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(54) Title: METALLURGICAL DUST RECYCLE PROCESS

(57) Abrégé/Abstract:

A method and apparatus for the treatment and recovery of metal values from metallurgical dust comprising the steps of preliminarily washing of the dust to remove chloride salts (62), leaching the cleaned dust with a nitric acid solution resulting in the substantially complete dissolution of contained zinc, cadmium, copper, magnesium, calcium manganese and lead values (64), collecting and recycling of exuded nitric acid fumes from the leach (92), removing iron from the resulting leachate as a reusable iron oxide precipitate via pH elevation with basic zinc carbonate (66), electrolytically recovering cadmium, copper, and lead from the iron free leachate (70), evaporating and decomposing the resulting anolyte to obtain oxides of zinc, magnesium, and manganese and anhydrous calcium nitrate (72), followed by calcium nitrate separation (74) and the ammoniacal dissolution (78) and recovery of zinc (84) with subsequent acid leaching (88) and separation of the magnesium and manganese values (90).



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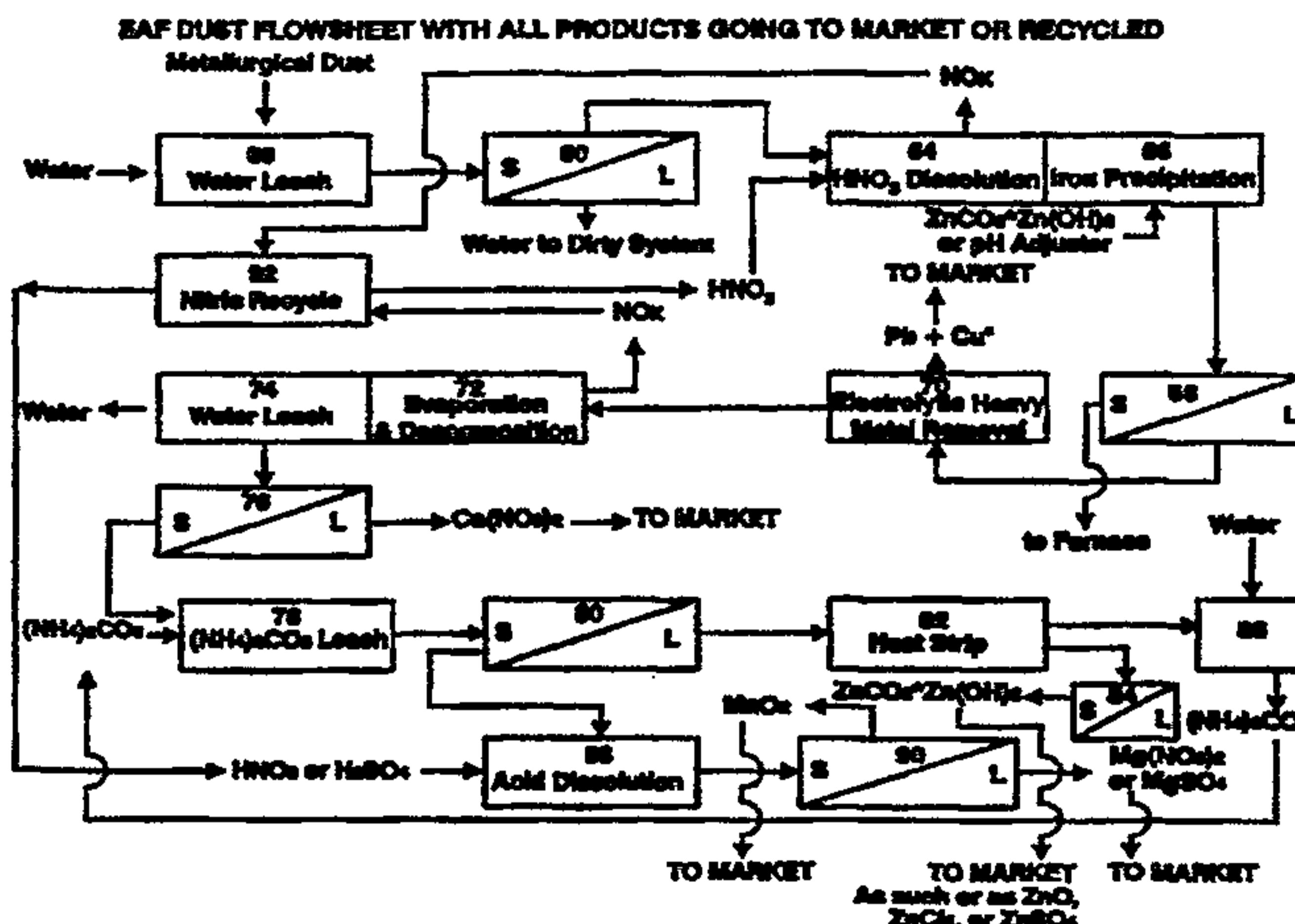
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(54) Title: METALLURGICAL DUST RECYCLE PROCESS



**(57) Abstract**

A method and apparatus for the treatment and recovery of metal values from metallurgical dust comprising the steps of preliminarily washing of the dust to remove chloride salts (62), leaching the cleaned dust with a nitric acid solution resulting in the substantially complete dissolution of contained zinc, cadmium, copper, magnesium, calcium, manganese and lead values (64), collecting and recycling of exuded nitric acid fumes from the leach (92), removing iron from the resulting leachate as a reusable iron oxide precipitate via pH elevation with basic zinc carbonate (66), electrolytically recovering cadmium, copper, and lead from the iron free leachate (70), evaporating and decomposing the resulting anolyte to obtain oxides of zinc, magnesium, and manganese and anhydrous calcium nitrate (72), followed by calcium nitrate separation (74) and the ammoniacal dissolution (78) and recovery of zinc (84) with subsequent acid leaching (88) and separation of the magnesium and manganese values (90).

## METALLURGICAL DUST RECYCLE PROCESS

## FIELD OF THE INVENTION

The present invention relates to a method and apparatus for the economically processing of Metallurgical Dust, such as Electric Arc Furnace Dust (hereinafter EAF dust [EPA hazardous waste No. 5 K061]) into marketable chemicals. EAF dust, which is currently treated as hazardous waste, can now be considered as a potential raw material for the recovery of the metal values contained therein as metals, inorganic chemicals, and as a potential raw material source.

## BACKGROUND OF THE INVENTION

10 The manufacture of steel using an electric arc furnace (EAF) is a highly advantageous process in the modern steel industry. A drawback in the EAF manufacture of steel is the production of EAF dust waste by-products. The EAF dust is generated during the steel making process by a variety of mechanisms, including droplet 15 ejection from the turbulent melt and vaporization. The vaporization mechanism is primarily responsible for the relatively high proportion of the non-ferrous metals in the dust such as zinc, lead and cadmium, which are vapors at a temperature of about 1600° centigrade (2,912° fahrenheit) in the EAF hearth. The droplets and 20 vapors of vaporized non-ferrous metals are carried in the exhaust gas stream from the furnace along with mechanically entrained iron oxides, lime, etc. The vaporized metals condense as oxides and ferrites and are collected downstream in a baghouse and/or electrostatic precipitator. The production of 1 ton of steel will 25 generate approximately 34 pounds (15.4 kg) of EAF dust as a by-product.

30 The rapid growth of the EAF steel process has made EAF dust one of the fastest growing and largest environmental problems worldwide. At present, there are approximately 600,000 metric tons of this hazardous waste generated annually in the USA and an additional 600,000 metric tons generated annually in the rest of the

world. EAF produced steel is currently forty percent (40%) of total US steel production. It is expected to become the major source of steel produced in the USA early in the next century.

There is also a similar but lower level contaminated dust 5 which is derived from the other major process for steel manufacturing, the basic oxygen furnace (BOF). The BOF can be either top or bottom blown. Because the levels of toxic metals such as cadmium, lead and zinc are lower, BOF dust is not currently classified by EPA as hazardous.

10 BOF dust may be considered hazardous in the future and its non-iron contaminants make it difficult to impossible to utilize in current steel manufacture resulting in substantial "stock piles" worldwide.

15 BOF dust can also be processed by the present invention to recover both the ferrous and non-ferrous values contained therein.

Many other metallurgical dusts also contain metal values which can be recovered and environmental concerns which can benefit from the application of this invention.

20 Currently EAF dust is disposed of by pyro metallurgical processing, land-filling, stabilization and to a small extent, fertilizer production.

Pyro processing which represents the substantial proportion of 25 all EAF dust treated, costs steel producers from US \$150 to US \$200 per metric ton. Assuming an average cost of US \$175 per metric ton of EAF dust, the annual cash burden on this major essential industry is US \$105,000,000 per year. This figure, however, greatly undervalues the true cost to the steel industry, to the public-at-large, and to our descendants from damage to the environment.

30 None of the known processes in practice totally eliminate economic and environmental waste.

Table 1 gives the average values of the EAF dust constituents for a sample plant for 1992 and 1993. Most notable are the high concentrations of iron (approximately 35%), zinc (approximately 20-

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23%), lead (approximately 1%), manganese (approximately 3.5%), and magnesium (approximately 2%). The nonferrous values represent potentially rich sources of metal values, such as zinc, lead, copper, cadmium, calcium and magnesium. The iron can be recycled back into the EAF furnace.

Table 1

SAMPLE PLANT EAF DUST CONSTITUENTS FOR 1992/1993

	%Zn	%Al	%Pb	%Fe	%Cd	%Cu	%Mn	%Na	%Ba
Avg. 1992	20.3	0.27	1.27	36.0	0.02	0.16	3.54	0.59	0.01
Avg. 1993	22.7	0.30	1.04	34.8	0.01	0.13	3.60	0.70	0.01

	%CaO	%Cr	%Mg	%Ni	%V	%As	%SiO <sub>2</sub>	%Cl
Avg. 1992	5.51	0.20	2.06	0.02	0.01	.0036	2.52	0.96
Avg. 1993	5.48	0.20	2.48	0.13	0.02	.0029	4.74	0.78

There are several problems associated with the disposal or processing of EAF dust. The high level of zinc in the dust is expected by many experts to cause problems with zinc build-up in a furnace if the dust is recycled directly to the furnace. High zinc vapors in the EAF furnace are known to cause shorting of the electrodes causing the electrical energy to be wasted instead of being used for making steel. A high proportion of the zinc in EAF dust is present in the form of ferrites (ZnO.Fe<sub>2</sub>O<sub>3</sub>) which have proven resistant to presently known leaching processes.

Currently, the steelmaker disposes of the EAF dust by shipping it to a company specializing in waste management, which charges a processing fee of up to \$200 per ton of dust. In addition to the

processing fee, there are freight costs and substantial potential liability in the over-the-road shipment of this hazardous waste.

The production of 1 ton of steel is generally expected to generate about 34 lbs. (15.4 kg) of EAF dust as a by-product. 5 Therefore, a 100 ton hearth will produce about 3400 lbs. (1542 kg) of EAF dust. A typical EAF hearth produces over 10,000 tons of EAF dust per annum. When a \$175 per ton cost is considered, the dust disposal cost for this typical plant is over \$1,750,000 per year. Many of the more substantial EAF Steel companies have two, three or 10 four hearths at a single steel complex. Their EAF costs rise proportionally.

#### DESCRIPTION OF THE PRIOR ART

Applicant is aware of the following U. S. Patents concerning process and apparatus for treating and recycling EAF dust.

15	<u>US Pat. No.</u>	<u>Inventor</u>	<u>Issue Date</u>	<u>Title</u>
	3,849,121	Burrows	11-19-1974	ZINC OXIDE RECOVERY PROCESS
20	4,332,777	Pazdej	06-01-1982	HYDROMETALLURGICAL TREATMENT OF METALLURGICAL DUST
	5,208,004	Myerson	05-04-1993	METHOD FOR THE RECOVERY OF ZINC OXIDE

Burrows, US 3,849,121, teaches a method for the selective recovery form a number of industrial waste material of various components, including zinc, copper, lead and iron, which comprises the steps of leaching the waste material with an ammonium chloride solution maintained at an elevated temperature, separating the undissolved iron component from solution, treating the solution with zinc metal to displace the copper and lead from the solution, and cooling the solution to precipitate therefrom the zinc component as zinc oxide. 25

Pazdej, US Patent 4,332,777, teaches a process and apparatus for hydrometallurgical treatment of metallurgical dust by acid leaching followed by a solid-liquid separation. The leaching phase is effected by moderate acid attack (pH at the end of the reaction about 4 or 5) and in which a supplementary solid-liquid separation 35

stage is provided, before the solid-liquid separation or after. The process is applicable to all dusts resulting from treatment of metals, notably ironworking dusts, and particularly those formed in blast furnaces so as to permit the separation and recovery of useful 5 elements contained therein, such as iron, zinc, and lead.

Myerson, US Patent 5,208,004, teaches a method for the recovery of zinc oxide from industrial waste materials of various components, including zinc, lead, iron, and cadmium, which comprises the steps of treating the waste material with an ammonium chloride 10 solution maintained at an elevated temperature, separating the undissolved components from the solutions, treating the solution with zinc metal to displace undesired metal ions from the solution, cooling the solution to precipitate therefrom zinc compounds, washing the precipitated zinc compounds to remove unwanted compounds 15 such as diamino zinc dichloride, and drying the remaining zinc compound which is essentially hydrated zinc oxide, resulting in essentially pure zinc oxide.

None of these inventions dissolve and recover the twenty to sixty percent of the zinc tied up in ferrites and similar insoluble 20 complexes.

#### SUMMARY OF THE INVENTION

The invention provides a method for totally converting toxic metallurgical dust into marketable products. This invention also provides a method for extracting and recovering the twenty to sixty 25 percent zinc values of EAF dust that has heretofore been unrecoverable.

During normal operation, the EAF dust is dissolved in a nitric acid solution, and iron is precipitated from the solution by raising its pH and/or by elevating the temperature. The dust may first be 30 leached in water. The resulting solution undergoes iron removal then heavy metal removal by electrolytic and/or sulfide precipitation then is evaporated and decomposed. The resulting product is leached in water to remove calcium nitrate. The resulting residue is treated with metal amine complexing agents such 35 as ammonium carbonate, ammonium hydroxides, mixtures thereof and similar agents to recover the zinc values leaving manganese and magnesium values which are separated by acid.

## OBJECTS OF THE INVENTION

The principal object of the invention is to provide an improved method of processing EAF dust which converts it totally from toxic waste to usable products.

5 An additional major object is to provide a process which can be operated at individual dust producing locations eliminating the transportation hazards and potential liabilities incurred in the shipment of hazardous and noxious wastes.

10 Another object is to provide a process which can be contiguous with EAF and similar metallurgical dust collection so as to eliminate the storage of hazardous waste.

A further object of this invention is to provide a method for removal of zinc, copper, cadmium, lead and other toxic or undesirable elements from EAF dust.

15 Another object of the invention is to provide a method for the separation of valuable calcium compounds from metallurgical furnace dusts.

Another object of the invention is to provide a method for eliminating existing and future environmental liability.

20 Another object of the invention is to provide a process for recovering the twenty to sixty percent zinc that current processes cannot obtain.

25 Another object of the invention is to provide a process for removing sufficient non-ferrous metals such as zinc and lead that the remaining iron residue can be recycled to the furnace without upsetting the required metallurgical balance of the bath and its coexisting vapors in the furnace.

Another object of the invention is to provide a method for the recovery of valuable zinc products from metallurgical furnace dusts.

30 Another object of the invention is to provide a method for the recovery of marketable magnesium and manganese compounds from metallurgical furnace dusts.

Another object of the invention is to provide a method for the separation of valuable zinc compounds from metallurgical furnace dusts.

Still another object of this invention is to provide an 5 apparatus to carry out this process.

Another object of this invention is to provide a method for the separation and recovery of valuable lead, cadmium, and copper.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects will become more readily 10 apparent by referring to the following detailed description and the appended drawings in which:

Figure 1 is a flow chart of the process for treating EAF dust to produce a number of profitable streams of inorganic chemicals.

Figure 2 is an expanded flow chart of Figure 1 which adds a 15 water leach to help control the corrosiveness of the process and improve the purity of the products.

Figure 3 is an expanded flow chart of Figure 2 which separates out further chemical products.

Figure 4 is a flow chart of the process which enables EAF dust 20 to be optimally utilized to produce a number of profitable streams of inorganic chemicals.

#### DETAILED DESCRIPTION

The invented method of treating metallurgical dust and recovering valuable chemical commodities, comprises the steps of: 25 reacting metallurgical dust in a nitric acid solution, resulting in a nearly complete dissolution of the zinc, cadmium, copper, iron, magnesium, calcium, manganese and lead; precipitating iron from the solution by raising the pH and/or elevating the temperature of the solution; and removing cadmium, copper and lead from the solution 30 in an electrolytic cell, where elemental copper and elemental cadmium are collected at the cathode, and lead dioxide is collected at the anode. Cadmium, copper and lead can also be removed using

a sulfide ion source such as hydrogen sulfide ( $H_2S$ ) or sodium bisulfide (NaSH). The nitric acid can be a solution of 10% to 100% nitric acid. Note that solutions of more than 70% nitric acid are more difficult to obtain and work with, so the working range is an aqueous solution of 30% to 70% nitric acid, and the preferred solution is 40% to 60% nitric acid.

Referring now to the drawings, and particularly to Figure 1, metallurgical dust, such as EAF dust is leached with nitric acid in the  $HNO_3$  Dissolution Stage 10 where it is leached with nitric acid from the Nitric Recycle 18.  $HNO_3$  Dissolution 10 generates  $NO_x$  which is sent to the Nitric Recycle 18. The  $HNO_3$  Dissolution mixture from the  $HNO_3$  Dissolution 10 is treated with a basic agent, such as zinc carbonate to cause Iron Precipitation 12. Increasing the temperature increases the iron precipitate. At 200°C or above, iron can be precipitated by temperature alone. This temperature requires a pressurized reaction vessel and is not therefore the preferred method. The resulting mixture is sent to a filter in filtration stage 14 where the iron oxide solid is separated for use as a feedstock for a steelmaking furnace or chemical applications. The liquid from the filtration stage 14 is sent to a electrolytic heavy metal removal 16 where elemental copper, cadmium and lead are removed at the electrodes. The resulting liquid is free from lead, cadmium, and copper and is suitable for agricultural and similar uses.

25

It is advantageous to employ a nitric recycle process 18, wherein nitric ( $NO_x$ ) gases exuded during the reacting of nitric acid solution with metallurgical dust are recycled into nitric acid by a nitric recycle process.

30

Reaction 10 of metallurgical dust with the nitric acid solution takes place at elevated temperatures, within the range of 70° to 130° centigrade (hereinafter C) or 158° to 266° fahrenheit (hereinafter F). A range of 95° to 125° C (203° to 257° F) yields good results. The mixture of nitric acid solution and metallurgical dust is reacted for a period of one quarter (1/4) to four (4) hours, with good results being obtained from reaction periods of one (1) to two (2) hours.

Iron removal 12 from the filtrate is accomplished by raising the pH of the solution from a range of 1 to 2.3 to a range of 1.8 to 3.5. This is accomplished through the introduction of a pH adjuster which, in this case, will be a basic agent. Examples of

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suitable basic agents include zinc carbonate  $ZnCO_3$ , zinc oxide  $Zn(OH)_2$ , or other mixed oxides, though any agent capable of adjusting the pH level can be used. At this same time the solution is heated to about  $80^\circ$  to  $130^\circ$  C ( $176^\circ$  to  $266^\circ$  F). The precipitate 5 is separated for use in the furnace, and the resulting filtrate is ready for further processing.

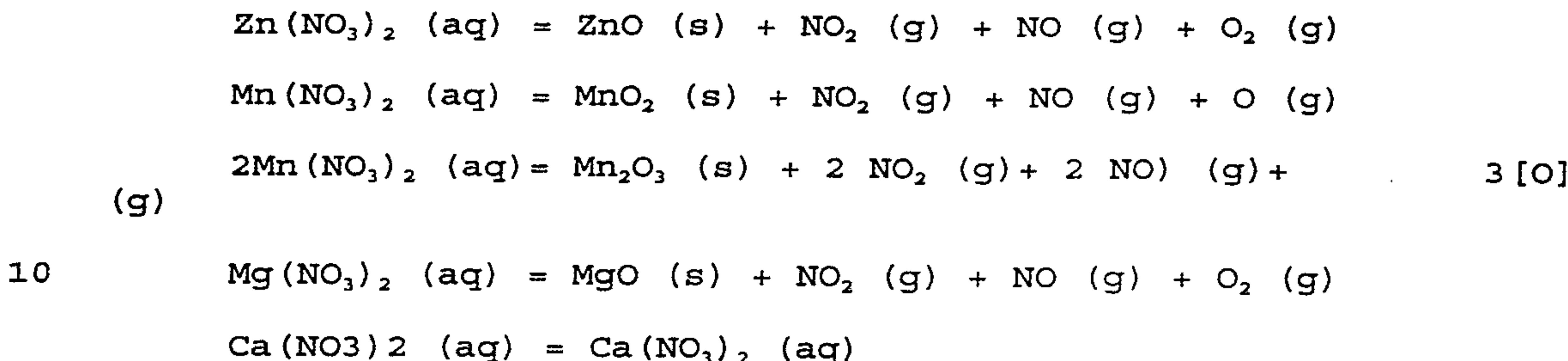
The resulting filtrate is then treated by either electrolysis 16 or by reaction with  $H_2S$  or other sulfide ion sources such as  $NaSH$ . Cadmium, copper and lead can be collected in an electrolytic 10 cell operated at ambient temperature, and the electrolysis is continued for sufficient time to insure quantitative deposition.

Alternatively if a separate cadmium product is required, electrolysis can be conducted so as to first remove copper and lead by electrolysis and then cadmium as a sulfide concentrate.

15 In many applications, it is desirable to add an initial step 20 of leaching metallurgical dust with water, Figure 2, creating and separating a filtrate and washed metallurgical dust 22. The filtrate is sent to a water treatment system, leaving washed metallurgical dust residue for reaction with nitric acid solution. 20 This step is quite effective in removing unwanted chloride from the system.

Using the water leach, the metallurgical dust is washed with water to remove chlorides in water leach stage 20, Figure 2. A resulting mixture is filtered in a first filtration stage 22, and 25 the liquid is sent for processing (which may be the dirty water system of a steel plant). The solid from filtration stage 22 is sent to  $HNO_3$  Dissolution 24 where it is leached with nitric acid from the nitric recycle 32.  $HNO_3$  Dissolution 24 generates  $NO_x$ , which is also sent to the nitric recycle 32. The  $HNO_3$  Dissolution 30 mixture from the  $HNO_3$  Dissolution 24 is treated with a basic agent, such as zinc carbonate, to cause iron precipitation 26. This resulting mixture is sent to a filter in a second filtration stage 28 where the iron oxide solid is separated for use in a steelmaking furnace. The liquid from the second filtration stage 28 is sent to 35 an electrolytic heavy metal removal 30 where elemental copper, cadmium and lead oxide are removed at the electrodes. This produces a heavy metal-free mixed metal nitrate solution which can be marketed.

A more refined product can be obtained by adding the steps of evaporating and decomposing 52, Figure 3, the filtrate to obtain a solid residue of metal oxides and calcium nitrate. Evaporating, decomposing and leaching the solid residue with water 54 produces  
5 the following products:



A third liquid solid separation 56 extracts aqueous calcium nitrate. Evaporation and decomposition steps can be added either with or without the initial water leach. Evaporating and decomposing 52 the  
15 filtrate to obtain metal oxides and calcium nitrate entails heating the filtrate to a temperature range of about 200° to 400° centigrade (392° to 752° F) for sufficient time to transfer the energy required for evaporation, concentration, and decomposition. Liberated NO<sub>x</sub> is then sent to the nitric recycle system 58. Leaching of solid  
20 residue with water takes place at ambient temperatures for one-half (1/2) to two (2) hours (see 54 and 56, Figure 3).

To enhance the value of the residual metals removed from the dust, further separations can be performed. It is possible to separate the zinc from the magnesium and manganese by leaching the  
25 precipitate of third separation 56 with aqueous ammonia, ammonia salts or other amine complexing solutions such as ammonium carbonate solution 78, Figure 4, to solubilize and filter to remove the zinc from the solids and filtrate 80. Stripping the leachate of ammonium carbonate 82 yields zinc precipitated as a zinc oxycarbonate.  
30 Leaching the residue with ammonium carbonate solution 78 is carried out at ambient temperatures for one (1) to three (3) hours. Stripping the leachant of the complexing ammonium carbonate solution requires a heat strip 82 to elevate the temperature to 70° to 110° C (158° to 230° F). These elevated temperatures are maintained for  
35 a sufficient time to transfer the energy, required for ammonium carbonate evaporation.

The basic zinc product obtained in the heat strip 82 is divided into a first stream and a second stream. The first stream can serve as a pH adjuster to precipitate iron at 66. The second stream 84 can be used to prepare highly pure zinc products for sale.

5 The zinc complexes come off as a cake or precipitate 84. The acid used to treat the zinc is selected from the group consisting of hydrochloric acid, nitric acid, organic acids, and sulfuric acid.

Referring again to Figure 4, the invented method includes

10 multiple process steps which enable metallurgical dust (such as EAF dust) to be optimally utilized to produce a number of profitable streams of inorganic chemicals. This process also has a high degree of versatility, in which different chemicals can be made to best exploit the market.

15 The first step in the invented system is to leach the chloride from the dust with water 60. The leach is performed at ambient temperature for a period of time sufficient to solubilize the majority of the chlorides. For the dusts sampled and the equipment used, this was one half (1/2) to two (2) hours, with good results

20 achieved from a 1 hour interaction. This leach can be performed at elevated temperatures. The leach can also be performed with various additives such as small amounts of alkali to reduce equipment corrosion or to enhance or restrict the water solubility of the water soluble elements. Results show that over 90% of the chloride

25 is removed in the water leach. This leach necessitates a second separation step 62 from which the leachant is sent to a dirty water system.

The third step is to react the washed dust in a 30% to 70% nitric acid solution 64. Higher and lower nitric acid

30 concentrations can be used but they are either much more costly or slower, respectively. Good results are achieved with a 40% to 60% nitric acid solution. The reaction step is normally performed at 90° to 130° C which is 194° to 266° F. A range of 100° to 120°C (212° to 248° F) is optimal. This elevated temperature should be

35 maintained over a time period sufficient to solubilize the non-ferrous metals contained in the dust. For the dusts sampled and the equipment used, this was from one half (1/2) to three (3) hours. A range of one (1) to two (2) hours is optimal, as good results can

be achieved at 1.5 hours. The result is the essentially quantitative dissolution of the zinc (100 percent can be obtained), cadmium, copper, magnesium, calcium, manganese and lead. Unexpectedly, the insoluble zincs such as zinc ferrite were totally 5 decomposed by nitric, and up to 100% of the zinc is recovered for sale. Nitric fumes exuded during this third step 64 are recovered as nitric acid by a nitric recycle process 92.

The fourth step 66 is to remove the iron from the second step 10 62 filtrate by raising the pH with basic zinc oxycarbonate 66 taken from the end of the process 84. Other alkaline sources, such as limestone ( $\text{CaCO}_3$ ), magnesium carbonate ( $\text{MgCO}_3$ ), magnesite or magnesium oxide ( $\text{MgO}$ ), magnesium hydroxide ( $\text{Mg(OH)}_2$ ), sodium carbonate ( $\text{NaCO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), potassium hydroxide (KOH), ammonium hydroxide or carbonate, zinc oxide ( $\text{ZnO}$ ), lime 15 (CaO), shaken lime  $\text{Ca(OH)}_2$ , or dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) could be used. For the samples tested, the step is performed within the range of 80° to 100° C (176° to 212° F), with a temperature of 90° C yielding good results, for a period of one (1) to three (3) hours, 2 hours yields good results. The precipitation of iron 66 is virtually 20 complete. The iron oxide precipitate 68 can be sent to the furnace as iron ore. The zinc reagent accumulates with the zinc already in the filtrate to be recovered later in the process. Other alkaline reagents, when used, are also recovered in subsequent processing steps.

25 The sixth step is to remove the cadmium, copper and lead in an electrolytic cell 70 or with  $\text{H}_2\text{S}$  or other sulfides. Using electrolysis, one needs sufficient Faradays to deposit (remove) the copper, cadmium, and lead. For the equipment and quantity of materials preset in our tests, this step was performed at ambient 30 temperature to 100° C (212° F) for one half (1/2) to two (2) hours, 1 hour providing good results. Elemental copper and elemental cadmium are collected at the cathode as:

Cu - copper metal

Cd - cadmium metal.

35 Lead is collected at the anode.

Removal of these metals is virtually complete, and the filtrate entering the next step is free of lead, cadmium and copper. It is comprised of:

$\text{Zn}(\text{NO}_3)_2$  (aq)

$\text{Mn}(\text{NO}_3)_2$  (aq)

$\text{Ca}(\text{NO}_3)_2$  (aq)

$\text{Mg}(\text{NO}_3)_2$  (aq).

5 The seventh step is to evaporate and decompose the filtrate 72 to obtain metal oxides. This step is performed by raising the temperature from 200° to 400° C (392° to 752° F), 400° C (752° F) being optimal, for a period of 4 to 6 hours, 5 hours being optimal. At this temperature, the zinc, magnesium and manganese form water 10 insoluble oxides, while the calcium remains as a water-soluble nitrate. The nitric gases given off during the evaporation and decomposition 72 are recycled to nitric acid by the nitric recycle 92. If the calcium content is such that it is desired in the oxide mixture, the mixed nitrates can be decomposed at temperature above 15 500° C to deposit all of them together.

The calcium nitrate is separated in a marketable form by leaching the solid residue with water 74. This leach is carried out at ambient temperature for a period of one half (1/2) to two (2) hours, 1 hour being optimal. A precipitate and filtrate 76 are the 20 products of the water leach. Calcium nitrate is recovered as the filtrate and can be sold as such or used to manufacture other chemicals. If the calcium content is low, this step may not be required.

Depending on the input level of the metallurgical dusts being 25 treated, the metal oxides obtained may be found to be of sufficient purity to be used as a crude zinc oxide suitable for refining to metal or for chemical manufacture.

The tenth step is to remove the zinc from the magnesium and manganese by leaching the residue with ammonium carbonate solution 30 78. For the materials being tested and the amount used, this leach is carried out at ambient temperature for a period of one (1) to three (3) hours, two (2) hours being optimal. Since none of the zinc is now in ferrite form, the leach quantitatively removes the zinc. Ammonia salts will effectively extract and recover the zinc. 35 After separation from the insolubilized magnesium and manganese 80, the filtrate is stripped of the ammonium carbonate (which is

recycled) by heating at 70° to 110° C (158° to 230° F) with a heat strip 82. A temperature range of 80° to 100° C (176° to 212° F) is optimal, for a period of one (1) to three (3) hours (2 hours being optimal) to yield zinc precipitated as a zinc oxycarbonate.

5 The zinc oxycarbonate obtained in the heat strip is divided into two streams. One stream is sent back to the beginning of the process (step four - iron precipitation 66), where it is used as a pH adjuster to precipitate iron. The other stream 84 can be used to prepare highly pure zinc products for sale.

10 The solids containing the magnesium and manganese are separated by dissolving the magnesium in either sulfuric or nitric acid 88. This can be performed at ambient temperature for one half (1/2) to two (2) hours. The liquid filtrate 90 contains marketable magnesium nitrate or sulfate.

15 This invention results in a thorough utilization of the metallurgical dust, such as EAF dust.

An apparatus for treating metallurgical dust and recovering valuable chemical commodities, comprises: a source of metallurgical dust, which may be from an electric arc furnace (EAF) or a BOF 20 furnace or some other metallurgical source; a source of water, which may either be city water or deionized (DI) water; a nitric acid recycle system; and a vessel is in communication with the source of metallurgical dust and the source of water providing a means for leaching chloride from the dust with water to create a washed 25 metallurgical dust. The same vessel or a second vessel is provided as a means for separating a residue with the filtrate. Filtrate is removed from this stage to a dirty water system and the resulting residue is collected for further processing. A third vessel is provided, in communication with said washed metallurgical dust, as 30 a means for reacting the washed metallurgical dust in a nitric acid solution. The nitric acid solution is provided by the nitric acid recycle system which is in communication with the third vessel. Nitric fumes exuded during this step are recycled into nitric acid by said nitric acid recycle system.

35 The mixture of nitric acid and washed metallurgical dust is then transferred to a fourth vessel. This vessel also has a input

for the addition of a basic or neutralized substance which is a means for removing iron from the mixture by raising pH in said system. This basic substance can be a zinc oxycarbonate produced at step 84, Figure 4, of the process. This mixture can optionally 5 be sent to a fifth vessel for separation or the separation may take place in vessel four. The resulting iron oxide precipitate can be sent to the furnace as iron ore.

The zinc reagent goes with the zinc already in the filtrate to be recovered later in the process. This filtrate is then sent to 10 a sixth vessel a means for removing cadmium, copper and lead is introduced. This may either be a reaction with  $H_2S$  or other heavy metal precipitation regents or the introduction of an electrolytic cell apparatus.

The filtrate entering the next step is free of lead, cadmium 15 and copper and is introduced into a seventh heated vessel for evaporating and decomposing the filtrate to obtain metal oxides and anhydrous calcium nitrate, the nitric gases given off during the evaporation and decomposition are recycled to nitric acid by the nitric recycle.

20 The resulting metal oxides are introduced into an eighth vessel along with water and leached. This results in a filtrate, calcium nitrate in a marketable form, and a precipitate or cake.

A ninth vessel is provided where the precipitate is mixed with an ammonium carbonate solution. This leach is a means for removing 25 the zinc from the magnesium and manganese. Residue is conveyed to a tenth vessel, filtrate is conveyed to a heat strip which liberates the ammonium carbonate from a zinc precipitate. This Zinc precipitate is zinc oxycarbonate.

A mechanical separator divides the zinc oxycarbonate obtained 30 in the heat strip into a first stream and a second stream. The first stream serves as a pH adjuster to precipitate iron. The second stream is used to prepare a highly pure zinc products for sale. Here the zinc complex is reacted with acid to produce a zinc product.

In the tenth vessel, the precipitate is mixed with either sulfuric or nitric acid and allowed to separate into a filtrate and a precipitate. The resulting residue is separated out which contains the manganese dioxide. The liquid filtrate contains 5 marketable magnesium as a salt such as nitrate or sulfate.

The advantages of the present invention include the complete recycle of iron to the furnace and sale of all other materials, and the great operational and environmental advantages. Further the present invention is unique in that it can be completely carried out 10 at atmospheric pressures as opposed to elevated pressures.

#### ALTERNATIVE EMBODIMENTS

While it has been suggested that this process and apparatus can be used effectively on metallurgical dust such as EAF dust, it will be readily apparent to one of ordinary skill in the art that 15 this process can be used on any materials which contain some or all of the following materials: zinc; lead, cadmium; copper; manganese; calcium; and magnesium.

#### EXAMPLES

##### Example 1

##### 20 PRELEACH OF DUST WITH WATER

A quantity of 4530 grams (hereinafter g) of water was heated to 60° C and agitated in a stainless steel reactor. A quantity of 906g of EAF dust was added and agitation at 60° C was maintained for 1 hour. The mixture was filtered and the residue was washed by 25 repulping with 60° C water. This produced the following results:

##### PERCENT EXTRACTED FROM EAF DUST

Al	Ca	Cd	Cu	Fe	Mg	Mn	Pb	Zn	Cl
2.2	7.0	0.2	0.4	0.0	0.1	0.0	15.1	0.0	93.4

The preleach with water removed the bulk of chloride while little 30 of the valuable metals were removed from the EAF dust.

Example 2

## NITRIC ACID LEACH OF WASHED DUST

A 3 liter agitated reactor was charged with 1200 g of 53% HNO<sub>3</sub>. A quantity of 400.0 g of washed dust were fed into the reactor over 5 75 minutes. The temperature was raised to 94° C and the solution was agitated for another 30 minutes. The solution was filtered and the residue was repulped with pH 2.5 water. This produced the following results:

## PERCENT EXTRACTED FROM WASHED DUST

10	Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
	97.3	99.8	97.2	91.0	94.9	89.1	98.5	96.3	99.4	98.4

The nitric acid leach solubilized the majority of the metal values from the EAF dust. Other elements, such as arsenic, would have also been solubilized if they were present. The remaining residue, if 15 any, is totally acceptable for direct recycle to the EAF furnace.

Example 3

## IRON PRECIPITATION

A 3 liter agitated reactor was charged with 11 of leachate. The mixture was brought to 90° C. A slurry of 30% calcium carbonate 20 (or, alternately, 20% ZnO or basic zinc carbonate) was added until the pH was raised to 2.2. The resulting precipitate was allowed to settle and the precipitated iron was separated from the solution by filtration. This produced the following results:

25	Ref. No.	611	628	729	740	750	757
	% Iron Removed	100	99.7	99.9	99.8	99.9	100.0

Example 4

## HEAVY METAL REMOVAL

100 ml of iron-free leachate is electrolyzed at 3.5 volts and 3.4 amp at 90°C for 15 minutes. (Ref. 768).

## PERCENTAGE PRECIPITATED

Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
		58.5	11.0	99.9			0.0	99.5	0.0

## GRAMS PRECIPITATED

Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
		.0034	.0003	.0194			0	.1310	0

5

Example 5

## EVAPORATION AND DECOMPOSITION

A quantity of 950 ml of iron free and heavy metal free leachate was placed in a 1l beaker and evaporated down to a concentrated solution on a hot plate. The concentrated solution was 10 transferred into a 2l glass reactor with a stirrer and was heated with stirring to evaporate and decompose the solids. After 235 minutes NOx ceased evolving from the reaction. The solids were allowed to cool. This produced the following results:

## PERCENTAGE OF SOLIDS

15	Al	Ca	Cd	Cr	Cu
	.140	5.868	.017	.008	.057

Fe	Mg	Mn	Pb	Zn
.034	2.323	1.600	.369	60.085

Example 6

20

## WATER EXTRACTION OF DECOMPOSED RESIDUE

A quantity of 360g of distilled water was charged into a 600 ml beaker. The water was agitated and 180g of decomposition residue was added. After 60 minutes of extracting, the solution was filtered. This produced the following results:

## PERCENTAGE EXTRACTED FROM DECOMPOSITION RESIDUE

Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
23.1	90.5	3.5			2.4	0.1	0.0		0.0

5 The percentages are for the extraction of the materials present in the decomposition residue. They have no bearing for the magnitude of these materials in the residue, only for their percent removal.

Example 7

## AMMONIUM CARBONATE EXTRACTION OF WASHED RESIDUE

10 A quantity of 524g of 50% ammonium carbonate was charged into an agitated 100 ml beaker. A quantity of 131g of residue was added and allowed to mix for 120 minutes at room temperature during which time hydrogen peroxide was added. The solution was filtered and the residue washed with 1% ammonia. This produced the following results:

15

## PERCENTAGE EXTRACTED BY AMMONIUM CARBONATE

Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
10.2	11.5	86.2	nil	nil	6.3	0.9	0.3	nil	94.9

These figures are the percent removal of the materials present in washed residue.

20

Example 8

## AMMONIUM CARBONATE STRIPPING

25 A quantity of 450g of ammonium carbonate leachate was charged into a 500 ml round bottomed flask. The solution was heated to boiling to strip off the ammonia. As the solution level got low distilled water was added. This procedure was continued until only a faint odor of ammonia remained. The solution was then filtered and the solid was scraped from the bottom of the flask. This produced the following results:

## RESULTING PRODUCTS

Al	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Pb	Zn
.006	.183	0.01	.011	.001	.004	.037	.005	.001	68.552

Example 9

5

## DISSOLUTION OF AMMONIUM CARBONATE LEACH RESIDUE

A quantity of 400g of 50% HNO<sub>3</sub> was charged into a 600 ml beaker. A quantity of 100g of ammonium carbonate leach residue was added and the mixture was agitated for 30 minutes. The solution was filtered through glass fiber filter paper. This produced the following results:

10

## PERCENTAGE IN RESIDUE

Al	Ca	Cd	Cr	Cu
.427	.381	.005	.060	.007

Fe	Mg	Mn	Pb	Zn
.194	2.469	57.404	.016	6.931

15 The filtrate contains 14.2 g/l of Mg and 7.9 g/l of Zn.

Example 10

## PRODUCTION OF ZINC SULFATE SOLUTION FROM ZINC CARBONATE

A quantity of 300 ml of distilled water was added into an agitated 11 beaker. A quantity of 70g of ammonium carbonate heat strip residue 20 was added along with 69g of 97% H<sub>2</sub>SO<sub>4</sub>. The solution was diluted to 900g with distilled water and the pH was adjusted to 2.0 with zinc carbonate. The mixture was diluted to 100g to make a 20% ZnSO<sub>4</sub>•7H<sub>2</sub>O solution. This produced the following results:

## GRAMS PER LITER IN SOLUTION

Al	Ca	Cd	Cr	Cu
0.35	.086	.014	.011	.002

Fe	Mg	Mn	Pb	Zn
.002	.113	.005	.003	51.927

SUMMARY OF THE ACHIEVEMENT  
OF THE OBJECTS OF THE INVENTION

From the foregoing, it is readily apparent that we have invented an improved method and apparatus for treatment of EAF dust and recovery of marketable products which is faster and more economical than heretofore has been possible. This process provides a method of removal of copper, cadmium and lead dioxide as well as separation of marketable calcium nitrate. Marketable zinc products, magnesium and manganese compounds are some of the valuable byproducts of the process as is high purity zinc sulfate. Yet, this process can be operated at individual dust producing locations, eliminating the need for transportation of hazardous waste and potential liabilities incurred in the shipment of hazardous and noxious wastes. This process, which can be contiguous with EAF and similar metallurgical dust collection, eliminates the storage of hazardous waste which helps eliminating existing and future environmental liability. Valuable calcium nitrates are separated from metallurgical furnace dusts using this process.

While other processes exist which recover zinc, the present invention obtains the twenty to sixty percent zinc that current processes cannot obtain. By removing sufficient non-ferrous metals, such as zinc and lead, allows the remaining iron residue to be recycled to the furnace without upsetting the required metallurgical balance of the bath and its coexisting vapors in the furnace. Valuable zinc products (e.g. high purity zinc sulfate and zinc chloride, zinc nitrate and other valuable zinc compounds) are obtained from the metallurgical furnace dusts as are marketable magnesium and manganese compounds.

It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the spirit and scope of this invention, which is therefore understood to be limited only by the scope of the appended claims.

CLAIMS

1. A method of treating metallurgical dust and recovering valuable chemical commodities, comprising the steps of:

a. leaching said dust with water to remove chlorides and other solubles, and filtering to remove a water filtrate and create a washed metallurgical dust;

5 b. reacting said washed metallurgical dust with a nitric acid solution therein dissolving the zinc, cadmium, copper, magnesium, calcium, manganese, lead and other metals into an acid filtrate;

c. precipitating iron from the acid filtrate of step (b) by raising the pH of the solution, where the pH range is 1.8 to 3.5;

10 d. removing cadmium, copper and lead through chemical or electrolytic processing;

e. evaporating and decomposing the acid filtrate to obtain a solid residue of metal oxides and calcium nitrate;

f. leaching the solid residue with water and separating and recovering the calcium nitrate in a marketable form;

15 g. separating the zinc from the magnesium and manganese by leaching the residue with ammonium carbonate solution to form a cake and an ammonium filtrate; and

h. stripping the ammonium filtrate of step (g) of ammonium carbonate to yield zinc precipitated as a zinc oxycarbonate.

20 2. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein said nitric acid is a solution of 10% to 100% nitric acid.

3. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 2, wherein nitric fumes exuded during the reacting of nitric acid solution with metallurgical dust are recycled into nitric acid by a nitric recycle process.

5

4. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein said reacting of metallurgical dust with said nitric acid solution takes place at elevated temperatures.

10

5. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein reacting of metallurgical dust with said nitric acid continues for a period of one quarter (1/4) to four (4) hours.

15

6. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein precipitating iron from the acid filtrate is accomplished by raising pH in said system with a basic pH adjusting agent and heating said acid filtrate to about 80° to 130° centigrade (176° to 266° F) wherein said basic pH adjusting agent is selected from the group consisting of zinc carbonate ( $ZnCO_3$ ),  $Zn(OH)_2$ , zinc oxide ( $ZnO$ ), zinc hydroxide ( $Zn(OH)_2$ ), and other oxides.

20

7. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein the step of precipitating iron from the acid filtrate by raising the pH of the solution further comprises heating said acid filtrate for one-half ( $\frac{1}{2}$ ) to three (3) hours.

25

8. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein precipitating iron from the acid filtrate further comprises heating said acid filtrate in an autoclave to a temperature above 150° C (302° F).

5 9. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein removing cadmium, copper and lead is performed by an electrolytic cell, where elemental copper and elemental cadmium are collected at a cathode, and lead is collected at an anode.

10 10. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein removing cadmium, copper and lead is performed by a reaction between the acid filtrate and a sulfide ion source wherein said sulfide ion source is selected from the group consisting of H<sub>2</sub>S, NaSH and other sources of sulfide ion.

15 11. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 9, wherein copper and lead are first removed by electrolysis and cadmium recovered separately by precipitating cadmium with a sulfide.

20 12. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, further comprising an initial step of leaching metallurgical dust with water, creating and separating a water filtrate and washed metallurgical dust, the water filtrate is sent to a water treatment system, leaving a residue of washed metallurgical dust for reaction with the nitric acid solution.

13. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein said leaching of solid residue with water continues until a majority of water soluble chloride has been extracted from the residue.

5

14. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, wherein stripping the ammonium filtrate of ammonium compounds takes place at 70° to 110° centigrade (158° to 230° F).

10

15. The method of treating metallurgical dust and recovering valuable chemical commodities according to claim 1, further comprising the step of:

i. dividing the zinc oxycarbonate obtained in the stripping of step (h) into a first stream and a second stream;

j. utilizing said first stream to adjust pH of the acid filtrate to precipitate iron;

k. reacting said second stream with acid to produce a zinc product, wherein said acid is selected from a group consisting of hydrochloric acid, nitric acid, organic acids and sulfuric acid; and

l. separating a residue containing magnesium and manganese by treating said residue with acid, said acid selected from the group consisting of hydrochloric acid, nitric acid, and sulfuric acid.

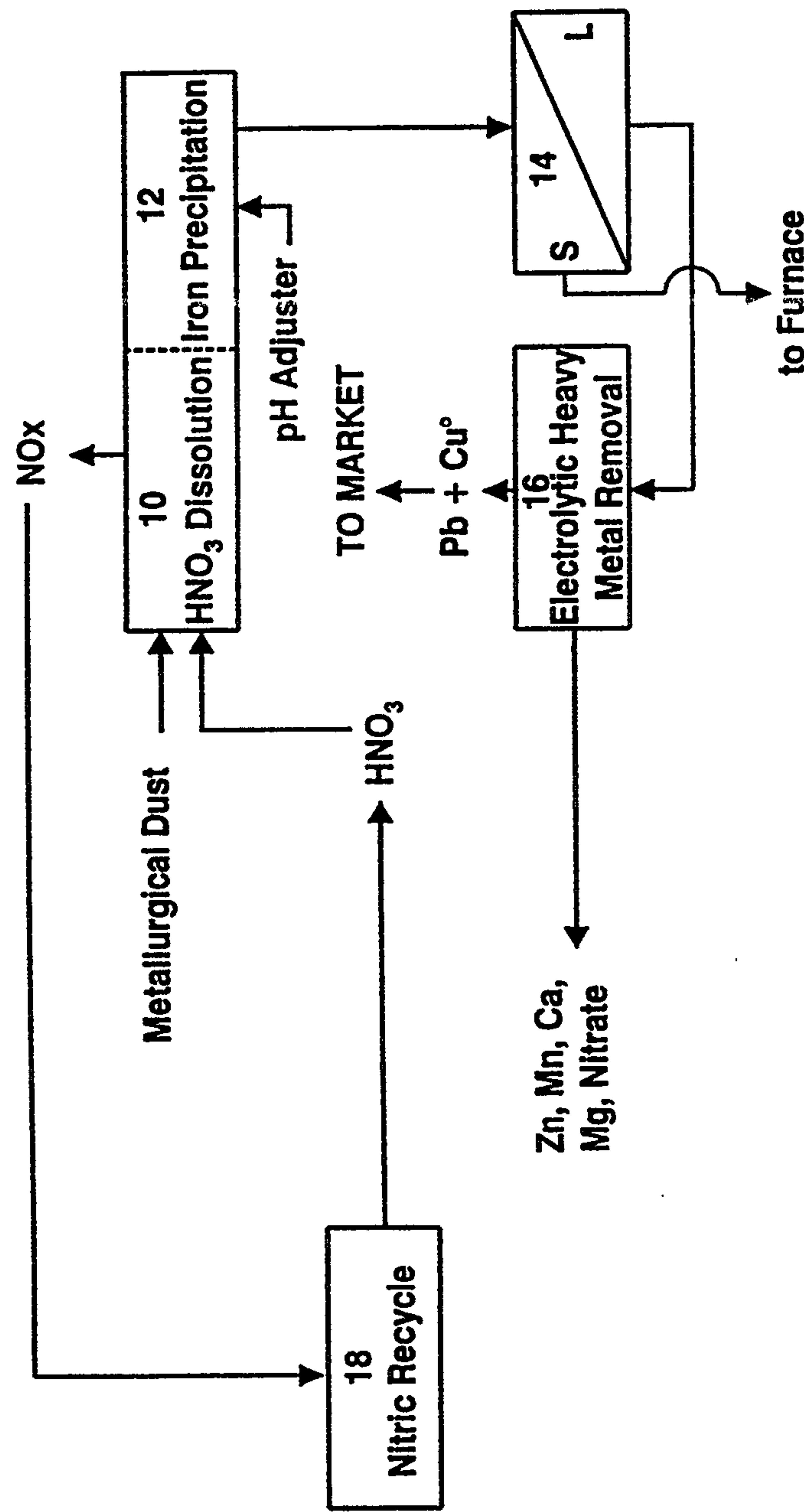
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16. A system for treating metallurgical dust and recovering valuable chemical commodities, comprising:

- a. a source of metallurgical dust;
- b. a source of water;
- 5 c. a nitric acid recycle system;
- d. a vessel in communication with said source of metallurgical dust and said source of water providing a means for leaching chloride from said dust with water to create a washed metallurgical dust;
- e. a means for removal of resulting liquid to a dirty water system;
- 10 f. a means for reacting said washed metallurgical dust in a nitric acid solution, in communication with said nitric acid recycle system, resulting in an acid filtrate, which are nitric fumes exuded during this step, where said nitric fumes are recycled into nitric acid by said nitric acid recycle system;
- 15 g. a means for removing iron from the acid filtrate by raising pH in said system with basic zinc oxycarbonate, where said iron in the form of iron oxide precipitate can be sent to the furnace as iron ore, zinc reagent goes with the zinc already in the filtrate to be recovered later;
- h. a means for removing cadmium, copper and lead in an electrolytic cell, the acid filtrate entering the next step is free of lead, cadmium and copper;
- 20 i. a means for evaporating and decomposing the acid filtrate to obtain metal oxides and anhydrous calcium nitrate, where the nitric gases given off during the evaporation and decomposition are recycled to nitric acid by the nitric acid recycle system;
- j. a means for leaching the solid residue with water separates calcium nitrate in a marketable form;

- k. a means for removing the zinc from the magnesium and manganese by leaching the residue with ammonium carbonate solution, where said solution produces an ammonium filtrate;
- 5 l. a means for stripping the ammonium filtrate of ammonium carbonate to yield zinc precipitated as a zinc oxycarbonate;
- m. a means for dividing the zinc oxycarbonate obtained in the stripping of step l into a first stream and a second stream, said first stream serves as a pH adjuster to precipitate iron, said second stream prepares highly pure zinc products for sale, by reacting the zinc complex with acid to produce a zinc product; and
- 10 n. a means for separating a residue containing magnesium and manganese by dissolving magnesium in either sulfuric or nitric acid, whereby liquid filtrate contains marketable magnesium nitrate or sulfate.

1/4



# Fig. 1

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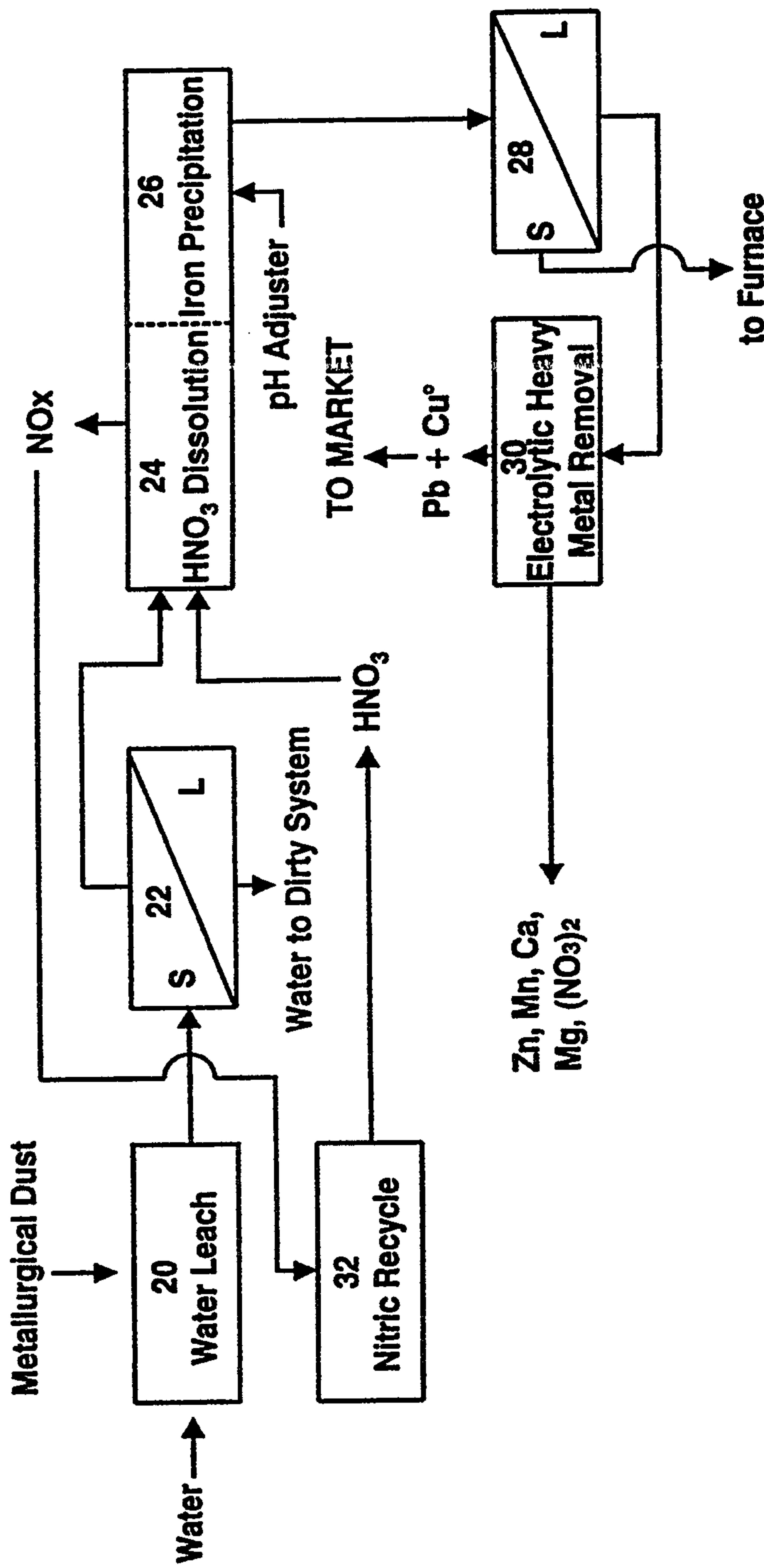


Fig. 2

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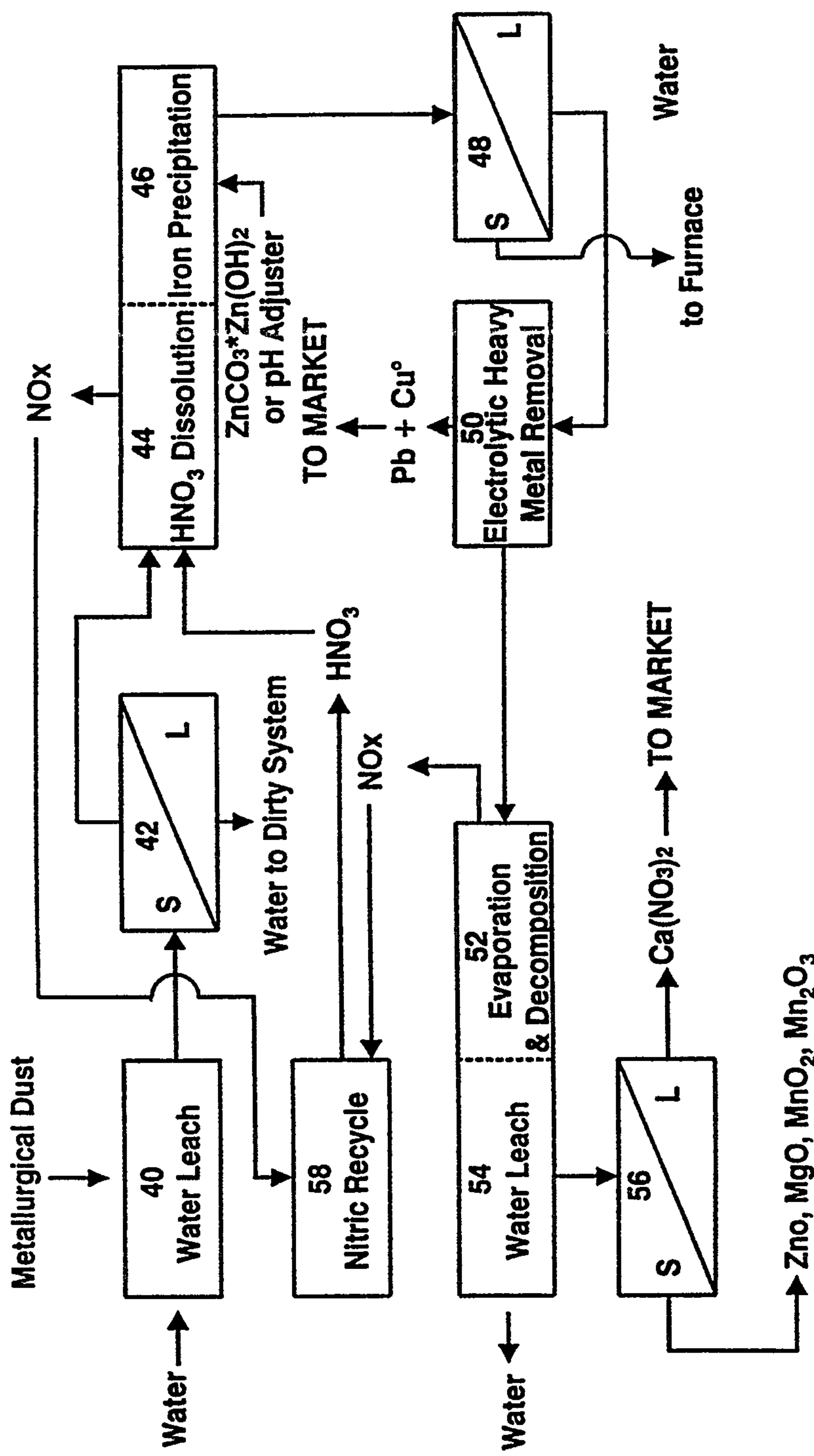


Fig.3

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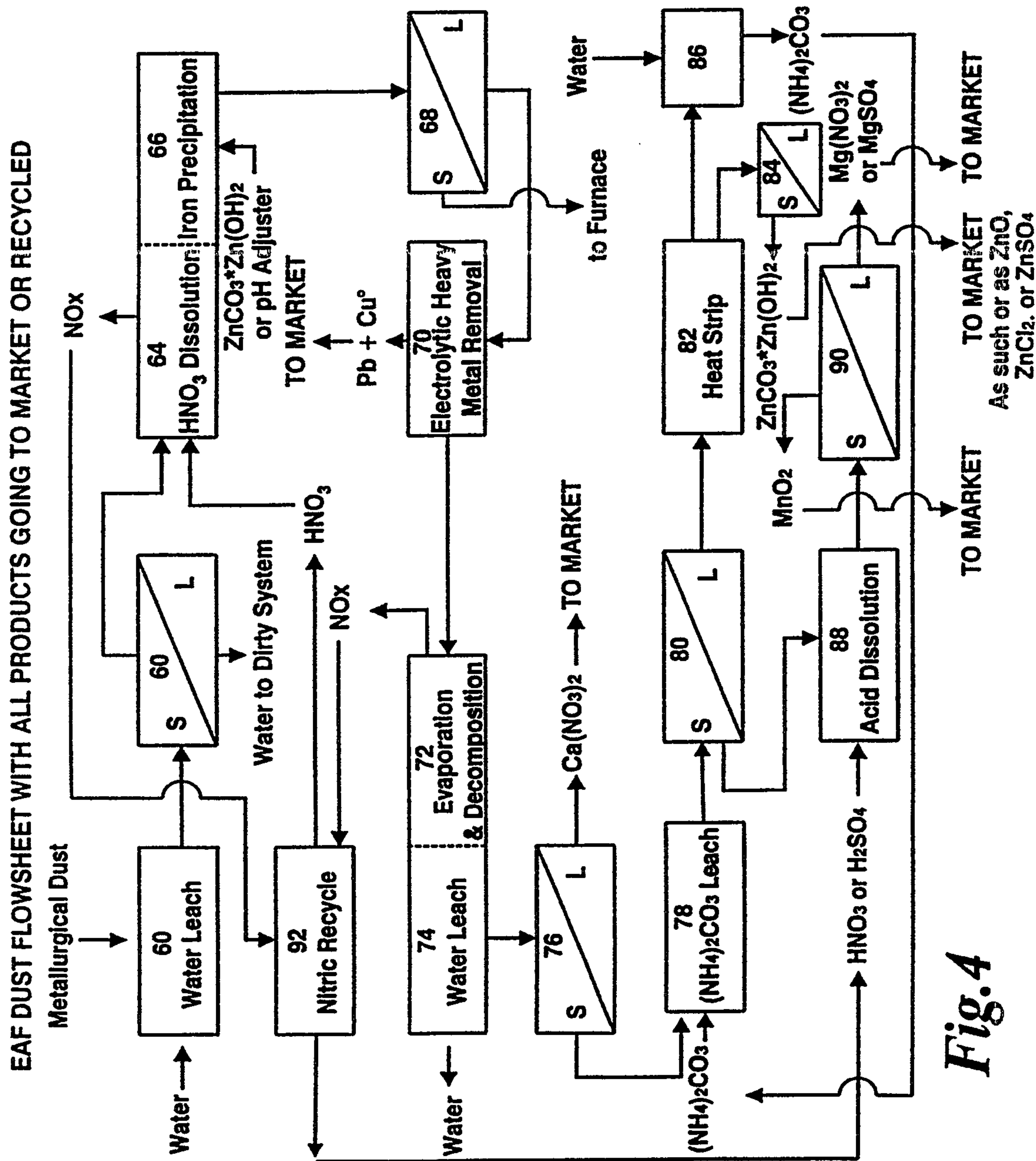


Fig. 4