ELECTROLYTIC PROCESS FOR TREATING A FERROUS SULPHATE SOLUTION

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ELECTROLYTIC PROCESS FOR TREATING A FERROUS SULPHATE SOLUTION

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1 Claim. (Cl. 204—93)

The steel industry produces very large quantities of used acid pickle liquor, the disposal of which presents vexatious problems. Used pickle liquor contains ferrous salt and excess acid, usually ferrous sulphate and sulphuric acid. It is possible to recover the iron salts and the residual acid, and to concentrate the latter for reuse, but the market for ferrous sulphate is so limited that it cannot absorb at an attractive price the product of waste pickle liquor of the entire steel industry. Laws designed to prevent pollution of streams and ground waters prohibit or prohibit in many places the discarding of spent pickle liquor even after it has been neutralized with lime. Thus, the disposal of spent liquor often costs as much as, or more than, the original pickle solution.

It has been proposed to oxidize the ferrous sulphate of waste pickle liquor to ferric sulphate, and to dry and decompose the ferric salt to iron and sulphur trioxide, thereby recovering in usable form substantially all of the sulphuric acid of the original pickle liquor. The principal problem to be solved in reducing this proposal to practical operation is to oxidize the ferrous sulphate cheaply and efficiently in strongly acid solution.

Anodic oxidation in an electrolytic cell, with the simultaneous deposition of iron offers a way to convert ferrous sulphate to ferric sulphate. However, there are two outstanding difficulties in such a method. Iron, being more anodic than hydrogen, can not normally be deposited from an electrolyte as acid as is ordinary waste pickle liquor. Further, if the ferric sulphate produced at the anode reaches the cathode any deposited iron is redissolved.

The object of this invention is to provide a novel continuous process for electrolytically treating an acidulous aqueous solution of a ferrous salt, for example a ferrous sulphate waste iron-pickle liquor, to produce a ferric salt and concurrently to electrodeposition iron in any desired form.

The process of this invention is practiced in a two-compartment cell, the compartments being inter-connected solely by a circulating body of mercury, for instance as in the Castner cell used for making caustic soda; a porous carbon anode in one compartment of the cell; and a suitable cathode to receive deposited iron in the other compartment. In the first-mentioned compartment, acidulous ferrous sulphate or other ferrous salt solution is electrolyzed; the anodically oxidized trivalent iron salt is withdrawn, as soon as it is formed, through the porous anode; and iron is deposited at the mercury which has a high hydrogen overvoltage and acts effectively as the cathode of that cell. The mercury-containing iron, is passed into the second compartment in which it serves as an anode. In the second compartment, there is maintained a suitable cathode and an electrolyte of a composition well suited to the deposition of iron as a smooth, coherent, solid sheet or, if desired, as a loosely adherent powder.

The sole figure of the accompanying drawing illustrates diagrammatically an apparatus suitable for use in practicing the invention. In the figure, there is shown in section a cell container 10 provided with an electrically insulating partition 11 which separates the container 10 into two compartments A and B which interconnect through one or more apertures at the bottom of the partition 11. A body of mercury rests on the bottom of the container 10 and is deep enough to cover the top of the aperture in the partition 11 during operation of the cell. Spent pickle liquor, or other acidulous aqueous solution of ferrous sulphate, is fed into a first compartment A in which there is maintained a porous carbon anode 12. An electrolyte 14 of a desired composition is maintained in a second compartment B, and in the latter electrolyte there is suspended a cathode 15 on which iron is deposited. The body of mercury 12 serves as the cathode of the first compartment A and also as the anode of the second compartment B. A cam 16 and a pivot 17, for which there may be substituted any suitable rocking means, are provided to rock the body of mercury 12 to force a circulation thereof between the compartments A and B and to accelerate distribution of iron in the mercury.

Electrolysis of the spent pickle liquor in the first compartment A deposits iron at the mercury cathode 12 and oxidizes ferrous sulphate to ferric sulphate at the anode 13. By promptly withdrawing anolyte through the porous carbon anode 13 as fast as ferric sulphate is formed, migration of ferric sulphate to the cathode is avoided. The rate of withdrawal of anolyte through the anode may be so adjusted that very little ferrous sulphate is withdrawn yet substantially all of the ferric sulphate formed is recovered.

The porous carbon anode 13 may be constructed as described in "Porous carbon electrodes" by George W. Heise, Transactions of The Electrochemical Society, vol. 75, pages 147 to 166, 1939. Mercury containing iron deposited in the first compartment A is circulated under the intercompartment partition 11 into the second compart-
ment B where the iron is removed by anodic action into the electrolyte 14 and thence deposited on the cathode 15 which may suitably be made of iron.

Other and less simple, though mechanically more efficient, means for circulating the mercury 12 may of course be used instead of rocking. For instance, the two cell compartments A and B may be in separate containers interconnected by pipes through which the mercury is circulated by pumps or stirrers. Circulation may be improved by imposing a rotating magnetic field or by other known expedients.

Liquors having an excess acid content up to about 2% or 3% by weight can be handled efficiently in the manner just described. With some sacrifice in efficiency an acidity as high as 4% or 5% can be tolerated. Much of the spent pickle liquor contains from 0.5% to 3% of free acid, and by mixing such acid with the more acid liquors, containing say 7% free acid, obtained from some pickling operations, it will readily be possible to treat the entire output of spent pickle liquor of nearly any steel producing locality.

The composition of the electrolyte in the second compartment B may be adjusted for optimum plating conditions. Successful results may be obtained with an electrolyte containing about 350 gm./liter of ferrous ammonium sulphate kept in a slightly acid condition, e.g. 0.01 N to 0.02 N sulphuric acid; but it is feasible to depart from this range of compositions without departing from the invention.

Although this invention was developed primarily to treat ferrous sulphate solutions, it will be apparent that other aqueous ferrous salt solutions, for instance a ferrous chloride solution, can be treated. Similarly, salts of other multi-valent metals, such as stannous tin or cuprous copper, may be substituted for the iron salts. Nor is it at all necessary that the same salt of iron be used in both of the compartments A and B.

Furthermore, porous conductors other than carbon, for instance porous metal conductors, may be substituted for the porous carbon anode. Likewise, it will sometimes be desirable to remove the iron from mercury cathode of compartment A in a physically separate cell, or even to dissolve out the iron by non-electrolytic chemical methods. Such modifications are deemed to be within the invention.

We claim:

A continuous process for treating an acidulous aqueous solution of ferrous sulphate containing 0.5% to 5% free sulphuric acid to produce iron and a solution of ferric sulphate which comprises the steps of electrolyzing such solution as an electrolyte in contact with a mercury cathode in which iron is deposited, and a porous carbon anode at which ferrous sulphate is oxidized to ferric sulphate; withdrawing through said anode electrolyte containing said ferric sulphate; removing the iron-containing mercury from contact with said electrolyte; electrolyzing an iron-sulphate containing second electrolyte, in which the contraction of free sulphuric acid is about 0.01 N to 0.02 N in contact with said iron-containing mercury as an anode, and an insoluble cathode, thereby stripping iron from the mercury and depositing iron on the last mentioned cathode; and returning mercury from the last-mentioned step to the first-mentioned step of the process.

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