

Dec. 5, 1950

E. H. KONRAD ET AL
METHOD OF ELECTRODEPOSITING IRON

2,532,629

Filed Nov. 7, 1947

2 Sheets-Sheet 1

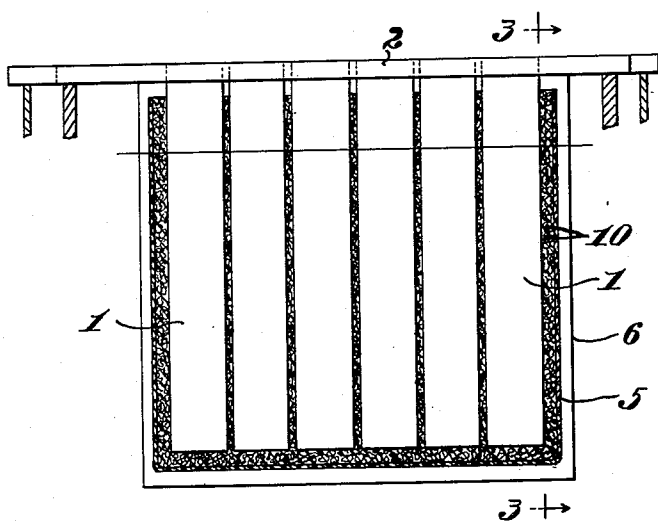


Fig. 1

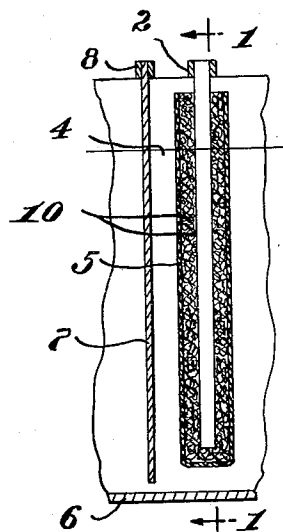


Fig. 3

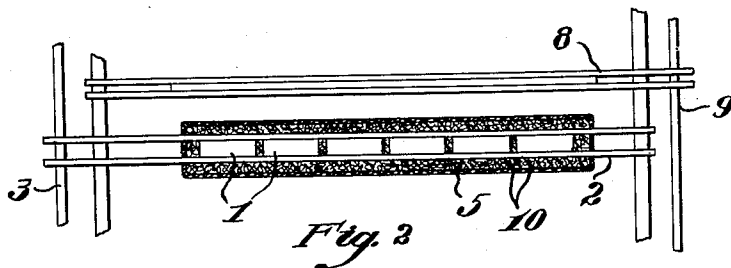


Fig. 2

Inventors
Erick H. Konrad
William E. C. Eustis
by Robert Cushman Grover
Attys

Dec. 5, 1950

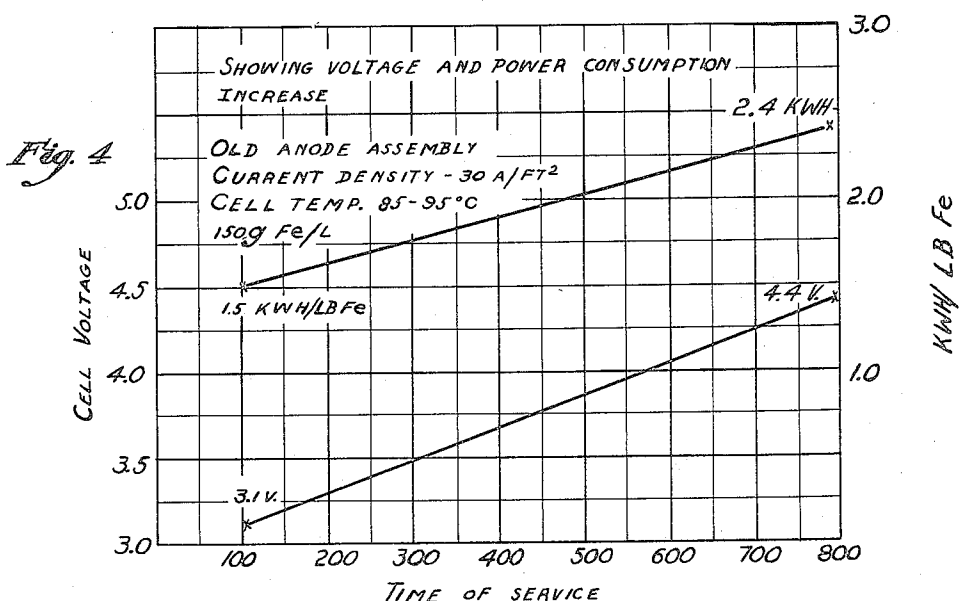
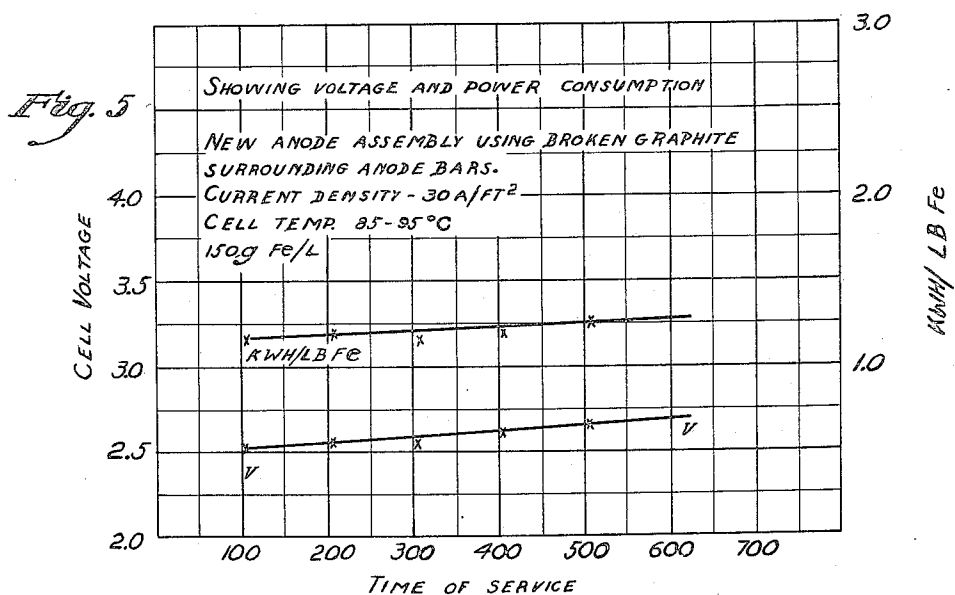
E. H. KONRAD ET AL

2,532,629

METHOD OF ELECTRODEPOSITING IRON

Filed Nov. 7, 1947

2 Sheets-Sheet 2



Inventors
Erick H. Konrad
William F. C. Fustis
by Robert Cushman & Gross
Attys

UNITED STATES PATENT OFFICE

2,532,629

METHOD OF ELECTRODEPOSITING IRON

Erich H. Konrad and William E. C. Eustis, South
Strafford, Vt., assignors to Sulphide Ore Process
Company, Inc., New York, N. Y., a corporation
of Delaware

Application November 7, 1947, Serial No. 784,686

2 Claims. (Cl. 204-48)

1

The present invention relates to a method of electrodepositing metals and to an electrolytic cell suitable for carrying out the method.

In the electrolytic deposition of metals from aqueous solutions of their soluble compounds, such as their soluble salts, it is customary to pass the electric current through the electrolyte between two opposed electrode surfaces, of which the anode, especially when insoluble in the electrolyte, is slightly smaller in area, in order to avoid excessive current densities at the edges of the cathode and concomitant thickening of the deposit and tree formation thereon.

There is therefore an inherent loss in efficiency in the operation of such an electrolytic cell, for the cross-sectional area, through which the electric current is transmitted, is reduced, and the corresponding electrodeposition of metal is effected relative to the total electrode surface areas. At the same time, with the same amperage across the cell, the current density per unit area of anode surface is increased and the potential or voltage across the cell is likewise increased in even greater proportion, for a given rate of electrodeposition of the metal.

The electric potential or voltage required is dissipated in such a cell in overcoming the resistance of the electrolyte and of the diaphragm, when used, as over voltage at the anode and at the cathode, and in polarization at the anode and cathode. Of these, the voltage required to overcome the resistance in the electrolyte and the over voltage at the electrodes may be reduced somewhat advantageously but is essential as representing the work performed by the cell in liberating and depositing the free metal. The polarization effects, however, represent loss of electrical energy and inefficiency of cell operation. Nevertheless such polarization effects are not readily overcome, for if they are sought to be corrected at the electrodes, the means employed for their correction may attack the electrode and if the electrolyte is altered in condition or composition a less desirable cell operation or deposit of the metal in question may result.

The extent of these losses in electrolytic cells having insoluble anodes may be indicated by comparison with electrolytic cells having soluble anodes. For example, in the electrolytic refining of copper using soluble anodes the average cell voltage at a current density of 15-20 amperes per square foot is 0.2-0.4 volt, whereas in an analogous electrodeposition of the copper using insoluble anodes the cell voltage required is 1.8-2.5 volts at a current density of 10 to 12 amperes per square foot, or approximately ten times as great an electric potential.

In the electrolytic recovery of iron from pyrrhotitic ores a pure solution of ferrous chlo-

2

ride is electrolyzed between an insoluble graphite anode, which is surrounded by a porous diaphragm, and an iron or stainless steel cathode. In the course of this type of operation, it has been found that the anode is attacked and deteriorates in use. It has been further found that when the anodic current density is increased there is a disproportionate increase in the cell voltage. For example, in a test run, the anode area was purposely decreased by one third, that is, from 10.2 square feet to 6.8 square feet, while the cell amperage was kept constant at 500 amperes per anode. This caused an increase in the anodic current density from 49 amperes per square foot to 73.5 amperes per square foot. Keeping all other conditions constant, in the cell, the voltage increased from 4.3 to 5.5 volts. In other words, the increase of 50% in the current density—while maintaining the same overall current of the cell constant at 500 amperes per anode—increased the voltage requirement of the cell by 28%. This voltage rise seems to be due chiefly to overcoming increased polarization and passivity phenomena at the anode face.

It is now found, in accordance with the present invention, that in the electrolytic deposition of metals between an insoluble anode and the cathode, a given current may be maintained at a lower initial potential or voltage and without appreciable increase in potential, throughout prolonged operation of the cell, by contacting the face of the anode, which opposes the cathode, with a layer of granular insoluble electroconductive material. The individual granules of this material are of cross-sectional dimensions considerably less than the space separating the electrodes (and preferably less than one-half of such dimension) and present at least approximately ten times as great a surface area as that of the anode surface, per se. The granular material may be of uniform size and shape or of non-uniform sizes or irregular shapes, but are adapted to form intimate and numerous contacts with the anode surface and with each other and are of high electrical conductivity and free from dust. Graphite granules or crushed graphite electrodes are especially suitable.

A typical instance of the practical application of invention will be described with reference to the electrodeposition of iron, using the apparatus, and obtaining the results which are shown in the accompanying drawings, in which:

Fig. 1 is a longitudinal diagrammatic elevation of the electrolytic cell;

Fig. 2 is a plan view of the same;

Fig. 3 is an end view of the cathode and an opposed anode;

Fig. 4 is a diagram showing the increase in voltage and power consumption per pound of de-

3

posited iron, in terms of time of service of the cell when using the anode plates of the cell only; and

Fig. 5 is a diagram showing the increase in voltage and power consumption per pound of deposited iron, in terms of time of service of the cell, with the anode plates, the cathode-opposed surfaces of which are provided with a layer of crushed graphite electrode granules in accordance with the present invention.

Referring to the drawings, a plurality of flat anode bars 1, of molded oil impregnated graphite, were suspended from copper crossbars 2, making contact with the main cell bus bar 3. Each anode was immersed in the electrolyte 4 and surrounded by a porous diaphragm 5, such as an asbestos bag, or other acid resistant, permeable material, the whole being contained in the tank 6.

The space between each anode surface (opposed to a cathode surface), and its porous diaphragm, or the entire free space in the bag, as shown, was filled by a charge of crushed graphite pieces, having a granule size of uniform or closely averaged overall diameter and preferably free from smaller sizes and dust. For convenience, all of the space between the diaphragm or anode bag and the anode may be filled with the granular graphite, but in those portions not directly opposed to a cathode surface, they are less effective, though they promote somewhat the overall conductivity of the cell.

The cathode 7 was composed of a single sheet of steel, suspended from crossbars 8 resting upon cathode bus bar 9 and the tank wall 6, and presenting its surface in opposition to the flat surfaces of the series of anode bars 1, as shown in Figs. 2 and 3.

In a particular instance of operation of the cell, as thus arranged and constructed, each of the six anode bars 1, as shown, was 6" wide by 1" thick and 40" long, 32½" of the length of the bar being submerged in the electrolyte 4, which comprised an aqueous solution of ferrous chloride containing 150 grams of ferrous iron per liter.

The cathode was a sheet of steel ⅛" thick and presented a submerged cathode surface 36" x 50" which was equal to 12.5 square feet per face. The area of the anodes was about 11.1 square feet per face.

The space between the anode and cathode was 4" from center to center.

The anode was surrounded by broken pieces of graphite electrode, 10 varying from ⅛" to ¾", and averaging about ⅜", which were packed firmly between the surface of the anode and the anode bag and formed a layer about 1¼" thick. The surface area of each such layer of crushed graphite on the anode surface was calculated to be about 180 square feet.

The cell was put into operation and maintained with the temperature of the electrolyte averaging about 88° C.

Operation I

Operating the cell first, before filling the anode bags with crushed graphite, a cathode current density of 30 amperes per square foot resulted in a cell potential of 3.1 to 3.4 volts.

Operation II

Upon filling the anode compartments with the layer of crushed graphite as above described and shown in the drawings, the cell voltage dropped to 2.6 volts, maintaining the same current density

4

of 30 a./ft.² (thirty amperes per square foot).

Part of this drop in voltage was no doubt due to the effective reduction in the space between the anode and cathode faces, namely, from 3½" to 2¼", or by 1¼". But only 0.2 volt per inch or 0.25 volt of the drop of .5 to .8 volt is attributable to this effect. The balance of the voltage drop can be attributed directly to the larger anode area and corresponding reduction in anode current density.

In separate operations of the cell under these parallel conditions for a prolonged period of time, it was found that whereas in Operation I deterioration of the graphite anode surfaces immediately set in, upon putting the cell into service, and considerable deterioration of the anode bars occurred, extending to a depth of ⅛" in 800 hours, in Operation II the anode bars were unaffected at the end of 500 hours' operation.

The deterioration of the set of anode bars used without the granular graphite layer is plotted in the diagram of Fig. 4 and shows that after 800 hours of service the voltage increased from 3.1 to 4.4 volts or 42% and that there was a proportionate increase in the power consumption, per pound of electrolytic iron deposited, from 1.5 to 2.4 kilowatt hours.

Results upon a set of graphite anode bars which were run under similar conditions, except that they were surrounded by pieces of crushed graphite, as above described, showed a lower initial voltage and power consumption per pound of electrolytic iron deposited and a much slower and lower rise in both voltage and power consumption, per pound of iron, upon continued operation of the cell.

The attack upon the anodes was not only reduced in this way but such as occurred was transferred to the granules of graphite contained in the anode chamber, forming contact with the anode surface and with each other. The granules thus consumed are easily and cheaply replaced, without interrupting the operation of the cell, by introducing fresh granules into the open tops of the anode bags.

During operation of the cell, some tendency to film formation may be observed upon the granule surfaces. If this occurs, it may be readily displaced by washing the granules with hydrochloric acid, preferably in concentrated solution and if necessary at elevated temperature.

It is further observed, as a part of the present procedure, that in an electrolytic cell, in which an insoluble anode is used, per se, as the anode deteriorates in the course of continued operation the nature of the anode reaction of the electrolyte changes, leading to the formation of an increasing amount of free acid at the anode.

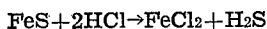
In the electrodeposition of iron, this increased formation of free acid at the anode leads to difficulties, especially when the anolyte is to be used as a leach liquor for the dissolving of fresh ores such as pyrrhotite. In such cases, any excess of free acid present must be neutralized in order to return the electrolyte to the original pH of 1.5 which is desirably maintained in the feed back to the electrolytic cell.

Ferric chloride anolyte even though containing free hydrochloric acid will react preferentially with pyrrhotite concentrates to form ferrous chloride and free sulphur as follows:



Under the proper conditions of operation of

the cell and of the leaching of the ore with the anolyte from the cell, the pH value of the resulting leach liquor after this reaction will be about 1.2 to 1.4. An excess of pyrrhotite may then be added whereupon the free acid in the electrolyte will then react therewith to liberate hydrogen sulphide from such excess of pyrrhotite, as follows:



Such liberation of hydrogen sulphide is desirable and effective to precipitate impurities dissolved from the ore and contained in solution in the leach liquor, whose sulphides are insoluble at a pH of 1.5 such as copper, silver, nickel and cobalt, and may then be filtered off, leaving a clear, purified solution to return to the catholyte of the electrolytic cell.

Thereupon the pH value of the solution will rise to about 1.5, which is a suitable condition in which to return it to the catholyte of the electrolytic cell.

But if appreciable anode deterioration has occurred and more free acid liberated, producing a lower pH value of the anolyte accordingly: either less pyrrhotite must be added thereto, to avoid excess hydrogen sulphide formation—which leaves the pH value lower than is desirable for return of the leach liquor to the electrolytic cell—or if sufficient pyrrhotite is added to neutralize the excess acid in the anolyte (after complete reduction of the ferric chloride) then an excessive amount of hydrogen sulphide gas is liberated which is undesirable in many ways which are well known and recognized.

For example, in operating a cell without the layer of graphite granules upon the anode surface, the pH value of the leach liquor, following the reaction of the anolyte with pyrrhotite as given above, was 1.2. As anode deterioration progressed, this pH of the leach liquor, at this stage of reaction upon the pyrrhotite dropped to an average of 1.0 during the second week and then dropped progressively until at the end of 800 hours of operation of the cell or 8 weeks of overall operation, it averaged 0.7–0.8.

Employing a crushed graphite granular layer as above described, but otherwise under like conditions of operation, the pH of the anolyte, after being employed as a leach liquor on pyrrhotitic ores, at the end of the first reaction, given above, averaged 1.5–1.7. Some addition of hydrochloric acid was therefore desirable to promote the second reaction for the liberation of hydrogen sulphide. Such addition of free hydrochloric acid to the leach liquor is desirable, not only as a matter of more accurate control of the leach liquor, of hydrogen sulphide liberation, and of the subsequent feed back to the electrolytic cell—but also to replace the necessary “drag out” loss of electrolyte which is entailed in the removal of insoluble matter and other unavoidable losses, such as spraying from the bath and leach liquor.

On the other hand, the areas of granular conductive surface and anode surface may possibly

be so adjusted and proportioned relative to each other and to the cathode surface that the pH value of the anolyte as withdrawn from the cell may be of the desired range, so that the leaching operation upon fresh ore therewith will dissolve the iron, precipitate acid-insoluble sulphides, without any or at least without excessive hydrogen sulphide formation, and acquire a suitable pH value for direct return to the catholyte of the electrolytic cell.

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. A method for the electrodeposition of iron, comprising as steps the passing of an electric current through an aqueous electrolyte containing ferrous chloride, between a cathode surface and a graphite anode bar, in spaced, opposed position to each other in the aqueous solution, and separated by a diaphragm which is pervious to said aqueous solution, the anode bar, on its surface opposed to the cathode surface, being in contact with a layer of granules of graphite having individual cross-sectional dimensions upward from one-eighth inch, and the granules being in electrical contact with each other and presenting a surface area to the aqueous solution of ferrous chloride which is greater than the area of the graphite anode bar, and electrodepositing iron on the cathode.

2. A method for the electrodeposition of iron, comprising as steps the passing of an electric current through an aqueous electrolyte containing ferrous chloride, between a cathode surface and a graphite anode bar, in spaced, opposed position to each other in the aqueous solution, and separated by a diaphragm which is pervious to said aqueous solution, the anode bar, on its surface opposed to the cathode surface, being in contact with a layer of crushed granules of molded graphite having individual cross-sectional dimensions upward from one-eighth inch, and the granules being in electrical contact with each other and presenting a surface area to the aqueous solution of ferrous chloride which is greater than the area of the graphite anode bar, and electro-depositing iron on the cathode.

ERICH H. KONRAD.
WILLIAM E. C. EUSTIS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
155,884	Mormandean	Oct. 13, 1874
830,918	Nelson	Sept. 11, 1906
1,239,443	Antisell	Sept. 11, 1917
2,273,036	Heise et al.	Feb. 17, 1942
2,464,889	Pike et al.	Mar. 22, 1949