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METHOD OF TREATING THE ELECTROLYTE IN THE ELECTRODEPOSITION OF IRON

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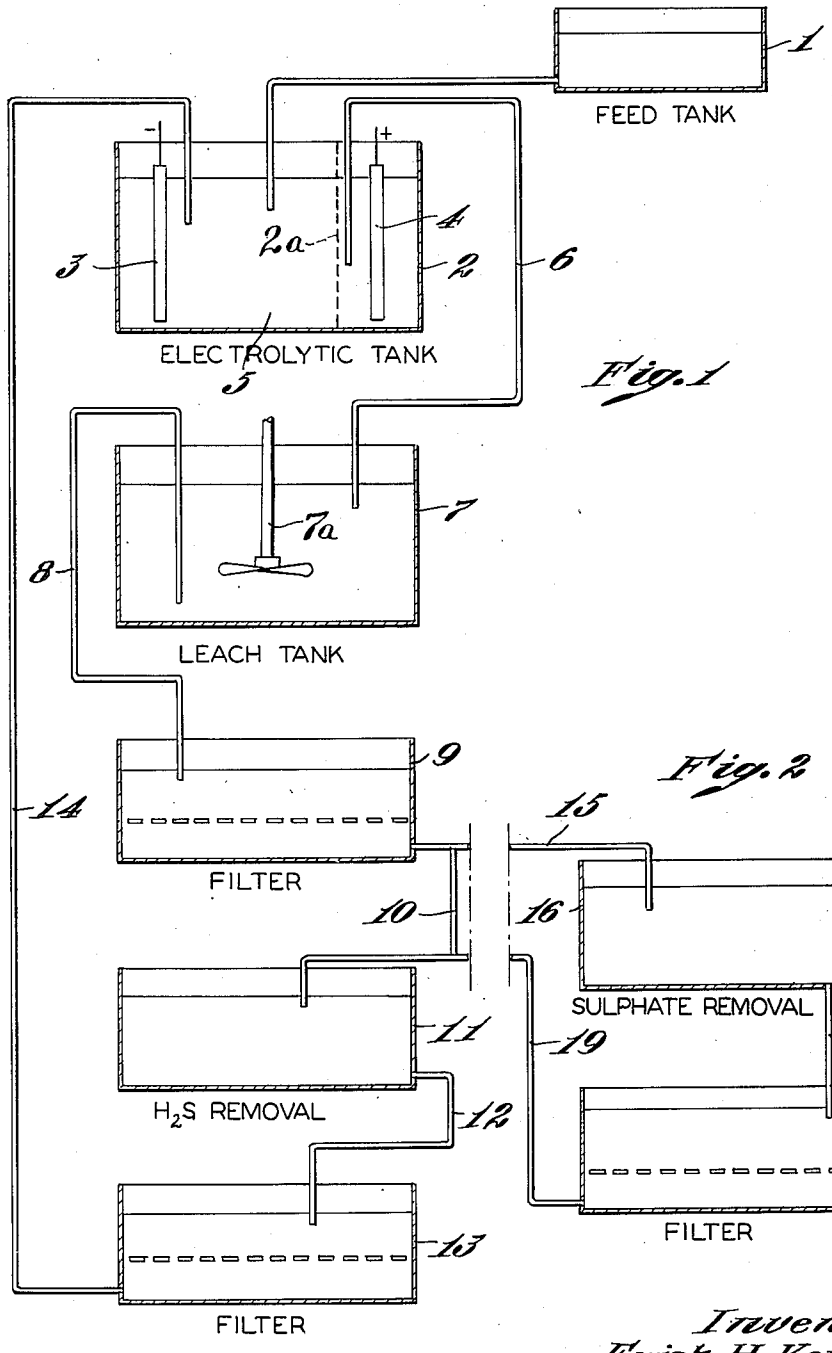


Fig. 1

Fig. 2

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METHOD OF TREATING THE ELECTROLYTE IN THE ELECTRODEPOSITION OF IRON

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6 Claims. (Cl. 204—113)

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This invention relates to a method of treating the electrolyte, in the electrodeposition of iron, for the replenishment of the iron content and for the improved conditioning of the electrolyte for continued electrolysis.

In the electrolytic deposition of iron, from an aqueous solution of one or more of its soluble salts, various views have been advanced and followed with respect to the condition of the iron content of the electrolyte used, during electrolysis. Corresponding procedures have been adopted in the preparation of the electrolyte and in the conduct of the electrodeposition of the iron metal therefrom. Such views and conditions have imposed themselves upon the raw materials which could be used effectively, upon the condition of electrolyte as withdrawn from and returned to the electrolytic tank, and upon the operation of the electrolytic deposition of the metal itself.

By the present invention it is found that the electrolytic deposition of iron from aqueous solutions may be advantageously effected, with the formation of smooth deposits of electrolytic iron of high purity, with relatively concentrated and strongly acidic solutions of a soluble ferrous salt, in which the ratio of ferric iron to ferrous iron is kept very low. It is further found that such an electrolyte may be replenished in respect of its iron content by frequently circulating it into intimate contact with ferrous sulphide ores of iron, such as pyrrhotite. Such ores not only contain and liberate sulphur, both as hydrogen sulphide and free sulphur, but usually—and especially in concentrates—present a considerable proportion of other metals of the copper and tin group, and nickel and cobalt whose sulphides are relatively insoluble in an acid medium at a pH of 1.2 to 2.0.

By the present invention, it is found that the electrolytic deposition of iron may be conveniently and economically effected from an aqueous solution of approximately 12% to 20% of iron, preferably as ferrous iron, such as ferrous chloride. Owing to the effect of the electrodeposition of metallic iron, at the cathode, and the correlative oxidation of the electrolyte, at the anode, however, some ferric iron may be introduced into the electrolyte, e. g., as ferric chloride. This is preferably maintained at 4 grams per liter or less in terms of ferric iron, in accordance with the present invention.

It is found that this condition may be maintained by continuously withdrawing the anolyte from the anolyte compartment of the electrolytic cell in which the electrodeposition of iron is being effected.

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It is further found that the anolyte, as thus withdrawn, for example, containing 35 to 100 grams ferric iron per liter, is effective preferentially to dissolve sulphide ores of iron, such as pyrrhotite, by the reaction of its ferric iron content, and that it is thereby reduced to ferrous iron. It is also found that the ferric iron content, particularly as ferric chloride, is effective to dissolve other metal components of the sulphide ore, whose sulphides are insoluble in acid solution, per se, such as copper, nickel, cobalt, silver, chromium, tin, lead, etc. This is probably due to the fact that such solvent action of the ferric salt does not effect the liberation of hydrogen sulphide.

But it is now also further found that if such contact between the electrolyte and the sulphide ores of iron and other metals is prolonged beyond the dissolving of the iron and other metals by the ferric iron content of the solution, and until it is completely reduced to ferrous condition, the free acid of the solution will then react upon the iron sulphide to liberate hydrogen sulphide gas as well as free sulphur and that these will react with sulphide-insoluble metals which have been dissolved by the ferric iron in solution, and thus precipitate such metals, substantially quantitatively and completely, as their sulphides.

Of course some of these metals may be initially present in the ore, or converted in storage, or otherwise, to some other forms, in which they may be attacked and dissolved by the free acid, as well as they are dissolved from the form of their sulphides, by reaction with the ferric chloride of the electrolyte. However, when dissolved, in either way, such metal salts will be equally completely precipitated out of solution by the subsequently liberated hydrogen sulphide and free sulphur, as their insoluble sulphides.

It may also be postulated that some of such sulphide-insoluble metals, will be present in the ore as sulphide and remain unaffected by either the ferric iron or the free acid content of the electrolyte.

In any event, the leach liquor thus obtained from the sulphide ore, consisting of the electrolyte, its reaction products with the fresh ore and the residues of the ore itself, etc., is filtered, thus removing solids such as insoluble ore residues, precipitated sulphides, free sulphur, and the like, in the form of concentrates which are high in metal values other than iron, such as

copper, and in sulphur content. The resulting filtrate, containing the soluble salts of iron substantially completely in ferrous condition, also contains hydrogen sulphide in solution and free sulphur in colloidal suspension, and free acid in solution.

This filtrate is accordingly further treated for the elimination and removal of the hydrogen sulphide and colloidal sulphur. This may be completely effected by contacting it with activated charcoal, either by adding the charcoal to it and agitating, or by passing the solution through a sufficient mass of activated charcoal, and then filtering. The adsorbent charcoal thus acquires and retains a high percentage of sulphur, both as free sulphur and as hydrogen sulphide, which may be recovered.

As thus completely liberated from both hydrogen sulphide and free sulphur, the resulting clear, strongly acid solution of ferrous chloride (or other ferrous salt) is especially adaptable to the continued electrodeposition of electrolytic iron therefrom.

If the liberated hydrogen sulphide or the free sulphur are oxidized, as they often are during the prolonged leaching treatment or re-cycling of the solution, so as to form sulphuric acid or soluble sulphur compounds in the electrolyte, these may be precipitated as calcium sulphate, by the addition of calcium chloride to the liquor during the leaching operation, and subsequently separated with the coagulated sulphur on the activated charcoal, or by separate precipitation and filtration.

The leaching liquor or solution containing hydrogen sulphide and colloidal sulphur may also be liberated of these components by agitating with a stream of compressed air or by allowing the solution to stand quiescent for a prolonged period of time (24 to 36 hours)—followed in either case by filtering out the thus coagulated sulphur.

The filtered, clarified solution of electrolyte, as thus obtained, is then returned to the electrolytic cell, for the continued electrodeposition of iron therefrom, and directed either into the electrolytic bath as a whole (if a non-diaphragm cell is used, as it may be) or into the catholyte compartment, in the case of a diaphragm cell. It may require some addition of acid to adjust the pH value to the desired degree of acidity as indicated above. But if sulphuric acid is formed in the leaching operation and the sulphate radical thereof precipitated by calcium chlorides, this will liberate free hydrochloric acid into the solution, which will in part or wholly compensate for the loss of acid due to solvent action of the acid of the solution upon the iron sulphide or the formation of hydrogen sulphide.

This invention accordingly provides a method of leaching sulfide ores or concentrates containing iron and copper sulfides in varying proportions and a variety of minor constituent metals in such a manner as to produce:

1. A solution of iron suitable for the production of smooth deposits of electrolytic iron of high purity;

2. A residue containing a high percentage of free sulphur which may be treated for the recovery of this sulphur;

3. A residue containing a high percentage of copper and the minor metallic constituents originally present in the ore suitable for their recovery.

The foregoing procedure may be carried out

as diagrammatically shown in the accompanying drawings in which

Fig. 1 is a diagrammatic flow sheet of the sequence of process steps; and

Fig. 2 is a diagrammatic showing of supplementary process steps which may be associated and conducted with the steps of Fig. 1.

The tank 1 may contain the initial supply of an aqueous solution of the ferrous salt, such as ferrous chloride, or a supply of acid such as hydrochloric acid, or both. The conventional electrolysis tank 2, with diaphragm 2a and anode 4 defining the anolyte portion, and cathode 3 is provided with the aqueous electrolyte 5 from tank 1 (or by recirculation as pointed out below) which is characterized, during electrolysis, by containing water, 12% to 20% of iron, in the form of a ferrous salt, such as ferrous chloride, an acid such as hydrochloric acid to a pH value of 1.2 to 2.0, and in the cathode portion not more than approximately 0.4% of iron in the form of a ferric salt, such as ferric chloride, and in the anode portion approximately 3.5% to 10.0% or iron in the form of a ferric salt such as ferric chloride.

In operation the electrolyte 5 may be withdrawn from the anolyte portion by the pipe 6 and circulated in the leach tank 7 having an agitator 7a over sulphide iron ore, such as pyrrhotite, characterized by containing a sulphide or sulphides of other metals such as of the copper or tin group, nickel or cobalt, the ore being fed to the leach tank in a conventional manner. The reduced leach liquor may be drawn off, with or without separation from attendant solids, through pipe 8, to the filter 9, from which the filtrate may be drawn off by pipe 10 and led into tank 11, for treatment for removal of hydrogen sulphide, e. g., by contact with activated charcoal. The thus treated liquor is then passed through pipe 12 to filter 13, to remove the charcoal with adsorbed gases and colloidal residues, and the resulting filtrate drawn off through pipe 14 and conducted back into the cathode portion of the electrolyte 5, as shown.

In the case of oxidized ores or leach liquors which may otherwise acquire the presence of sulphates, as above-described, the leach liquor, after being removed from the ore in leach tank 7 and passed through the filter 9, may be bypassed from pipe 10 to pipe 15 and thence into tank 16 for treatment with calcium chloride. The resulting mixture then may be withdrawn through pipe 17 to filter 18, the filtered solution then being returned through pipe 19 to pipe 10 and thence into the treating tank 11.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

We claim:

1. Method of treating the anolyte in the electro-deposition of iron, which anolyte has a pH of 1.2 to 2.0 and contains 35 to 100 grams per liter of iron in ferric condition, comprising contacting the anolyte with an excess of an acid soluble iron sulphide ore containing another metal whose sulphide is insoluble in said anolyte after the ferric ions have been reduced to ferrous ions, such excess of ore being sufficient to completely reduce all ferric iron present in the anolyte to ferrous iron and to subsequently react with the free acid present in the anolyte to form hydrogen sulphide, dissolving the iron

and other metals soluble in the anolyte and continuing the leaching of the ore by the anolyte until the ferric iron is completely reduced to ferrous iron and hydrogen sulphide is then formed from the free acid and precipitates the other metal as insoluble sulphide, separating the resulting mixture of solution and solids, treating the solution portion therefrom to remove the hydrogen sulphide and the free sulphur content, and returning the clear solution as catholyte to the electrolytic cell.

2. The method according to claim 1 in which the anolyte has a pH of 1.2 to 2.0 and contains 35 to 100 grams per liter of iron as ferric chloride.

3. The method according to claim 1 wherein separating of the resulting mixture of solution and solids is conducted by filtering the mixture and treating the filtrate with activated charcoal to remove the hydrogen sulphide content.

4. The method according to claim 1 wherein separating of the resulting mixture of solution and solids is conducted by filtering the mixture and treating the filtrate with compressed air to remove the hydrogen sulphide content.

5. The method according to claim 1 wherein separating of the resulting mixture of solution and solids is conducted by filtering the mixture and allowing the solution portion to stand quiescent to remove hydrogen sulphide.

6. Method of treating the anolyte in the electrodeposition of iron, which anolyte has a pH of 1.2 to 2.0 and contains 35 to 100 grams per liter of iron as ferric chloride, comprising contacting the anolyte with an excess of an acid soluble iron sulphide ore containing another metal whose sulphide is insoluble in said anolyte after the ferric ions have been reduced to ferrous ions, such excess of ore being sufficient to completely reduce all ferric iron present in the anolyte to ferrous iron and to subsequently react with the free acid present in the anolyte to form hydrogen sulphide, dissolving the iron and other metals soluble in the anolyte and continuing the leaching of the ore by the anolyte until the ferric iron is completely reduced to ferrous iron and hydrogen sulphide is then formed from the free acid and precipitates the other metal as insoluble sulphide, separating the resulting mixture of solution and solids, treating the solution portion therefrom with calcium chloride to precipitate any sulphate ion content in the solution portion, filtering, treating the clear solution to remove hydrogen sulphide, filtering and returning the clear solution as catholyte to the electrolytic cell.

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