractions in series. These sequential extractions may be performed with scCO_2 in one or more supercritical fluid (SCF) extraction columns. Increasing the number of supercritical fluid extraction columns increases throughput of extractions. That is, the sequential use of various co-solvents may be done in parallel with two or more supercritical fluid

(SCF) extraction columns in order to increase throughput of the process. In a preferred embodiment, there are five or more sequential extractions with six different co-solvents and one or more supercritical fluid (SCF) extraction columns.

[0098] In this embodiment, the industrial waste is fly ash. The sequential extractions are done with scCO_2 and may also be done in different supercritical fluid extraction columns. Each of the extraction processes is optimized to remove the desired metal based on the solubility of the co-solvents with scCO_2 . The optimization is controlled with one or more of type of co-solvent, co-solvent flow rate, extraction time, and operating pressure and temperature, which are adjusted to allow for sufficient purity of individual metal in the extracts.

[0099] In one embodiment, metals may be extracted from the fly ash with magnetic separation, acidic digestion, caustic digestion and combinations of the same as described herein; this is an optional step and the extraction of metals in the fly ash **710** may be treated prior to the SCF Extractors 1-5, the fly ash **742** and **744** may be treated after SCF Extractors and before carbon removal **702** and/or the fly ash may be treated after the carbon removal processes of FIG. 8. The fly ash may be treated before the SCF Extractor **718** and **720** with techniques as known in the art to remove metals from rare earth oxides (REO) including the techniques as described in Gupta, et al., *Extractive Metallurgy of Rare Earths*. CRC Press: Boca Raton, 2005, which is hereby incorporated by reference as if fully set forth herein. The extraction techniques may include common techniques for separation of metals from REO including magnetic separation, acidic digestion, caustic digestion and combinations of the same. Sulfuric acid may be used at variations in temperatures and concentrations to selectively solubilize the various and desired metals in the fly ash. Once digested, the metals such as uranium, thorium, cerium and other metals can be removed from nitric acid solutions using solvent extraction. In addition, similar techniques can be utilized to extract metals from fly ash with caustic soda (sodium hydroxide). In a preferred embodiment, the caustic soda method may be used when high phosphate content is present in the fly ash. In one embodiment, other methods as known in the art to extract rare earth metals using both acid and basic extraction and different combinations of complexing ligands may also be used. See Meawad, et al., An overview of metals recovery from thermal power plant solid wastes. *Waste Management* 2010, 30 (12), pp. 2548-2559, which is hereby incorporated by reference as if fully set forth herein.

[0100] Yet another technique for removing rare earth metals from fly ash based on the acid treatment may be used as described in U.S. Pat. No. 4,649,031, which is hereby incorporated by reference as if fully set forth herein. In one embodiment, vanadium extraction can be utilized on the fly ash to remove metals as a whole, but this is not selective isolation of the metals. The solubility of each metal is influenced by pH, so using a combination of both acidic and basic conditions is important in the separation of the metals. In another embodiment, extraction and separation of individual metals is performed with the use of different complexing ligands. These complexing ligands can be used in conjunction with an extraction technique such as column extraction or liquid-liquid extraction techniques. However, these techniques can require a significant amount of organic solvents, which can be hazardous as well as harm the environment.

[0101] The use of scCO_2 is attractive for the extraction of metals from solid material due to it being a relatively cheap

solvent, environmentally benign in nature, and its low viscosity and high diffusivity, which allows it to penetrate the fly ash particles easily. Furthermore, the properties of supercritical CO₂ can be easily tuned by just changing the pressure, which allows a wide variety of extraction choices in a single solvent that is easily recycled and can be used elsewhere such as EOR or sequestration.

[0102] In this embodiment, each of the extractions are configured to selectively target a one more predetermined metals, e.g., scandium, yttrium and others, in the fly ash. The first, second, third, fourth, fifth and sixth extractions are configured to target extraction of strategic and rare metals or metals that are toxic and can therefore be considered hazardous. This is done by a combination of operating conditions including temperature, pressure and co-solvents. In a preferred embodiment, the selection of the co-solvents and metals to be extracted in a series of extractions may be optimized by order of operations.

[0103] Moreover, before or after the extracting with SCF Extractors 1-5 the metals from the fly ash may be extracted with acid/base extractions as described herein. In addition or optionally, the fly ash may be treated with a polishing step to remove calcium from the fly ash or other contaminants in the fly ash in order to make the selective metal extraction more effective. In one embodiment, the preprocessing step is configured to remove calcium from the fly ash by treating the fly ash with ethylenediaminetetraacetic acid. In addition and optionally, the iron from the fly ash may be removed in a preprocessing step by using acetylacetone.

[0104] Referring again to FIG. 7, subsystem 702 is configured to optimize the particle size of the fly ash and includes a first conveyor 704 configured to transport fly ash 706 to vibrator mill 708. The fly ash 706 input into the vibrator mill 708 is typically on the range for 60 microns or greater. However, the fly ash 706 may be about 20 microns or greater. The vibrator mill 708 is configured to size the fly ash 706 to about 15 microns or less, thereby creating milled or sized fly ash 710. The sized fly ash 710 is transported with a second conveyor 712 to a hopper 714. The milled fly ash 710 is transported with a third conveyor 716 to reactor for processing or metal extraction.

[0105] In this embodiment, the milled fly ash 710 is sent to one or more supercritical fluid (SCF) extraction columns 718, 720 for extraction of a predetermined metal. In this embodiment there are five supercritical fluid (SCF) extraction columns (1 and 5 shown). Extraction column 1 is depicted as reference 718 and extraction column 2 is depicted as reference 720. The number of extraction columns is dependent on throughput and may be increased to more than five columns, e.g., 1-20 or more, or decreased to only one column. The first through fifth columns may be operated simultaneously in parallel.

[0106] In this embodiment, five chelating agents as co-solvents are input into each extraction column (1-5) in a series to exact metals. Any combination of chelating agents may be utilized and additional or less chelating agents may also be used. Moreover, scCO₂ is used at various temperatures and pressures as well. The chelating agents are chosen to exact predetermined metals based on selectively metal extraction via the chelating agent. The chelating agent 722 is sent to column 718 along with scCO₂ from the compressor 734. This chelating agent 722 is chosen to remove scandium. However, any other chelating agents may also be used as desired for extraction of a predetermined metal. The scCO₂ may also be

recycled in tank 736 and received from the removal process 436. The process conditions for the first chelating agent 722 in operating the Extractors (1-5) are 1100 psi to 10,000 psi and ambient to 85° C.

[0107] The Extractors (1-5) are operated in one of two modes, a static mode and dynamic mode. The static mode includes operating at a fixed or dynamic pressure for a period of time, e.g., residence time, under conditions where the co-solvent is unchanged and not flowing into or out of the extractor at a flow rate. The residence time may be in a range from about 0.5 hours to 6 hours or greater, in a preferred embodiment the residence time is about 1 hour. In this mode the temperature is in a range from about ambient to about 85° C. and in preferred embodiment operating at a temperature of about 60° C. to 70° C. The operating pressures in this mode can be in a range from about 1100 psi to about 10,000 psi, and in a preferred embodiment at about a pressure in a range from about 2500 psi to about 3500 psi.

[0108] The dynamic mode of operation requires a fixed or variable flow rate of co-solvent into and out the extractor. The flow rate may be in a range from about 1 to about 10 mL/min, e.g., into a 100 mL extractor, or about 1-10% of total CO₂ volume.

[0109] The description of the supercritical fluid column 2-5 and inputs are similar to the supercritical fluid column 718 and inputs are not repeated. The fifth column 720 includes a compressor 740. The scCO₂ may also be recycled in tank 738 and received from the removal process 436.

[0110] The second chelating agent is sent to column 718 along with scCO₂; the process conditions as described herein. The second chelating agent 724 is chosen for selective extraction of a one or more predetermined metals. Any combination of chelating agents may be used. The third chelating agent 726 is sent to column 718 along with scCO₂; the process conditions are described herein. The fourth chelating agent 728 is sent to column 718 along with scCO₂; the process conditions are described herein. The fifth chelating agent 730 is sent to column 718 along with scCO₂; the process conditions are described herein.

[0111] Outputs 746, 748 from the SCF extractors 1-5 are sent to liquid liquid extractors 750, 752, 754, 756 and 758, respectively. The outputs 746, 748 include a class of compounds called coordination compounds. In the case of typical ligands such as acetylacetone and hexafluoroacetylacetone the emergent metal-containing complex is called an organo-metallic complex. For phosphines it is usually called a metal-phosphine complex.

[0112] The LL extractors (1-5) are configured for solvent extraction to separate the co-solvents from the predetermined metals and water or dilute acid solutions based on their relative solubility. The separation is done as known in the art by operating under conditions such that a soluble compound is separated from an insoluble compound or a complex matrix.

[0113] Liquid liquid (LL) extractor 750 has a water or dilute acid input 760 and is configured to extract co-solvent 722 via output 762 and returned to an input of the SCF extractor 718, thereby recycling the co-solvent 722. In addition, an output 764 is for water and iron product. The recycled co-solvent 722 can also be sent to the other SCF Extractors 2-5. The processing conditions of the LL extractor 750 are ambient temperature and atmospheric pressure in a preferred embodiment.

[0114] Liquid liquid (LL) extractor 752 has a water or dilute acid input 766 and is configured to extract co-solvent

724 and the predetermined metal product. The co-solvent **724** is recycled and returned to SCF extractors 1-5 via output **768**, thereby recycling the co-solvent **724**. The processing conditions of the LL extractor **750** are ambient temperature and atmospheric pressure in a preferred embodiment. The output **770** includes water and the predetermined metal.

[0115] Liquid liquid (LL) extractor **754** has a water or dilute acid input **772** and is configured to extract co-solvent **726** and the predetermined metal product. The co-solvent **726** is recycled and returned to SCF extractors 1-5 via output **774**, thereby recycling the co-solvent **726**. The processing conditions of the LL extractor **754** are ambient temperature and atmospheric pressure in a preferred embodiment. The output **776** includes water and the predetermined metal.

[0116] Liquid liquid (LL) extractor **756** has a water or dilute acid input **782** and is configured to extract co-solvent **728** and the predetermined metal product. The co-solvent **728** is recycled and returned to SCF extractors 1-5 via output **780**, thereby recycling the co-solvent **728**. The processing conditions of the LL extractor **756** are ambient temperature and atmospheric pressure in a preferred embodiment. The output **784** includes water and the predetermined metal.

[0117] Liquid liquid (LL) extractor **758** has a water or dilute acid input **786** and is configured to extract co-solvent **730** and the predetermined metal product. The co-solvent **730** is recycled and returned to SCF extractors 1-5 via output **788**, thereby recycling the co-solvent **730**. The processing conditions of the LL extractor **758** are ambient temperature and atmospheric pressure in a preferred embodiment. The output **790** includes water and the predetermined metal.

[0118] In addition, after the LL Extractors 1-5 further separation and/or isolation of one or more metals extracted from the fly ash may be conducted. This separation and/or isolation may be done with one or more of an ion exchange column followed by isolation by precipitation of the metal oxide, oxalate, or other insoluble complex or by metallothermic reduction to obtain the elemental metal as known to one of ordinary skill in the art.

[0119] FIG. 8 illustrates a carbon removal system and process according to another embodiment of the invention. Referring to FIG. 8, the system **800** is an optional system and configured to remove carbon from fly ash. The removable of carbon is configured to make the fly ash a more commercially relevant product. In one embodiment, carbon is removed so that the residual solid is comprised of mostly inert silicates (with no or substantially minimized attendant black color and with no or substantially minimized leachable metals), thereby the fly ash can then be used as a filler for building products or other products. The fly ash **742**, **744** from system **700** of FIG. 7 may be provided on conveyor **802**. In a preferred embodiment, the fly ash **742**, **744** includes a substantially ineffective concentration of metal and calcium. The fly ash **742**, **744** is provided to a mixing tank **806** via conveyor **802**. Water **804** is also provided to the mixing tank **806**. An output of the mixing tank **806** is mixed with input **822**. Input **822** is in communication with frothing agent tank **810**, collector tank **814** and collector tank **818** having outputs **812**, **816**, and **820**, respectively. The frothing agent is known in the art, e.g., tall oil, pine oil, combinations of the same and the like. The collector tank **814** and collector tank **818** are optional additions to the frothing agents. They can be anything configured to fine tune the frothing agent's action, e.g., methyl isobutyl carbinol. Input **824** includes the outputs of mixing tank **806**, frothing agent

tank **810**, and collector tanks **814**, **818** and are input into a first frothing tank (stage 1) **826**. The number of frothing tanks may be increased in order to achieve the desired separation of carbon. That is, as the number of frothing tanks increases so does the number of stages. In one embodiment, the froth units **826**, **832** are operated at ambient temperature and pressure.

[0120] An input of air **840** is sent to compressor **842** for compression and input **844** to a first frothing tank (stage 1) **826** and input **846** to second frothing tank (stage 2) **832**. In operation, compressed air **844** is bubbled through the bottom of the frothing unit **826** and carbon floats to the top of the unit. The carbon is skimmed or scraped off and the output **830** includes skimmed carbon.

[0121] An input of air **840** is sent to compressor **842** for compression and input **846** to a second frothing tank (stage 2) **832**. In operation, compressed air **846** is bubbled through the bottom of the frothing unit **836** and carbon floats to the top of the unit. The carbon is skimmed or scraped off and the output **834** includes skimmed carbon. The input **830** includes an output from the first frothing tank (stage 1) **826**, frothing agent tank **810**, and collector tanks **814**, **818** via input **828**.

[0122] Belt filter **858** is configured to dry or remove moisture from the carbon of input **838**. Dried carbon rich fly ash is output **860** to a conveyor **862**. Output **836** is water and sent to mixing tank **806** with a recycle loop.

[0123] Residue of the frothing unit **832** is output **852** and sent to belt filter **850** for drying clean fly ash which is composed of mostly silicates. Clean fly ash is output **854** to conveyor **856** from the belt filter **850** and water **848** is output **848** and sent to mixing tank **806** with a recycle loop.

EXAMPLES

[0124] Without intending to limit the scope of the invention, the following examples illustrate how various embodiments of the invention may be made and/or used.

Example 1

[0125] In this example, metal was extracted from Class C fly ash obtained from a coal fired power plant. The fly ash sample was analyzed with inductively coupled plasma mass spectrometry (ICP-MS) and results of this analysis are shown in FIG. 9. The fly ash sample before extraction is shown by scanning electron microscope (SEM) picture **902** which shows an individual particle of fly ash **904** surrounded by silica and calcium oxide particles **906**. In the individual particle **904** rare earth metals are concentrated. Image **908** shows an elemental mapping image of particle **904**, which shows lanthanum. Image **910** shows an elemental mapping image of particle **904**, which shows cerium. Image **912** shows an elemental mapping image of particle **904**, which shows neodymium. Accordingly, images **908**, **910**, and **912** show rare earth metals lanthanum, cerium and neodymium which are substantially comingled in the particle **904**. The elemental map was conducted with scanning electron microscope. In addition, graph **916** also shows the comingled nature of lanthanum, cerium and neodymium highlighted with circle **920**. Moreover, an analysis of metals in the pre-treated fly ash sample was conducted and is shown in Table 3.

TABLE 3

Initial Concentration of Metals in Fly Ash Sample	
	Concentration [mg/Kg]
Ce	407.7
Dy	32.3
Eu	14.0
Ga	91.8
Ge	2.8
Ir	1.8
La	163.6
Lu	2.7
Nd	140.5
Sc	42.2
Tb	5.6
Y	75.6

[0126] The experimental setup included a 100 mL supercritical fluid (SCF) extraction column obtained from Supercritical Fluid Technologies, Inc. having a model number SFT-110. About 30 grams (g) of fly ash in a nylon bag was placed into the 100 mL SFT-110 reactor.

[0127] CO₂ (g) was provided from a cylinder of CO₂ (g) to an operating pressure in the extractor of 1100 psi or above to achieve supercritical CO₂. Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. In this example, the operating supercritical operating pressure was about 3500 psi in the extractor. The chelating agent or co-solvent used was a mixture of thenoyltrifluoroacetone (TFA) and methanol. The mixture included about 1 g of TFA in 1 L of methanol. The temperature of the reactor was increased from an ambient temperature to about 45° C. to achieve the operating temperature.

[0128] The extractor was run in two modes of operation a first static mode and second dynamic mode of operation. In the static mode of operation the extractor was run for one-half hour at the operating temperature and pressure with the co-solvent. In the dynamic mode of operation, a restrictor valve was opened to flow the co-solvent mixture at a flow rate of about 1 mL/min for 1 hour at the operating pressure and temperature. This cycle was repeated four additional times. The SCF extraction column was turned off and the fly ash was collected and analyzed for metal.

[0129] This example was successful in selectively extracting rare earth metals from the fly ash. FIG. 10A illustrates results of the extraction in a graphical form. The y-axis of the graph is the relative % extraction and the x-axis of the graph denotes various metals in the retrieved solvent. FIG. 10B illustrates results of the extraction in a graphical form. The y-axis of the graph is the concentration [mg/L] of extraction and the x-axis of the graph denotes various metals in the retrieved solvent. These figures highlight the selective nature of the extraction process. The selective nature of the extraction is adjustable based upon at solubility and co-solvent section. More specifically, FIGS. 10A-10B show about a 100% extraction of scandium and about 50% extraction of yttrium. Thereby, the process of this example shows selective extraction of rare earth metals. Moreover, it was found that the selective extraction was based on the co-solvent utilized and was a function of solubility. To further separate these metals a liquid liquid extraction may be done. Moreover, an ion exchange column may be used to separate the extracted metals from each other followed by either precipitation of the metal as the oxide, oxalate, or other insoluble metal contain-

ing complex or by metallothermic reduction to obtain the elemental metal from solution.

Example 2

[0130] In this example, metal was selectively extracted from Class C fly ash obtained from a coal fired power plant. The fly ash sample was analyzed with inductively coupled plasma mass spectrometry (ICP-MS) and the analysis of metals present in the pre-treated fly ash sample is shown in Table 4. The metals in the fly ash were selectively extracted with an acidic extraction process, basic extraction process and scCO₂ extraction process. The extraction process was done in series and the results are shown in Table 4.

[0131] The acid extraction process was done in a glass container with a magnetic stir plate. In this extraction, 30 grams of fly ash was added to the container with 1 M (mol) of sulfuric acid at atmospheric pressure and 60° C. for 1 hour and stirred. After the extraction a vacuum filtration step was conducted to separate the extracted fly ash from the fluid.

[0132] The base extraction process was done in a glass container with a magnetic stir plate. In this extraction, the extracted fly ash from the acid extraction was added to the container with 1 M (mol) of sodium hydroxide at atmospheric pressure and 60° C. for 1 hour and stirred. After the extraction a vacuum filtration step was conducted to separate the extracted fly ash from the fluid.

[0133] Next supercritical fluid (SCF) extraction was performed and compared to the acidic and basic extraction. In this extraction a column obtained from Supercritical Fluid Technologies, Inc. having a model number SFT-110. The extracted fly ash was placed into the 100 mL SFT-110 reactor. About 30 grams (g) of fly ash in a nylon bag was placed into the 100 mL SFT-110 reactor. The fly ash sample is described with reference to Table 4.

[0134] CO₂ (g) was provided from a cylinder of CO₂ (g) to an operating pressure in the extractor of 1500 psi or above to achieve supercritical CO₂. Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. In this example, the operating supercritical operating pressure was about 3500 psi in the extractor. The chelating agent or co-solvent used was a mixture of thenoyltrifluoroacetone (TFA) and methanol. The mixture included about 1 g of TFA in 1 L of methanol. The temperature of the reactor was increased from an ambient temperature to about 45° C. to achieve the operating temperature.

[0135] The extractor was run in two modes of operation a first static mode and second dynamic mode of operation. In the static mode of operation the extractor was run for one-half hour at the operating temperature and pressure with the co-solvent. In the dynamic mode of operation, a restrictor valve was opened to flow the co-solvent mixture at a flow rate of about 1 mL/min for 1 hour at the operating pressure and temperature. This cycle was repeated four additional times. The SCF extraction column was turned off and the fly ash was collected and analyzed for metal. The results of this example are shown in Table 4. To further separate these metals a liquid liquid extraction may be done. Moreover, an ion exchange column may be used to separate the extracted metals from each other followed by metallothermic reduction to obtain the elemental metal from solution.

TABLE 4

Concentration of Metals in Fly Ash Sample, Amount Extracted and Percent of Extraction					
	Concentration of metals in fly ash [mg/kg]	Amount Extracted from Fly Ash [mg/kg]		Percent Extraction	
		acid/base	ScCO ₂	acid/base	ScCO ₂
Ce	408	368	82	90%	20%
Dy	32	21	9.0	65%	28%
Eu	14	9.3	8.5	66%	61%
Ga	92	17	60	18%	65%
Ge	2.8	0.56	1.8	20%	65%
Ir	1.8	0.49	0.9	28%	51%
La	164	73	30	44%	18%
Lu	2.7	2.6	0.51	97%	19%
Nd	141	77	111	55%	79%
Sc	42	30	42	70%	99%
Tb	5.6	3.2	2.2	57%	40%
Y	76	64	45	84%	59%

[0136] Referring to Table 4 shows selective extraction with acidic, basic and scCO₂ extractions. This process shows that with co-solvent having one ligand primarily one metal is selectively extracted, which in this case is scandium (Sc). Moreover, it shown that extraction processes are complementary. Accordingly, the extraction process orders may be readily optimized by utilizing the complementary extraction processes in an optimized order.

[0137] It was found that Sc and Y were selectively removed together from the supercritical carbon dioxide (scCO₂) extraction process. In addition, by changing the co-solvents other rare earths metals would be selectively extracted together. Any other co-solvents may be used. For example, in another example, the co-solvent was changed to hexafluoroacetylacetone with methanol in the supercritical carbon dioxide (scCO₂) extraction process described herein La and Nd were selectively extracted together.

[0138] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

[0139] Moreover, though the present disclosure has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the disclosure, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

1. A method of selectively extracting metals from a metal containing substance, comprising the steps of:
providing the metal containing substance; and
simultaneously treating the metal containing substance with supercritical carbon dioxide (scCO₂) and a chelating agent (ligand) to selectively remove one or more metals from the metal containing substance.

2. The method of claim 1, wherein the metal containing substance comprises a non-aqueous solid waste.

3. The method of claim 1, wherein the metal containing substance one or more of an industrial waste, a fly ash waste, a soil, a fluorescent bulb waste, and an electrical component waste.

4. The method of claim 1, wherein the metal containing substance comprises fly ash.

5. The method of claim 4, further comprising the step of processing the fly ash to reduce a concentration of calcium in the fly ash prior to the simultaneously treating step.

6. The method of claim 5, wherein the processing the fly ash to reduce a concentration step comprises

processing the fly ash with a chelating agent to chelate calcium (Ca) from the fly ash to reduce the concentration of calcium to a first concentration.

7. The method of claim 6, wherein the chelating agent is ethylenediaminetetraacetic acid (EDTA).

8. The method of claim 6, wherein the resulting concentration is in parts per million (ppm).

9. (canceled)

10. The method of claim 6, wherein the simultaneously treating step comprises the steps of treating the fly ash with the supercritical carbon dioxide (scCO₂) and the chelating agent (ligand) in a supercritical fluid (SCF) extraction column at a first pressure and temperature for a first time to remove a predetermined metal from the metal containing substance.

11. The method of claim 10, further comprising the step of treating the fly ash with the supercritical carbon dioxide (scCO₂) and a second chelating agent (ligand) in a supercritical fluid (SCF) extraction column at a second pressure and temperature for a second time to remove a predetermined metal from the one or more metals, wherein the second pressure and temperature is different than the first pressure and temperature and the second chelating agent (ligand) is different than the first chelating agent.

12. The method of claim 10, wherein the chelating agent (ligand) is a selected group consisting of acetylacetone, hexafluoroacetylacetone, fluorinated crown ether, bis(2,4,4-trimethylphenyl)phosphinic acid, tributylphosphate, thenoyltrifluoroacetylacetone, lithium bis(trifluoroethyl) dithiocarbamate and combinations thereof.

13.-14. (canceled)

15. The method of claim 14, wherein the one or more metals comprises rare earth metals comprising one or more of scandium, lanthanum, dysprosium, europium, neodymium, and yttrium.

16.-19. (canceled)

20. The method of claim 1, wherein the simultaneously treating the industrial waste step further comprises treating the industrial waste with one or more of a sulfuric acid (H₂SO₄) and a nitric acid (HNO₃) to extract the one or more metals from the industrial waste.

21. A method of selectively removing one or more metals from fly ash, comprising the steps of:

providing the fly ash;

selectively removing a first metal from the fly ash with supercritical carbon dioxide (scCO₂) and a first chelating agent (ligand) at a first pressure and temperature in a supercritical fluid (SCF) extraction column;

selectively removing a second metal from the fly ash with supercritical carbon dioxide (scCO₂) and a second

chelating agent (ligand) at a second pressure and temperature in the supercritical fluid (SCF) extraction column;

selectively removing a third metal from the fly ash with supercritical carbon dioxide (scCO_2) and a third chelating agent (ligand) at a third pressure and temperature in the supercritical fluid (SCF) extraction column;

selectively removing a fourth metal from the fly ash with supercritical carbon dioxide (scCO_2) and a fourth chelating agent (ligand) at a fourth pressure and temperature in the supercritical fluid (SCF) extraction column;

selectively removing a fifth metal from the fly ash with supercritical carbon dioxide (scCO_2) and a fifth chelating agent (ligand) at a fifth pressure and temperature in the supercritical fluid (SCF) extraction column; and

selectively removing a sixth metal from the fly ash with supercritical carbon dioxide (scCO_2) and a sixth chelating agent (ligand) at a sixth pressure and temperature in the supercritical fluid (SCF) extraction column.

22. The method of claim **21**, wherein the first chelating agent (ligand) is a mixture of thenoyltrifluoroacetylacetone (TFA) and methanol and the first metal is scandium.

23. The method of claim **22**, wherein the second chelating agent (ligand) is hexafluoroacetylacetone and the second metal includes lanthanum and neodymium.

24. The method of claim **23**, wherein the third chelating agent (ligand), the fourth chelating agent (ligand), the fifth chelating agent (ligand) and the sixth chelating agent (ligand) are selected from the group consisting of acetylacetone, hexafluoroacetylacetone, fluorinated crown ether, Bis(2,4,4-

trimethylpentyl)phosphinic acid, tributylphosphate, thenoyltrifluoroacetylacetone, lithium bis(trifluoroethyl)dithiocarbamate and combinations of the same.

25. A method of removing metals from industrial waste, comprising the steps of:

providing the industrial waste from a fossil fuel-fired system, wherein the industrial waste comprises fly ash;

removing SO_x from a flue gas of the fossil fuel-fired system and processing the SO_x to form sulfuric acid (H_2SO_4);

removing NO_x from the flue gas of the fossil fuel-fired system and processing the NO_x to form nitric acid (HNO_3);

removing CO_2 from the flue gas of the fossil fuel-fired system and processing the CO_2 to form supercritical carbon dioxide (scCO_2);

extracting one or more metals from the industrial waste with one or more of the supercritical carbon dioxide (scCO_2), the nitric acid (HNO_3), the sulfuric acid (H_2SO_4) and a chelating agent (ligand); and

selectively extracting one or more metals from the industrial waste with the supercritical carbon dioxide (scCO_2).

26. The method of claim **25**, wherein the chelating agent (ligand) is selected from the group consisting of acetylacetone, hexafluoroacetylacetone, fluorinated crown ether, Bis(2,4,4-trimethylpentyl)phosphinic acid, tributylphosphate, thenoyltrifluoroacetylacetone, lithium bis(trifluoroethyl)dithiocarbamate and combinations of the same.

27.-29. (canceled)

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