Sept. 2, 1969 E. C. BRACE 3,464,904

METHOD FOR TREATING METALLIC SULFIDE COMPOUNDS

Filed Dec. 21, 1964 3 Sheets-Sheet 1

FIG. 1.

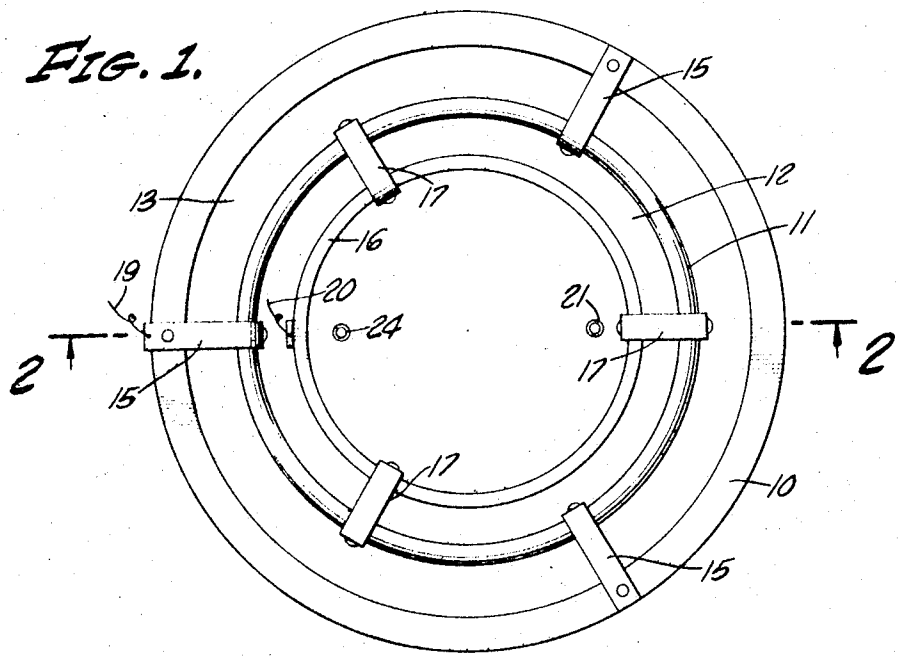
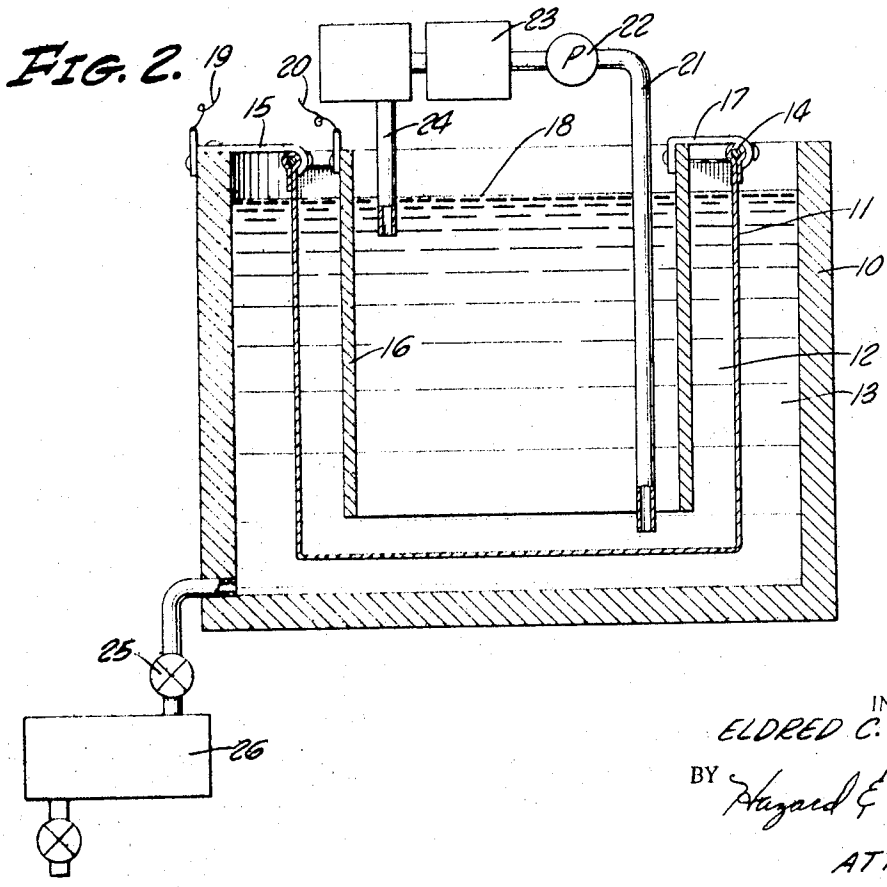


FIG. 2.



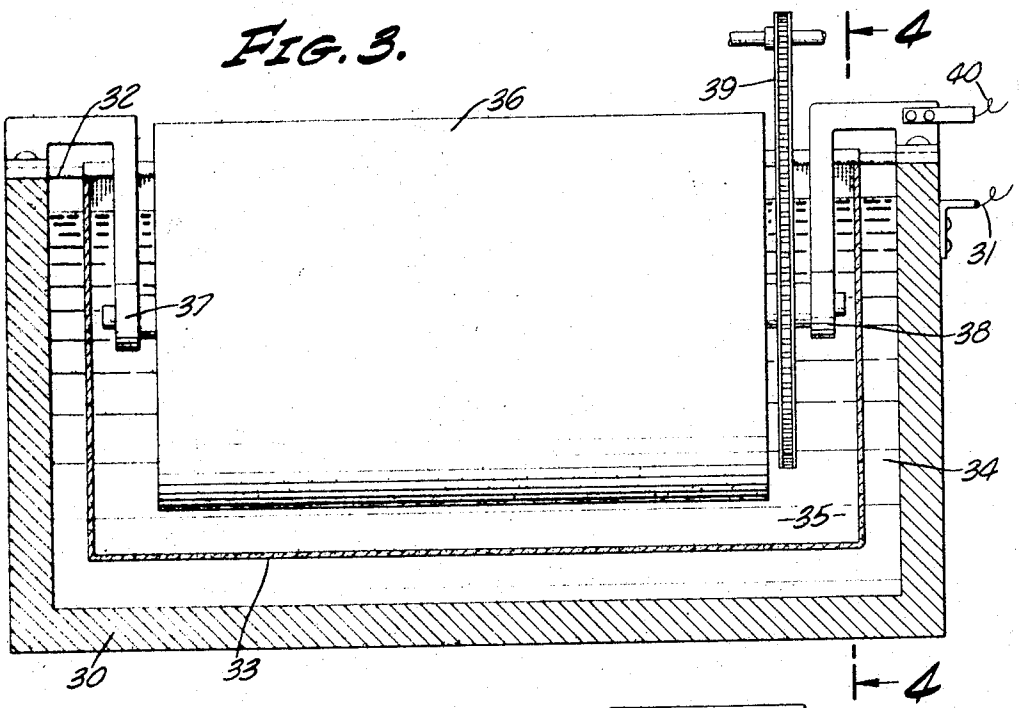
INVENTOR.
ELDRED C. BRACE
BY Hazard & Miller
ATTORNEYS

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Filed Dec. 21, 1964 3 Sheets-Sheet 2

FIG. 3.



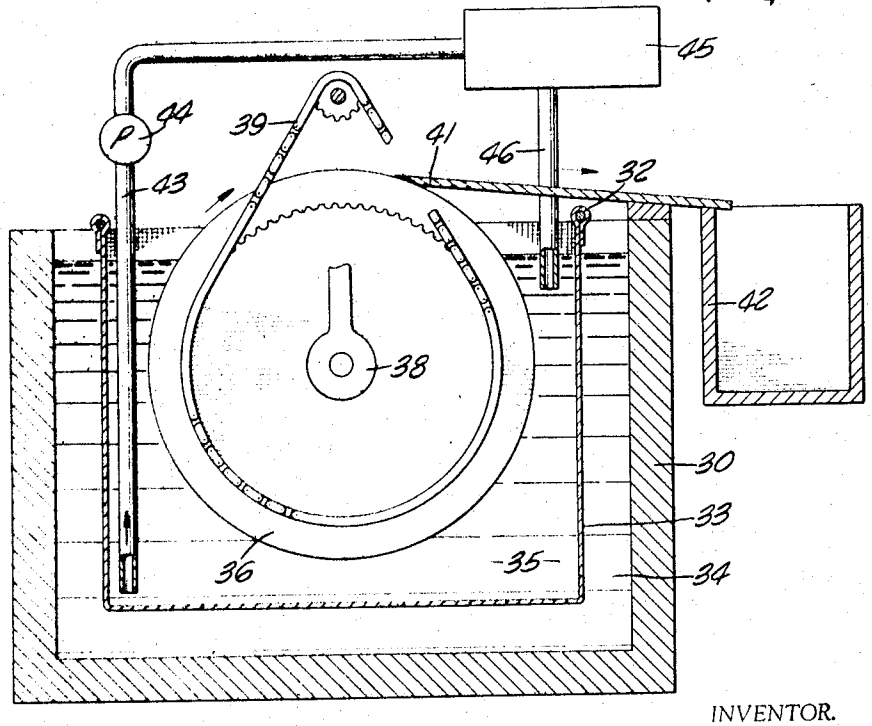


FIG. 4.

INVENTOR.
ELDRED C. BRACE
BY Hazard & Miller
ATTORNEYS

Sept. 2, 1969 E. C. BRACE 3,464,904

METHOD FOR TREATING METALLIC SULFIDE COMPOUNDS

Filed Dec. 21, 1964 3 Sheets-Sheet 3

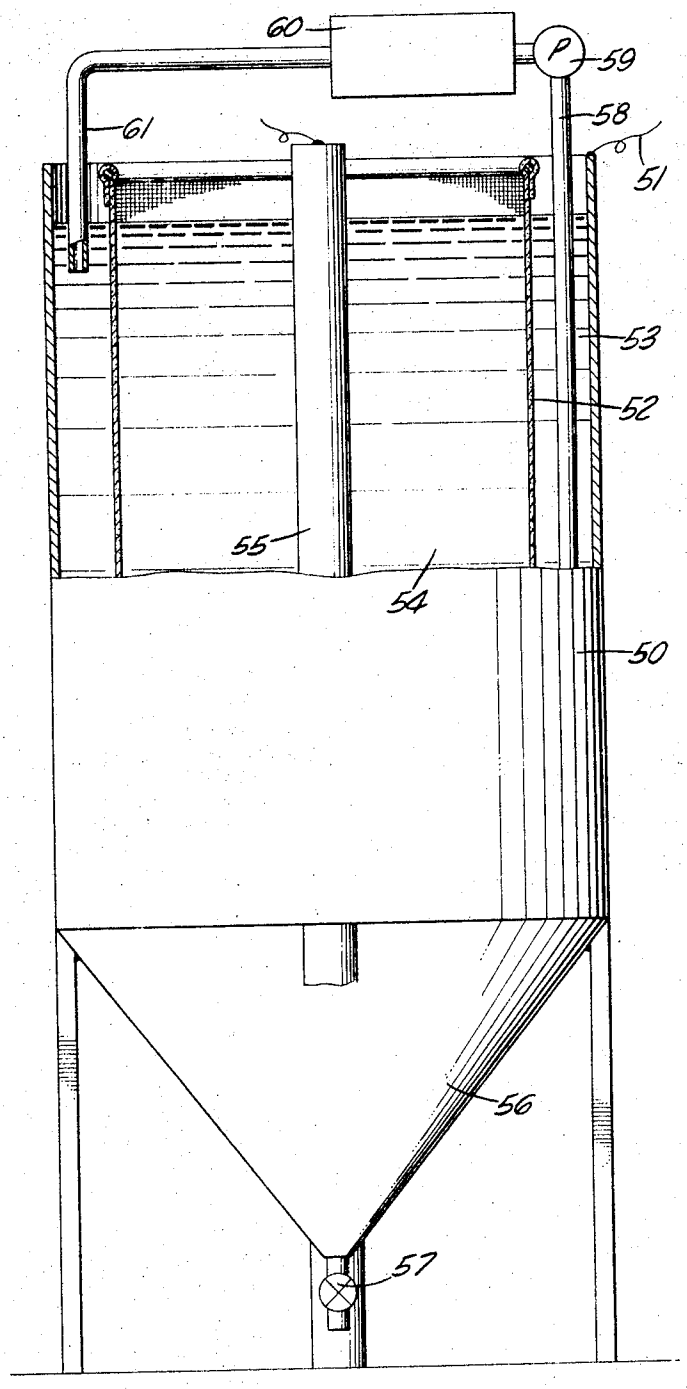


FIG. 5.

INVENTOR.
ELDRED C. BRACE
BY Hazard & Miller
ATTORNEYS

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METHOD FOR TREATING METALLIC SULFIDE COMPOUNDS

Eldred C. Brace, Tucson, Ariz., assignor to Banner Mining Company, Tucson, Ariz., a corporation of Nevada

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Int. Cl. C22d *1/22, 1/16;* C23b *3/10*
U.S. Cl. 204—105 1 Claim

ABSTRACT OF THE DISCLOSURE

A method of treating metallic sulfide compounds including copper and zinc sulfides to recover the metals therefrom which includes subjecting the compounds to electrolysis, utilizing a graphite anode which forms a tank or cell for the electrolyte, and a porous diaphragm between the anode and the cathode of a material selected from the group consisting of Dynel, polyvinyl chloride, polyethylene, polypropylene chloride and Teflon, removing the catholyte from the catholyte side of the diaphragm, reducing the ferric iron therein to ferrous iron and returning the catholyte to the catholyte side of the diaphragm.

This invention relates to a method and apparatus for treating metallic sulfide compounds for the purpose of recovering the metals therefrom, either in the form of metallic oxides or in other useable forms.

The invention has been primarily designed for recovering copper from concentrates containing copper sulfides and for recovering zinc from concentrates containing zinc sulfide compounds.

Copper is usually recovered from copper sulfide compounds as copper oxide. Zinc, however, may be recovered from zinc sulfides either as zinc sponge or in the form of a zinc salt, commercially useable as such.

One aspect of the invention concerns or is related to the material that is used as an anode in an electrolytic cell in which the metallic sulfide compounds are treated. Heretofore, it has been proposed that the walls of an electrolytic cell or tank used for this purpose be formed of such material as wood, concrete, iron, stainless steel, nickel, various metal alloys, lead, tungsten, tantalum, or the precious metals. The basic metals all corrode very rapidly in the presence of the electrolyte and must be frequently replaced so that their use is usually regarded as uneconomical. The precious metals and more noble metals may withstand corrosion by the electrolyte, but when used as anodes, anodic corrosion occurs to a limited extent. The use of precious metals and noble metals has generally been regarded as uneconomical, because of their initial costs, and due to anodic corrosion when used as anodes, their use has been regarded as prohibitive.

One aspect of the present invention, therefore, resides in the discovery and use of a relatively inexpensive material which may serve as the walls or the tank of the electrolytic cell and which even when used as an anode in the cell will remain relatively inert for an indefinite length of time not only to the corosive action of the electrolyte, but under the conditions that exist when used as an anode. Such a material is solid graphite, preferably formed of one piece with no joints or rough surfaces present.

This material can be used as the tank of the electrolytic cell itself and also as the anode. When so used, even though the electrolyte is a water solution of hydrochloric acid and chlorine is evolved at the anode surfaces during electrolysis, the graphite withstands corrosion indefinitely.

Another aspect of the invention relates to the treatment of the catholyte. The electrolytic cell employed is divided into two compartments or chambers, namely, the anolyte chamber and the catholyte chamber. These chambers are defined from each other by a porous diaphragm. The metallic sulfide compounds to be treated are placed in the anolyte chamber, and any iron present in the compound will be oxidized in the anolyte chamber and result in the formation of ferric iron compound. A ferric iron compound, such as ferric chloride in the anolyte greatly enhances the oxidation of the desired metal in the sulfide compound. However, as electrolysis proceeds, the ferric iron compound in the anolyte passes through the porous diaphragm or partition and enters the catholyte chamber and is considerably reduced at the cathode to ferrous iron. This is occasioned by the liberation of hydrogen at the cathode. At the cathode, the metal that is being recovered from the sulfide compound must be reduced to as near its metallic state as possible. Consequently, any ferric iron compound in the catholyte that has not been reduced will tend to oppose or counteract any reducing reaction on the metal that is being precipitated at the cathode.

I have found that if the iron present in the catholyte chamber can be kept or maintained in the ferrous state, it will act as a reducing agent and aid in the reduction of the desired metal in the catholyte chamber from the sulfide compound, whereas if it is allowed to remain in the catholyte chamber in the ferric state, it will oppose or detract from the obtaining of the desired metal at the cathode.

It is, therefore, another object of the present invention to treat the catholyte so that ferric iron compounds that may exist therein will be alered or changed from ferric iron to ferrous iron, and in that way assist or contribute to the deposit or precipitation of the desired metal on the cathode. Essentially, this treatment consists of removing a portion of the catholyte from the catholyte chamber and subjecting it to a treatment which will convert the ferric iron therein to ferrous iron after which the treated portion of the catholyte is returned to the catholyte chamber.

Another aspect of the present invention is concerned with the type of material used as a diaphragm or partition to define the anolyte chamber from the catholyte chamber. Heretofore, natural materials, such as paper and asbestos have been used. Ceramics have also been employed. The consumption of natural materials by dissolution or disintegration in the electrolyte under the conditions of electrolysis proved to be so excessive as to be uneconomical in a commercial process. The material employed should be of such a character as to withstand the corrosive action of the electrolyte and of the gas that is evolved at the anode, such as chlorine. It also should be a material which would be relatively inexpensive. I have found that the material sold on the market under the name of Dynel is ideally suited for this purpose and that allied synthetic materials can also be used.

Another object of the present invention is to provide an electrolytic cell suitable for the treatment of metallic sul-

fide compounds, wherein a rotating metallic cathode is employed which is largely submerged in the electrolyte and slowly rotated therein. This cathode has the desired metal precipitated or deposited thereon from which the desired metal which is deposited in the nature of a metallic sponge can be continuously scraped as the cathode rotates and promptly conducted to a launder or other instrumentalities which will minimize the sponge being oxidized by exposure to air.

With the foregoing and other objects in view, which will be made manifest in the following detailed description, and specifically pointed out in the appended claim, reference is had to the accompanying drawings for an illustrative embodiment of the invention, wherein:

FIGURE 1 is a top plan view of one form of apparatus embodying the present invention.

FIGURE 2 is a vertical section taken substantially upon the line **2—2** upon FIGURE 1 in the direction indicated.

FIGURE 3 is a vertical section through another form of apparatus which may be employed and which embodies the present invention.

FIGURE 4 is a sectional view taken substantially upon the line **4—4** upon FIGURE 3 in the direction indicated.

FIGURE 5 is a view in side elevation parts being broken away and shown in vertical section, illustrating still another form of apparatus embodying the present invention.

Referring to the accompanying drawings, wherein similar reference characters designate similar parts throughout and referring particularly to that form of apparatus illustrated in FIGURES 1 and 2, **10** indicates the tank of an electrolytic cell. The interior of the tank is divided by means of a partition or diaphragm **11** into a catholyte chamber **12** on the interior of the partition and an anolyte chamber **13** on the exterior of the partition. The partition which may be in the form of an open topped cylindrical bag is suspended in the tank **10** from an annular rod or ring **14** which is supported from the top edges of the tank **10** such as by supporting arms **15**. In the catholyte chamber **12**, a cathode **16** preferably in the form of a hollow metal cylinder is suspended such as by arms **17**. This cathode is preferably arranged concentrically with respect to the walls of the tank **10**. The electrolyte which is in the form of a dilute acid is indicated as largely filling the tank and by the reference character **18**. Leads **19** and **20** are connected to the tank **10** and cathode **16**, respectively, and supply electric current from a direct current source (not shown). The metallic sulfides, such as for example copper sulfide concentrates, are placed in the anolyte chamber **13** and are subjected to electrolysis.

The electrolyte **18** may be a water solution of either sulfuric acid or hydrochloric acid. However, hydrochloric acid is preferable due to the fact that oxidation of the metallic sulfides is more rapid when hydrochloric acid is employed. This is probably due to the catalytic properties of the chlorine that is released from the acid at the anode **10** constituting the tank of the electrolyte cell. While hydrochloric acid is preferred because of the rapidity of its action on the metallic sulfide, it is more corrosive than sulfuric acid in this type of an electrolytic process. For this reason, the nature of the material employed for the tank **10** is one of the features of the present invention.

The tank **10** is formed of graphite, and in the preferred form of construction, it is formed of a single unitary or integral piece of graphite. Joints in the walls or bottom of the tank **10** are to be avoided, as these joints are apt to leak with prolonged usage of the tank. The tank **10** being formed of graphite and being electrically connected by the lead **20** so as to function as an anode is subject to the corrosive action of the electrolyte **18**, and the chlorine that is released on the interior surfaces of the tank as electrolysis proceeds. Nevertheless, being formed of graphtie, the tank **10** effectively resists corrosion under the circumstances and conditions existing within the electrolytic cell.

The cathode **16** is formed of a metal which will resist

corrosion in the electrolyte **18**. Usually, the cathode **16** will be formed of metallic copper.

As electrolysis proceeds, the metallic sulfides in the anolyte chamber **13** are anodically oxidized.

OXIDATION REACTIONS

$Cu_5FeS_4 \leftrightharpoons CuFeS_2 + 2Cu_2S$

$CuFeS_2 + 2O_2 + 2Cl = CuS\ (Covelite) + FeCl_2^{++}$

$2Cu_2S + O_2 = 2CuS\ (Covelite) + 2CuO$

$CuS + 3O = CuO + SO_2$

$CuO + 2HCl = CuCl_2 + H_2O$

$CuO + Cu\ (Native\ or\ Metallic) = Cu_2O$

$Cu_2O + 2H = 2Cu + H_2O$

$Cu_2O + 2HCl = CuCl + H_2O$

$CuCl + H = Cu + HCl$

$2CuCl + Electrolysis = 2Cu + 2Cl$

Metal ion migration occurs through the porous bag or partition **11** toward the cathode **16** and with the passage of time the metallic constituent of the sulfides collects as sponge on the cathode and ultimately drops therefrom by gravity as sponge. This can be withdrawn from the catholyte chamber **12** such as through a tube **21** in which there is a pump **22** that pumps the catholyte **12** and the collected sponge metal through a filter or the equivalent indicated at **23**. The sponge may be recovered from the filter, and the filtrate returned to the catholyte chamber **12** through a return tube **24**.

Any insoluble constituents in the residue from the electrolysis of the sulfide compounds that are present in the anolyte chamber **13** remain in the anolyte chamber. If these residues contain other metals of value, such as gold and silver, the residues may be drained from the bottom of the anolyte chamber **13** by opening valve **25** and conducting some of the anolyte and the residues to a treatment tank **26** where they may be recovered by conventional or preferred methods.

The concentration of the acid in the electrolyte **18** is preferably between 5% and 10% by weight. Lower concentrations are ordinarily uneconomical.

The current that is supplied through the leads **20** and **21** has its amperage and voltage adjusted to the desired condition. A typical adjustment would be to supply three volts and ten amperes per square foot of cathode surface that is submerged in the acid electrolyte. If the electrolyte is maintained at an elevated temperature of up to 150° F., this elevated temperature has a marked effect in reducing power costs and increasing the quality of the product.

Most metallic sulfides, such as copper sulfides obtained from mineral sources contain various amounts of iron. The iron enters the anolyte chamber **13** along with the metallic sulfide compounds that are deposited therein. The iron constituents are apparently converted into ferric iron salts in the anolyte chamber, and these iron salts remain in solution in the acid electrolyte. In the anolyte chamber, ferric iron salts apparently aid or assist in the oxidation of the sulfides. However, as the iron salts remain in solution, they diffuse through the pores of the porous diaphragm or partition **11** and enter the catholyte chamber **12**.

In an effort to ascertain accurately what occurs in the electrolytic cell, I prepared a synthetic electrolyte containing 10% acid by weight. A ferric salt and finely divided particles of pure copper were placed in the anolyte compartment **13**. Electrolysis was conducted in the manner described, and the precipitate was formed on the cathode. The precipitate finally settled in the bottom of the membrane or diaphragm partition bag **11**. Examination of the washed and dried precipitate showed that it was almost entirely metallic, but was encased in a film of oxide. The quality of the metallic precipitate was approximately 97% to 99% copper. This indicated that the presence of ferric salts in the catholyte chamber **12** resulted in slight oxidation of the metal that was being recovered.

At the cathode, the metal that is being recovered from the metallic sulfide compounds, should be reduced to as near its metallic state as possible. Any ferric iron existing in the catholyte chamber will oppose or counteract this reduction of the metal that is being recovered in that it tends to oxidize it as it is precipitated at the cathode. In order to avoid oxidation in the catholyte chamber of the metal that is being recovered from the sulfides, it is desirous to maintain all of the iron in the catholyte in its ferrous state. If the iron in the catholyte chamber is in the ferrous state, it will act as a reducing agent and aid in the ultimate reduction of the metal that is being recovered from the sulfide. To this end, the catholyte that is removed from the catholyte chamber by the tube **21** and pump **22** and conducted to the filter **23** for the purpose of extracting the metal sponge, after passing the filter **23** is subjected to further treatment. This treatment consists of reducing the ferric iron in the catholyte to ferrous iron before the catholyte or filtrate is returned to the catholyte chamber through the tube **24**. This may be accomplished in one of several ways, such as to conduct the filtrate over or in contact with metallic iron. Another way is to induce an ion exchange employing resins which absorb ferric iron. Such a resin is Dowex 1–X8. Another manner in which to reduce the ferric iron in the catholyte to ferrous iron is to subject the filtrate to a chelating agent, as an example of a suitable chelating resin Dowex A–1 is suitable. It will, therefore, be appreciated that one aspect of the present invention is to maintain the catholyte as free of ferric iron as is reasonably possible and reducing or altering the ferric iron to ferrous iron as soon as reasonably possible. This may be performed periodically or continuously. It will, therefore, be understood that the container **23** may contain not only the filter, but also other treating apparatus for treating the filtrate to change the ferric salts to ferrous salts before the filtrate is returned to the catholyte chamber through the tube **24**.

A feature of the invention resides in the construction of the partition or diaphragm bag **11**. Heretofore, when an electrolytic cell has been divided into an anolyte chamber and a catholyte chamber by a porous partition or diaphragm, the material used has usually been paper, porous ceramics, asbestos, and the like which materials are subject to deterioration, such as by dissolution or disintegration in the electrolyte. In accordance with the present invention, the material used is a synthetic fabric or plastic that will withstand the extreme corrosive action of the electrolyte even in the presence of chlorine gas developed at the anode. Such fabrics are Dynel, polyvinyl chloride, polyethylene, polypropylene chloride, Teflon, and the like, and the porous partition is preferably selected from this group. Of the group, I have found that Dynel is most suitable from the cost standpoint and its resistance to acid electrolytes. Because of the fact that Dynel is so highly inert to the electrolyte, its use in the same electrolytic cell can be continued indefinitely.

While the process and apparatus have been primarily designed for the recovery of copper from copper sulfides, it is not restricted thereto. In addition, the process and apparatus can be employed to recover zinc from zinc sulfide compounds, wherein zinc sponge metal is deposited at the cathode and ultimately dropped therefrom to the bottom of the bag or partition **11**. Zinc chloride has value as such in many industries, and if desired, zinc chloride may be produced by anodic oxidation in the electrolytic cell without carrying the process to the extent of depositing the zinc metal to any great extent on the cathode. When preparing metallic zinc sponge from zinc sulfide compounds, the porous partition or diaphragm **11** must be used to separate the anolyte from the catholyte. However, when zinc chloride is to be produced, the use of the partition can be dispensed with. When metallic zinc is being recovered at the cathode, it should, of course, be promptly removed from the electrolyte prior to its being redissolved therein.

The apparatus illustrated in FIGURES 3 and 4 is designed to enable the metal that is recovered and deposited on the cathode to be quickly removed therefrom. In this form of construction, the graphite tank is illustated at **30**, and this tank has connected thereto a lead **31** to render it an anode. Within the tank, there is suspended as by rods **32** a porous diaphgram or partition **33**, preferably formed of Dynel cloth. This divides the interior of the tank into an anolyte chamber **34** and a catholyte chamber **35**. The cathode consists of a hollow metal cylinder or tube **36** which has its ends preferably closed and which is mounted for rotation in the catholyte chamber **35** by means of bearings **37** and **38**. These bearings mount the cathode for rotation about a horizontal axis and in a position wherein the major portion of its exterior surface is submerged in the electrolyte. The cathode is slowly and continuously rotated, such as by a chain drive **39** driven by a source of power (not illustrated). The lead **40** like the lead **31** is supplied with electric current from the source of direct current electricity (not illustrated) to render the cathode **36** a cathode in the electrolytic cell. A scraper **41** is disposed adjacent the top surface of the rotary cathode **36** and will continuously remove the metallic deposits therefrom as the cathode rotates and deliver them into a launder or the equivalent illustrated at **42**. In this form of construction, the metallic sulfides are delivered in the form of a pulp into the anolyte chamber **34** and are subjected to electrolysis, as previously described. The metal that is to be recovered is deposited largely in metallic form on the exterior surface of the rotary cathode **36** and is scraped therefrom by the scraper **41** as the cathode slowly rotates. As previously explained, ferric compounds that are frequently present in the metallic sulfides will contribute or assist in anodic oxidation in the anolyte chamber **34**, but these ferric compounds in the catholyte chamber **35** tend to oppose the reduction of the metal and its deposit as metal on the cathode. To convert or change the ferric salts in the catholyte chamber **35**, the catholyte chamber is provided with a suction tube **43** and pump **44** which will withdraw a portion of the catholyte from the catholyte chamber and conduct it to a treating tank **45**. This treating tank may contain merely metallic iron or it may contain either an ion exchange resin or a chelating agent which will cause the ferric compound in the catholyte to be converted into ferrous compounds prior to the catholyte being returned to the catholyte chamber through the tube **46**. In all other respects, the apparatus shown in FIGURES 3 and 4 functions in the same manner as that previously described in connection with the construction illustrated in FIGURES 1 and 2. The rotary cathode **36** and the scraper **41**, however, do provide a mechanism that facilitates the deposit of the metal to be recovered on the cathode and its prompt removal from the electrolyte and from the cathode, as the cathode rotates.

The construction illustrated in FIGURE 5 is a further variation, wherein the tank **50** that contains the electrolyte is formed of metal such as copper and constitutes the cathode. A lead leading thereto from electrical source of supply being indicated at **51**. Within the tank there is suspended a porous diaphragm or partition **52**, preferably formed of Dynel cloth or the equivalent, and this divides the interior of the tank into a catholyte chamber **53** and an anolyte chamber **54**. In this form of construction, the anode **55** is formed of graphite and is suspended centrally of the tank within the anolyte chamber **54**. The metallic sulfides that are to be treated are delivered in pulp form into the anolyte chamber **54**, as before, and the metal that is to be recovered passes by ionic migration through the partition **52** to the cathode **50**. Ultimately, this metal in the form of metallic sponge particles descends by gravity onto the conical bottom **56** from which it may be periodically removed through a valved outlet **57**. In this form

of construction, as before, provision must be made for changing ferric compounds in the catholyte chamber **53** to ferrous compounds, and to this end, a suction tube **58** extends downwardly in the catholyte chamber **53**, and is equipped with the pump **59**. Catholyte in the catholyte chamber **53** is either periodically or continuously withdrawn from the catholyte chamber and delivered to a treating tank **60**, in which there may be metallic iron, ion exchange resins, or chelating agents, which will effect a conversion of ferric compounds in the catholyte to ferrous compounds before the removed catholyte is returned by the return tube **61** to the catholyte chamber.

From the above described constructions, it will be appreciated that an improved method and apparatus have been provided for treating metallic sulfide compounds to recover their metallic constituents in useable form. This may be merely in the form of zinc chloride where the metallic sulfide compound is a form of zinc sulfide. Usually, however, in the case of copper and frequently in the case of zinc, the ultimate product that is recovered is metallic sponge, wherein the particles are principally of the metal, but may have a very slight oxide coating. By constructing the anode of graphite, its life in the electrolytic cell will be prolonged indefinitely, and by using a synthetic cloth that is inert to the electrolyte, such as Dynel, the cloth defining the anolyte chamber from the catholyte chamber will last indefinitely. Where removal of the metallic particles from the cathode must occur promptly, the use of the rotary cathode illustrated in FIGURES 3 and 4 will enable this to be accomplished.

Various changes may be made in the details of the process and in the apparatus without departing from the spirit or scope of the invention, as defined by the appended claim.

I claim:

1. The method of treating metallic sulfide compounds to recover the metallic constituents therefrom which includes subjecting the compounds to electrolysis in a tank or cell formed of solid impervious graphite and which constitutes a chemically inert anode.

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JOHN H. MACK, Primary Examiner

D. R. JORDAN, Assistant Examiner

U.S. Cl. X.R.

204—106, 114, 115