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[54] **PROCESS FOR THE CONCURRENT RECOVERY OF ACID AND METAL VALUES FROM SPENT PICKLE ACID CONTAINING THE SAME**

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[57] **ABSTRACT**

A process for the concurrent recovery of acid and metal values from spent pickle acid containing the same which comprises:

a. adding a quantity of sulfuric acid to the spent pickle acid other than sulfuric acid at least sufficient to convert the soluble salts in the pickle acid to soluble metal sulfates and at the same time, regenerate the pickle acid;

b. recovering the pure pickle acid by distillation;

c. oxidizing the soluble metal sulfates if iron sulfate is present to insoluble metal hydroxides;

d. neutralizing any excess sulfuric acid which may be present with a base to form an insoluble metal sulfate;

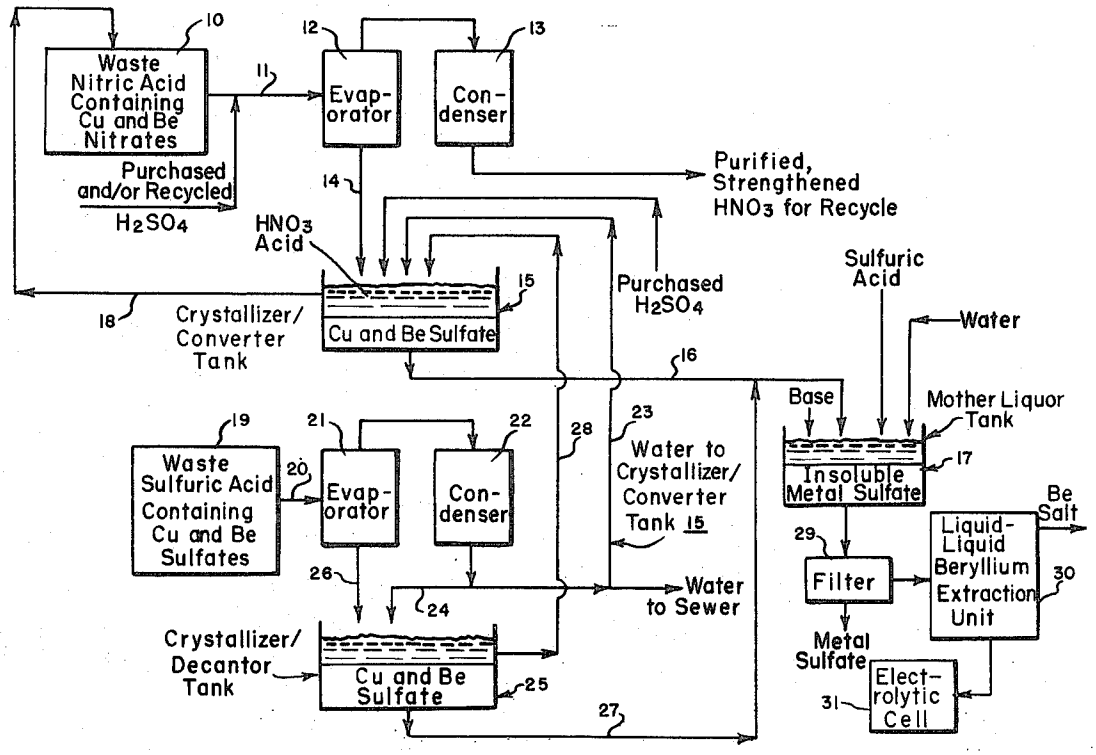
e. adding a quantity of sulfuric acid sufficient to convert the insoluble metal hydroxides other than ferric hydroxide which may be present to soluble sulfate salts;

f. removing the insoluble ferric hydroxide and/or insoluble metal sulfate, is present, by filtration to result in a filtrate containing iron-free soluble metal sulfates;

g. adjusting the pH and the concentration of the filtrate to that suitable for an electroplating solution; and

h. recovering the metals from the electroplating solution by electrolysis.

13 Claims, 2 Drawing Figures



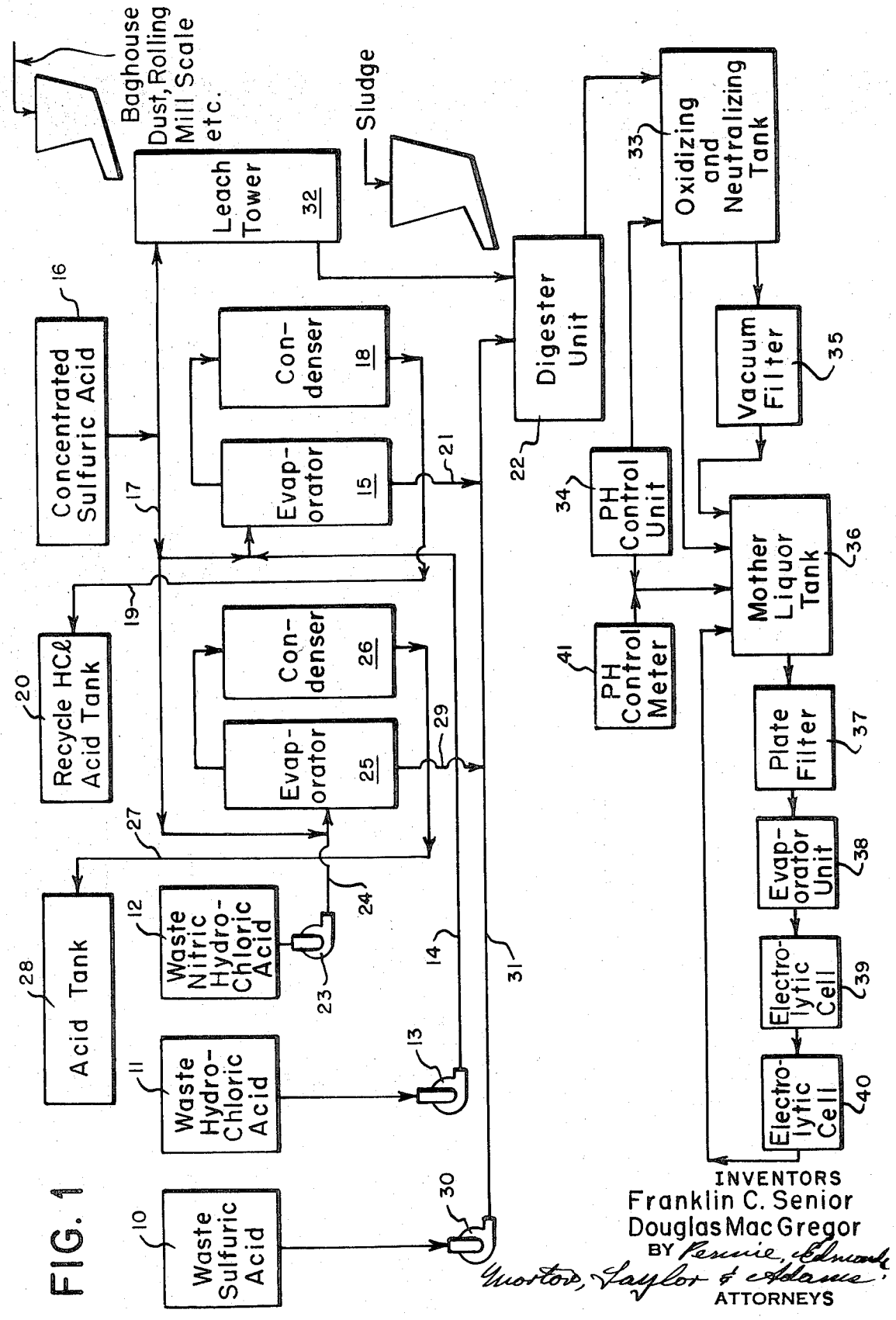


FIG. 1

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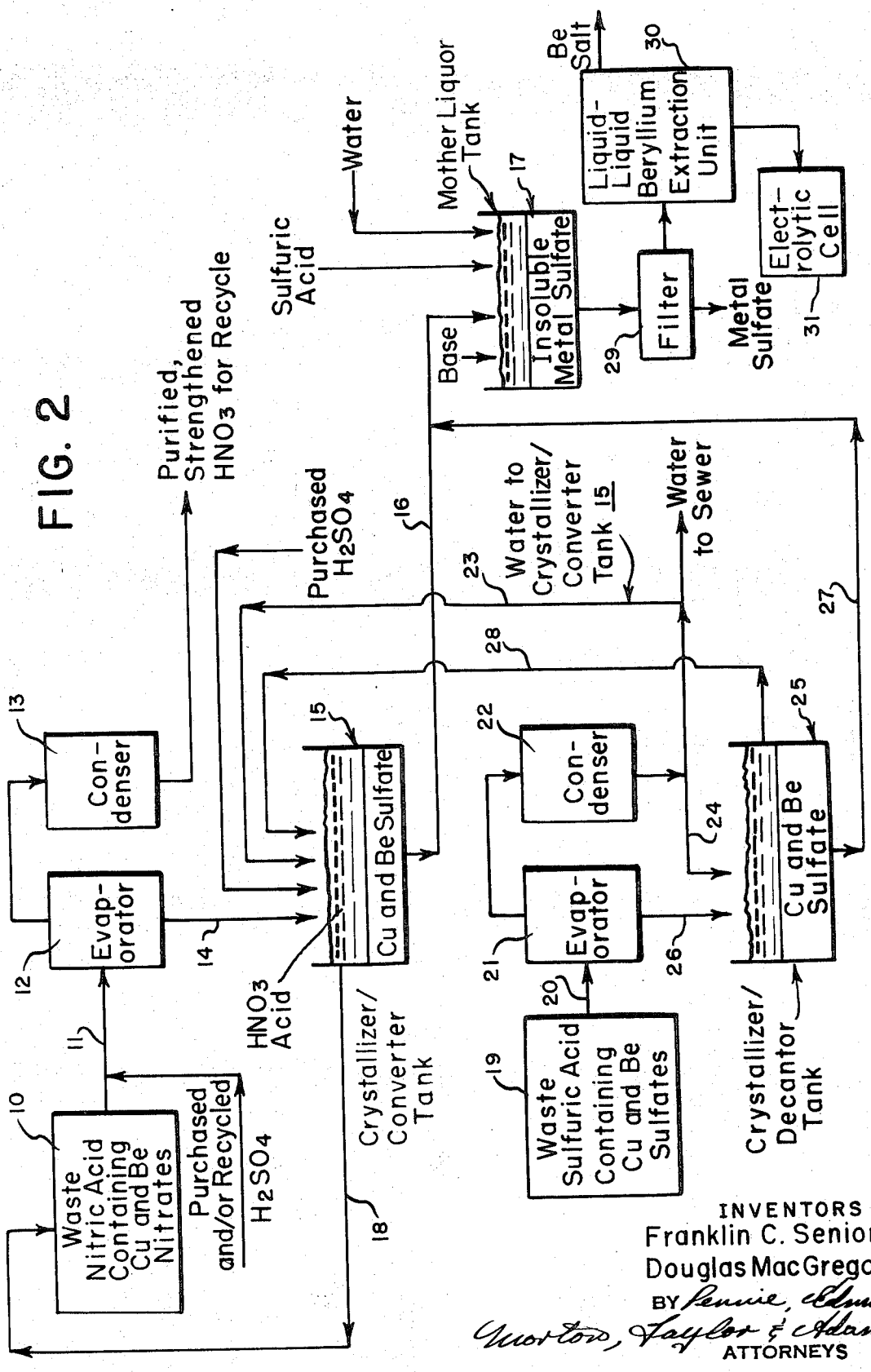
FIG. 2



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PROCESS FOR THE CONCURRENT RECOVERY OF ACID AND METAL VALUES FROM SPENT PICKLE ACID CONTAINING THE SAME

BACKGROUND OF THE INVENTION

The making, shaping and finishing of stainless, high alloy and super alloy steel, copper, beryllium and other metals normally involves a pickling step in which the metals are immersed in strong acid baths to remove oxidized surface scale in order to place the metal in suitable condition for further processing and forming. In addition to the employment of various acids to clean and remove oxide and mill scale in stainless steel and other metals production, most electroplating and galvanizing operations are required to discard many thousands of tons of acid a year which contain valuable metal values such as nickel, chromium, silver, beryllium and copper. The acids most commonly used for these purposes are among the most corrosive and poisonous known, namely, sulfuric, nitric, nitric-hydrofluoric and hydrochloric. The steel and metal plant acid pickle solutions may be used until their acid content is decreased by the formation of salts of iron and other metals through the removal of mill scale and oxide. At this point, they must be discarded and fresh pickling acids used because of the acids' reduced effectiveness in removing mill scale and oxide from stainless steel and other alloy steels and metals. It has been found that such waste acid streams contain salts having approximately 3–10 percent iron, 0.4–1.2 percent nickel, 3.5–5 percent chromium, 0.04–0.06 percent cobalt and 0.1–0.2 percent zinc, 0.05–15.0 percent copper, 0.01–0.04 percent beryllium and other metals.

Depending on the pickle acid used, the oxides or scale enters solution in the acids as sulfates, chlorides, nitrates or fluorides. The iron oxide scale is at first an insoluble material. It is converted by the acid to a substantially soluble salt. In the case of iron, the ferric salt which is derived from ferric oxide is reduced to the ferrous state which is substantially soluble in the pickle acid. The extent of the use of pickling acids in steel manufacture or production may be appreciated by the fact that from 50 to 400 pounds of strong acid solutions are used for each ton of finished steel produced in this country. The typical ranges of the percent acid in the initial solutions are 20–50 percent for nitric acid streams, 15–25 percent nitric plus 5 to 15 percent hydrofluoric in nitric-hydrofluoric streams and 30–50 percent for hydrochloric streams, parts of which are converted to salts and sludges. The neutralization of waste acid streams of nitric, hydrochloric, hydrofluoric and nitric-hydrofluoric acids results in the production of large quantities of highly soluble salts. Discarding these salts in the earth, streams, rivers, etc. has resulted in a serious level of pollution and ecological disruption. In addition to the effect on the ecology of these highly corrosive obnoxious acids and the salts of these acids as they are dumped into the earth and into streams making them toxic to all life, there is a great economic loss of 4–5 million dollars which is required to replace up to 200,000 tons of various acid solutions which are annually consumed in pickling and electroplating operations. The spent waste acid streams may also be neutralized by the addition of a base such as calcium or sodium hydroxide forming large quantities of obnoxious slude. In addition, it has been estimated that in the production of a million tons of stainless steel there is a loss

of 3 million pounds of nickel and cobalt in the waste acid streams. There is also a loss of some 8,000 tons of iron and several million pounds of zinc, copper, beryllium, tungsten and chromium. The total annual economic loss for the cost of new acids and the loss of metal values in the acids in the United States alone is conservatively 20 million dollars a year.

SUMMARY OF THE INVENTION

We have now discovered a method for treating large volumes of spent acid streams other than sulfuric acid streams by the controlled addition of sulfuric acid to convert the metallic salts to soluble sulfates and the evaporation and condensation of the acid to recover the acid in a pure state and in a concentration which may be higher than original and suitable for recycling in the acid pickling operations or for other uses. The method also provides for the concurrent recovery of metallic values from the thus treated waste acid streams and also from wet sludge and dry solid metal bearing wastes such as baghouse dust rolling mill scale and grinding dusts through the digestion of the sludge and dust with sulfuric acid to convert the metallic hydroxides and oxides to soluble sulfates, the oxidation and neutralization of the resulting solution to remove iron, chromium and calcium compounds by filtration, controlling the dilution and the pH as required by the addition of suitable acids and bases to redissolve and recover nickel, cobalt and copper valves and the electrolytic deposition of the metal values from the clear filtrate and the recycling, if desired, of the demetallized sulfuric acid solution.

In addition to the recovery of acid and metal values from the waste acid streams, the process of this invention eliminates the problems associated with the disposal of highly soluble, toxic salts since the salts herein are ecologically harmless, substantially insoluble sulfate salts.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 and 2 are schematic flow sheets each illustrating an embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, storage tanks 10, 11 and 12 contain waste acids that are contaminated with soluble metallic salts which have been obtained from steel plants or other metal pickling processes. Storage tank 11 holds a spent hydrochloric acid solution containing ferrous nickel chloride and other metal salts. The hydrochloric acid solution stream is delivered by a one-half horsepower pump 13 through line 14 at a rate of several gallons per minute to evaporator 15. Concentrated sulfuric acid is delivered from tank 16 through line 17 to evaporator 15 to be mixed with the waste hydrochloric acid stream to convert the soluble ferrous chloride and other salts to soluble ferrous sulfates and ferric chloride to ferric sulfate. The concentrated sulfuric acid and metal sulfates contained in the still bottoms are kept well under the fuming temperature of 600°F in order to capture and retain approximately 15 to 30 percent of the water in the incoming hydrochloric acid stream. In this manner, the hydrochloric acid which is recovered from condenser 18 is advantageously concentrated so that the acid which is delivered through line 19 for recycling in pickling operations is a 20–25

percent acid solution or substantially stronger than the hydrochloric acid normally used in fresh acid pickle baths in a typical steel mill.

Metal sulfates remain in solution in the still bottoms. Since hydrochloric acid evaporates at atmospheric pressure at 230°F, the 25 percent hydrochloric acid solution that is returned through line **19** to acid tank **20** for reuse in new pickling operations is substantially free of iron or other metallic compound contaminants.

The solution of sulfuric and metal sulfates contained in evaporator **15** is then pumped through line **21** to line **31** to be mixed with the spent sulfuric acid stream and then to digester unit **22.**

Waste nitric-hydrofluoric acid solution is similarly pumped at a rate of several gallons per minute from storage tank **12** by acid pump **23** through line **24** to evaporator **25.** As was the case with the hydrochloric acid stream, concentrated sulfuric acid is delivered from acid tank **16** and is mixed with the nitric-hydrofluoric acid solution stream to convert metal nitrates and fluorides to soluble sulfates. Since nitric acid vaporizes at about 225°F and hydrofluoric acid vaporizes at about 183°F, both acids boil off at evaporator **25** while leaving metal sulfates such as iron, nickel, copper and beryllium sulfates, which are stable up to 630°F, in solution. The acid vapors are condensed at condensor **26** and pumped along line **27** to acid tank **28.** In place of waste nitric-hydrofluoric acid, storage tank **28** may contain waste nitric acid without altering the process of the present invention.

The metallic salt solution in evaporator **25** is fed through line **29** and is mixed with the waste sulfuric acid solution which has been pumped from acid storage tank **10** by pump **30** at a rate of several gallons per minute through line **31** to digester **22.**

In addition to the hydrochloric, sulfuric and nitric-hydrofluoric acid streams, waste wet sludge comprising about **20** percent solid metal hydroxides may be introduced into digester unit **22** at a rate of 20 to 40 tons per day. The gelatinous sludge results from the neutralization of waste acid streams with suitable bases and is performed by some steel or metal plant operators. The gelatinous sludge contains ferric, nickel, copper and cobalt hydroxide and other salts of manganese, zinc and chromium.

The sludge is extremely difficult or even impossible to filter and dewater to less than 20 percent solids contents and presents considerable disposal problems for steel plants due to its vast accumulation. It is usually discarded in a lagoon which results in the loss of significant amount of nickel, cobalt, iron, manganese, zinc and chromium. However, the solid hydroxides are readily solubilized and converted to sulfates when they are introduced into the digester containing the confluence of two suluric acid and metal sulfate streams from the stills and the sulfuric acid and metal sulfate stream from tank **10.** Concentrated sulfuric acid from holding tank **16** may also be pumped into the digester unit **22** to replace the sulfuric acid consumed by the formation of iron, chromium, calcium and other metallic sulfates. The conversion to sulfates takes place at a pH of about 0.2 to 1.5. It has been found in a typical operation that about 27 percent of the iron in digester **22** is in the ferrous state and about 73 percent of the iron is present as ferric or insoluble compounds.

Dry solid wastes consisting of mill scale, mill sludge, grinding dust or baghouse dust can also be treated and disposed of by the process of the present invention. Such dry solid wastes are more refractory than sludge and require several hours of contact time with strong sulfuric acid in leach tower **32** before being added to the digester unit. The reaction is exothermic with a relatively large gas evolution, principally carbon dioxide and steam, as the conversion to sulfates takes place. The recycle leach tower **32** is provided with means to digest the several hundred pounds per hour of dust for dissolution in the sulfuric stream, and to baffle the violent foaming that occasionally occurs.

The digested sulfate stream is pumped from digester **22** to oxidizing and neutralizing tank **33** which is subjected to sparging air at a rate of several hundred cubic feet per minute and proper pressure to oxidize the ferrous ions in solution to the ferric or insoluble state. Other oxidizing agents such as hydrogen peroxide and nitric acid are also suitable for this purpose.

pH controller unit **34** feeds calcium hydroxide or other suitable base to control and adjust pH during oxidation to a value advantageously from about 3 to 7. Advantageously, the base is a very finely ground powder of about 325 mesh and is carefully added as a slurry to prevent local deposition of iron-nickel hydroxide. Advantageously, oxidation is permitted to continue after the pH has reaced 4.0 in order to obtain a complete oxidation of the ferrous ions for subsequent removal. At this point, concentrated sulfuric acid is carefully added to the solution to reduce the pH to about 3.0 to 3.5 to redissolve the nickel and copper compounds. The solution is then filtered in vacuum filter **35** at a suitable rate. The insoluble ferric hydroxide and calcium sulfate is removed with the filter cake and the clear filtrate containing the nickel and copper values is pumped to mother liquor tank **36.** The mother liquor from tank **36** is extracted at a constant rate and delivered to plate filter **37** to remove the insoluble metal sulfates formed by the addition of a corresponding metal hydroxide from pH meter **40** to control the pH of the electroplating solution.

The clear filtrate then passes to evaporator unit **38** where water obtained from washing, sludge and incoming acids is removed and the pure condensate is passed to a sewer or recycled as wash water.

For example, a stream of about 3 gallons per minute carrying 88 pounds per hour of sulfates of nickel, cobalt, copper, etc., including **44** pounds per hour in constant recycle, passing to electrolytic cell **39** for the removal of copper results in a pure copper plate out substantially free of nickel. The clear filtrate stream then passes to electrolytic cell **40** where nickel and cobalt are substantially removed from the plating circuit as cathode plates.

The depleted electrolyte has a lower pH due to the release of acid at the cathode and is returned to the mother liquor tank **36.**

pH control meter **41** is provided to feed milk of lime or other base to control the pH of the plating solution in mother liquor tank **36** at a suitable pH.

Referring to FIG. **2,** waste nitric acid in storage tank **10** contains by weight about 10 percent copper as cupric nitrate, about 0.20 beryllium as beryllium nitrate, about 8 percent free nitric acid and about 30 percent combined metal salts. The waste nitric acid is fed through line **11** at a suitable rate to evaporator unit **12** where a sufficient amount of heat is applied to vaporize the free nitric acid and about 25 percent of the nitrate

anion as nitric acid. The nitric acid vapors are condensed in 13 and are discharged through recycle line 14 at about 27–30 percent. Concentrated sulfuric acid made up with recycled sulfuric acid and/or purchased acid is advantageously added to evaporator 12 through line 11. The hot still bottoms in distillation unit 12 are discharged through line 14 to crystallizer/converter tank 15. Sufficient amounts of water, concentrated sulfuric acid and sulfuric acid from evaporator 21 in the required amounts are added to the hot still bottoms and the solution is cooled. The copper and beryllium sulfates thus formed settle to the bottom of tank 15 and are delivered through line 16 to mother liquor tank 17. The supernatant, now containing regenerated nitric acid is decanted from tank 15 and delivered thorugh line 18 to storage tank 10.

Tank 19 contains waste sulfuric acid containing about 3 percent copper and a small amount of beryllium as the sulfates thereof, as well as about 20 percent free sulfuric acid. The waste acid is delivered through line 20 to evaporator 21 where most of the water is evaporated and condensed in 22. The water may be passed through line 23 to tank 15 or withdrawn through line 24 to cyrstallizer/decantor tank 25. The hot still bottoms in evaporator 21 containing sulfuric acid and metal sulfates is delivered to crystallizer/decantor tank 25 through line 26. Upon cooling of the still bottoms, the beryllium and copper sulfates crystallize and are delivered through line 27 to mother liquor tank 17. The supernate containing concentrated sulfuric acid is delivered to crystallizer/converter tank 15 through line 28.

Mother liquor tank 17 now contains copper and beryllium sulfates. Suitable amounts of water and sulfuric acid are added to the sulfates to produce the desired plating solution at a pH of from about 1.0–3.0. The solution in tank 17 is extracted with a suitable base, for example, hydrated lime and the calcium sulfate is filtered off at 29. The clear filtrate then passes through a conventional liquid — liquid beryllium beryllium extraction unit 30 where a suitable beryllium salt for example, beryllium chloride is produced. The plating solution, now containing only copper sulfate, is delivered to electrolytic cell 31 where the copper is removed as a cathode plate or as a powder as desired.

EXAMPLE 1

1,610 pounds per hour of waste hydrochloric acid pickle liquor having a specific gravity of 1.19 and containing about 8 percent metallic chlorides was mixed with 220 pounds per hour of concentrated sulfuric acid in an evaporator/converter which was lined with teflon or other similar material. 1,460 pounds per hour of 25 percent by weight of hydrochloric acid was distilled from this mixture and recycled for reuse in pickling operations. At the same time, 1,470 pounds per hour of waste nitric-hydrofluoric acid pickle liquor and 200 pounds of concentrated sulfuric acid were mixed in a teflon lined evaporator/converter and 1,240 pounds per hour of nitric-hydrofluoric acid having a specific gravity of 1.10 was distilled from this mixture and recycled for reuse in pickling operations. A third waste pickle liquor stream of waste sulfuric acid was added to the residue of the distillation of both the hydrochloric and nitric hydrofluoric waste acid streams at the rate of 350 pounds per hour and was delivered to the digester tank. The hydrochloric waste acid stream was fed into the digester at the rate of 370 pounds per hour and the residue of the nitric-hydrofluoric distillation was fed into the digester at the rate of 430 pounds per hour for a total of 1,150 pounds per hour that was delivered to the 6,000 gallon digester.

In addition, 2,500 pounds per hour of waste gelatinous nickel-iron hydroxide sludge was added to the digester. 140 pounds per hour of dry dust, processed with 80 lbs sulfuric acid, was also added to the digester. Digestion and converstion to sulfates was accomplished at a pH of about 0.2 to 1.5. The digested and converted sulfuric stream was then transferred to a 3,000 gallon tank into which several hundred cubic feet per minute of air was introduced at 5 to 6 pounds per square inch for a period of three to six hours. A pH controller unit fed milk of lime into the 3,000 gallon oxidizing and neutralizing tank to adjust the pH during air oxidation from about 1.5 to about 7.0. 1,600 pounds of finely ground calcium oxide was used during the six hour oxidizing neutralizing cycle. 100 pounds of concentrated sulfuric acid was then introduced to lower the pH slowly to about 3.6 to redissolve the nickel and copper compounds. The solution in the oxidizing tank which contained approximately 262 pounds of nickel, cobalt and copper sulfate was filtered to remove ferric hydroxide and calcium sulfate and then the filtrate was transferred to a 10,000 gallon holding tank. A controlling pH meter fed calcium oxide into the 10,000 gallon holding tank to maintain pH at about less than 3 to 3.5. Precipitated calcium sulfate was removed by a pressure filter and removed to the land fill. The filtrate was then transferred to an evaporator where 3,300 pounds of water were removed. The pure water condensate was passed to the drain. The remaining sulfate filtrate was transferred at a rate of 3 gallons per minute at a small 2 cathode 1,500 ampere 2.5 volt cell where pure copper was plated out on the cathode substantially free of any nickel. The remaining sulfate solution was transferred at a rate of 3 gallons per minute to a 20 cathode electrolytic cell having 4 feet by 4 feet cathode sheets and a capacity of 20,000 amperes and 10 volts. After removal of the nickel the depleted electrolyte, having a decreased pH was transferred at a rate of 3 gallons per minute back to the 10,000 gallon holding tank.

EXAMPLE 2

A procedure similar to that set forth in Example 1 was followed except that the mother liquor in the crystallizer/decantor tank was adjusted to a pH of about 10.0 with lime and the nickel and copper hydroxides thus formed settled to the bottom of the tank and were filtered off. The filtrate and the supernate water were recycled. The nickel and copper hydroxides were delivered to the mother liquor tank for reconversion to soluble sulfates for plating. This procedure eliminated the need for evaporating the water from sludge washings and incoming acids.

EXAMPLE 3

11,350 pounds of nitric acid pickle waste containing 9 percent free nitric acid by weight, 1,110 pounds of copper as copper nitrate and about 18 pounds of beryllium as beryllium nitrate and some cobalt nitrate were delivered to a tank. The tank had previously contained 5,680 pounds of a 30 percent by weight nitric acid stream from the decantor tank. The mixture of 17,200 pounds were delivered to a small still where 12,200

pounds of a 27 percent pure nitric acid were evaporated and 3,700 pounds of still bottoms containing metal nitrates were delivered to the converter/decantor tank. 1,270 pounds of sulfuric acid and 440 pounds of reflux sulfuric acid from a companion still were added to this tank.

Simultaneously, 2,100 pounds of a waste sulfuric acid stream containing by weight, approximately 3.0 percent copper as copper sulfate, about 1 pound of beryllium as beryllium sulfate and about 20 percent free sulfuric acid were delivered to a still where 1,180 pounds of water were evaporated, condensed and refluxed to process.

The hot still bottoms, containing anhydrous copper sulfate and free sulfuric acid, were delivered to a small crystallizer/decantor tank where the copper sulfate settled upon cooling and the strong sulfuric acid supernate was decanted and delivered to the converter/decantor tank noted above.

About 4,700 pounds of a hydrated copper sulfate from these tanks were delivered to the 3,000 gallon mother liquor tank. 1,250 pounds of sulfuric acid and 2,500 gallons of water were added to this tank to produce the desired plating solution. pH of the plating solution was controlled by the addition of lime. The 2,000 pounds of insoluble calcium sulfate (gypsum) formed by lime addition was discarded.

The filtrate, containing beryllium and copper sulfates was delivered to a conventional liquid — beryllium extractor unit. 156 pounds of beryllium chloride were recovered for recycling to the mill. The beryllium-free plating liquid was delivered to the plating tanks and 1,170 pounds of copper plated out on the cathode for sale back to the mill or on the open market.

The stripped plating solution was recycled back to the mother liquor tank.

Analysis of the recycled nitric acid solution showed 27.0 percent by weight of nitric acid, 7 parts per million of copper, 1 part per million of beryllium and no trace of cobalt.

EXAMPLE 4

11,300 pounds of nitric acid pickle waste containing about the same quantities of components as in Example 3 were mixed with 2,000 pounds of concentrated sulfuric acid and delivered to the evaporator. The sulfuric acid was made up of recovered sulfuric acid from the mill and purchased acid.

The nitric acid recovered from the waste stream was 31 percent by weight and of high purity. The copper and beryllium sulfate still bottoms were treated in a manner similar to Example 3 and 1,100 pounds of pure copper were recovered as plate out on cathode starter sheets at 0.92 Kwhr/lb and 1.8 volts.

We claim:

1. A process for the concurrent recovery of acid and metal values from spent pickle acid containing the same which comprises:
   a. adding a quantity of sulfuric acid to a spent pickle acid stream other than a spent sulfuric acid stream to convert the soluble metal salts to soluble metal sulfates and at the same time, regenerate the pickle acid;
   b. recovering the pickle acid by distillation;
   c. oxidizing the soluble metal sulfates present in the distillation residue resulting from step (b) to convert the soluble metal sulfates to insoluble metal hydroxides;
   d. neutralizing excess sulfuric acid present in the medium of step (c) with lime to adjust the pH from about 3 to 7 and to form metal hydroxides and calcium sulfate;
   e. adding a quantity of sulfuric acid to the medium resulting from step (c) to lower the pH to about 3.0 to 3.5 to redissolve all of the insoluble metal hydroxides except iron hydroxide;
   f. removing the insoluble calcium sulfate and iron hydroxide by filtration to provide a filtrate containing iron-free soluble metal sulfates;
   g. adjusting the pH and the concentration of metal salts in the filtrate to that suitable for an electroplating solution; and
   h. recovering the metal values from the solution of step (g) by electroplating.

2. The process of claim 1 wherein the spent pickle acid is nitric acid, nitric-hydrofluoric acid or hydrochloric acid.

3. The process of claim 2 where in addition to iron, the spent pickle acid contains one or more metals in the form of a salt or salts of the waste pickle acid, said metal selected to be copper, beryllium, nickel, chromium, cobalt or zinc.

4. The process of claim 1 wherein excess sulfuric acid is added at step (a) and the distillation step (b) is carried out well under the fuming temperature of sulfuric acid.

5. The process of claim 1 wherein the oxidizing step is carried out with air, hydrogen peroxide or nitric acid as the oxidizing agent.

6. The process of claim 1 wherein the pH adjustment of step (g) is carried out with sulfuric acid or lime.

7. A process for the concurrent recovery of acid and metal values from spent pickle acid containing the same which comprises:
   a. adding a quantity of sulfuric acid to a spent pickle acid stream other than a spent sulfuric acid stream to convert the soluble metal salt or salts to soluble metal sulfates and at the same time, regenerate the pickle acid;
   b. recovering the pickle acid by distillation;
   c. adding to the distillation residue of (b) which comprises a solution of soluble metal sulfates; at least one member of the group consisting of an iron-containing mill scale, mill sludge, grinding dust and baghouse dust reacted with strong sulfuric acid, and insoluble metal hydroxide including iron hydroxide sludge;
   d. digesting the insoluble metal hydroxides with sulfuric acid to form soluble metal sulfates;
   e. oxidizing the soluble metal sulfates to insoluble metal hydroxides;
   f. neutralizing excess sulfuric acid present in the medium of step (e) with lime to adjust the pH from about 3 to 7 and to form metal hydroxides and calcium sulfate;
   g. adding a quantity of sulfuric acid to the medium resulting from step (f) to lower the pH to about 3.0 to 3.5 to redissolve all of the insoluble metal hydroxides except iron hydroxide;
   h. removing the insoluble calcium sulfate and iron hydroxide by filtration to provide a filtrate containing iron-free soluble metal sulfates.

i. adjusting the pH and the concentration of metal salts in the filtrate to that suitable for an electroplating solution; and

j. recovering the metal values from the solution of step (i) by electroplating.

8. The process of claim **7** wherein the spent pickle acid is nitric acid, nitric-hydrofluoric acid or hydrochloric acid.

9. The process of claim **8** wherein the spent pickle acid contains one or more metals in the form of a salt or salts of the waste pickle acid, said metal selected to be copper, beryllium, iron, nickel, chromium, cobalt or zinc, further provided, that when the metal is iron, at least one other of the aforementioned metals is also present.

10. The process of claim **7** wherein excess sulfuric acid is added at step (a) and the distillation step (b) is carried out well under the fuming temperature of sulfuric acid.

11. The process of claim **7** wherein the oxidizing step is carried out with air, hydrogen peroxide or nitric acid as the oxidizing agent.

12. The process of claim **7,** wherein the insoluble metal hydroxide added in step (e) is iron hydroxide or a mixture of iron hydroxide and at least one other hydroxide of nickel, cobalt, manganese, zinc or chromium.

13. The process of claim **7** wherein the pH adjustment of step (h) is carried out with sulfuric acid or lime.

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