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ELECTROLYTIC RECOVERY OF METALS FROM SOLUTIONS

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Fig. 1.

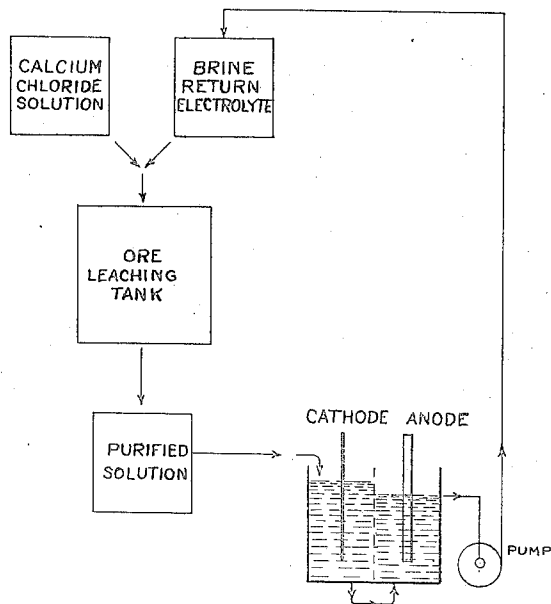
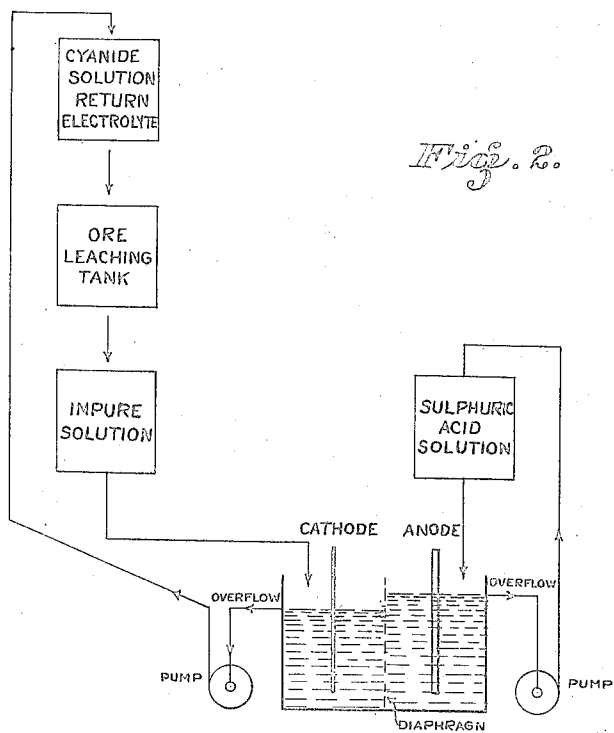


Fig. 2.



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ELECTROLYTIC RECOVERY OF METALS FROM SOLUTIONS.

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This invention relates to the electrolysis of solutions with insoluble anodes and is intended especially to prevent the disintegration of these anodes which is apt to occur during this operation.

The problem of finding an anode which will not disintegrate on continued use is one which for many electrolytic operations has not yet been solved. For example, in the electrolysis of cyanide solutions there is no available commercial material which does not disintegrate under anodic service with greater or less rapidity. The same is true of the electrolysis of brine solutions for the production of chlorine and especially in the electrolytic precipitation of metals, such as lead and silver, which have been dissolved from ores in the acid brine leaching process. This anode problem often becomes more acute where it is necessary to employ diaphragms to separate the electrodes.

I have found that the disintegration of the anode is due to the presence in the solution of certain substances (often in minute quantities) which bring about this deleterious effect. If these substances are removed or kept from contact with the anode, the disintegration is minimized or eliminated. For instance in the electrolysis of brine solutions with carbon or graphite anodes, I have found that the presence of sulphate ions is the principal factor in the disintegration. Similarly in the electrolysis of cyanide solutions with lead or lead peroxide anodes, it is mainly the presence of chlorides which bring about the anode disintegration. A lead anode is practically permanent in a solution containing only sulphate ions. And in the same way for each given insoluble anode, a solution can be prepared which has no disintegrating effect.

In order to carry my invention into effect, I make use of a diaphragm which separates the electrolytic cell into two compartments, such as illustrated in the accompanying drawings, in which Fig. 1 is a diagrammatic view showing an arrangement of apparatus where it is desired to make use of a precipitated cathode solution for circulation through the anode chamber.

Fig. 2 is a diagrammatic view showing an arrangement of apparatus where it is not practicable to remove the impurities from a lead solution and where a separate solution may be used for the anodes. The anode may be of any suitable material, for instance,

lead, graphite, etc., and it is surrounded by a solution of appropriate composition. For example, with a lead anode a solution of sulphuric acid or sodium sulphate, substantially free from chlorides, is employed as illustrated in Fig. 2. For a graphite anode a solution of a chloride, substantially free from sulphates, should be used as illustrated in Fig. 1.

If the solution in the cathode compartment contains acid radicles or anions capable of attacking the anode in question, these anions will tend to drift into the anode compartment under the influence of the potential gradient. In order to avoid this condition it is necessary to feed in fresh solution to the anode chamber either intermittently or continuously so that the static head so created inside the anode chamber will tend to carry back these anions as they tend to drift in through the diaphragm. This effect may also be secured by providing two ports, an inlet and an outlet port, to the anode chamber and arranging for a fairly rapid feed of the proper solution through the anode chamber whereby the objectionable anions are carried out before they can attain a concentration sufficiently high to be detrimental.

As an example of the practical operation of this invention as applied to the electrolysis of cyanide solutions, an apparatus of the general type described in my Patent No. 1,231,967, July 3, 1917, entitled "Recovery of metals from solutions and apparatus therefor" may be used. The cathode is of a porous conducting material and the solution to be precipitated is passed through this cathode. The anode may be of lead and is separated from the current cyanide solution by a permeable diaphragm of canvas, wood veneer, or similar material. To the anode chamber so formed, there are two ports and a steady stream of a solution of pure sodium sulphate is arranged to flow in at one port and out at the other. The level of the outlet port is preferably so arranged that there is a slightly higher pressure inside the anode chamber than there is in the cathode chamber so that the anolyte tends to drift outwards and prevent the entry of anions (such as chlorides) which would tend to cause disintegration of the anode.

In the same way in the recovery of lead and silver which have been dissolved in

brine solutions, an apparatus of the kind described in my prior Patent No. 1,251,302, December 25, 1917, entitled "Electrolytic recovery of metals from their solutions", may
 5 be used. In this case a graphite anode may be conveniently employed and a solution of a chloride (such as sodium chloride) substantially free from sulphates may be employed as an anolyte. This solution may be
 10 prepared by treating a brine solution with barium or calcium chloride. It is often convenient to make use of the leaching solution itself for this purpose and in order to do this a small quantity of calcium chloride is added
 15 to the leaching solution.

After the lead and silver are taken up from the ore, the solution is passed through the electrolytic cell and the metals precipitated. The precipitated solution, now
 20 substantially free from lead and silver, as well as from sulphates, is fed through the anode compartment as above described before being returned to the ore. In this way two beneficial results are attained, for not
 25 only is the disintegration of the anodes prevented, but the solution is oxidized and saturated with chlorine—a condition favorable to high metal extractions in the leaching operation.

I have found further that by employing the above mentioned arrangement, it is possible not only to prevent disintegration of the anode surface but actually to build it up
 30 and improve it. This is done by using an anode solution, containing a salt of a metal, which will deposit on, and form a protective layer over, the face of the anode. The best metal for this purpose is manganese, although lead, cobalt, and antimony, may be
 35 employed in special instances.

In carrying out the above process as applied for instance to graphite anodes, the same mechanical arrangement as described above is employed but as an anolyte solution, a solution of sodium chloride containing
 40 a small quantity of manganese chloride is used. Under continued electrolysis an adherent coat of manganese dioxide is formed on the anode and as this is continually renewed, the surface of the anode is
 45 effectually protected from disintegration.

A brief description of Figs. 1 and 2 in the drawing is herewith submitted. Where it is desired to make use of the precipitated
 50 catholyte solution for circulation through the anolyte chambers, an arrangement of apparatus is employed as shown in Fig. 1. In this case the objectionable impurities are removed from the solution either before or
 55 after passing through the cathode chamber.

The drawing illustrates the leaching of a lead ore with a brine solution. The ore is leached with the brine solution returning from the electrolytic cells. Before this
 60 solution goes on the ore it is mixed with

calcium chloride solution. This calcium chloride precipitates the sulphates which would otherwise cause disintegration of the anode. The purified solution is run first through the cathode chamber to precipitate
 65 the lead and then through the anode chamber (note that in this instance the catholyte is at a higher pressure). Where it is not practicable to remove the impurities from the lead solution, a separate solution may be
 70 used for the anodes as illustrated in the diagrammatic drawing marked Fig. 2. This drawing illustrates the leaching of a silver ore with cyanide solution. In this case the solution, after precipitation of the metal in
 75 the cathode compartment of the cell, returns to the leaching tank. The anode department is filled with a dilute solution of sulphuric acid and a lead anode is employed. The anolyte solution is kept at a slightly higher
 80 pressure to offset the ionic draft through the diaphragm.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:—

1. In the electrolysis with insoluble anodes of solutions which tend to cause disintegration of said anodes, a method of operation which consists in enclosing the anode with
 85 a porous partition and feeding to the compartment thus formed, concurrently with the process of the electrolysis, a solution of a kind which will not attack the anodes.

2. In the electrolysis with insoluble anodes of solutions which tend to cause disintegration of said anodes, a method of operation which consists in enclosing the anode with
 90 a porous partition and feeding to the compartment thus formed, concurrently with the process of the electrolysis, a solution of a kind which will not attack the anodes, and regulating the feed of the solution to the
 95 anode compartment so that there is created a pressure higher than that in the cathode compartment, thus causing a flow through the diaphragm from the anode to the cathode compartment, and preventing harmful substances from entering the anode compartment from the cathode compartment.

3. In the electrolysis with insoluble anodes of solutions which tend to cause disintegration of said anodes, a method of operation which consists in enclosing the anode with
 100 a porous partition and feeding to the compartment thus formed, concurrently with the process of the electrolysis, a solution of a kind which will not attack the anodes, and withdrawing said solution from the anode compartment at a rate sufficiently rapid to prevent accumulation of harmful anions from the catholyte solution which would
 105 tend to disintegrate the anode.

4. In the electrolysis with insoluble anodes of solutions which tend to cause disintegration of said anodes, a method of operation

which consists in enclosing the anode with a porous partition and feeding to the compartment thus formed, concurrently with the process of the electrolysis, a solution of a kind which will not attack the anodes, and adding to the solution a salt of a metal which will form a deposit of an oxide on the anode surface and protect it against corrosion.

5. In the electrolysis with insoluble anodes of chloride solutions which contain substances (anions) of a kind which tend to cause disintegration of said anodes, a method of operation which consists in separating the anodes from the catholyte by permeable diaphragms to form a cathode compartment and an anode compartment, maintaining a circulation of a catholyte solution through the cathode compartment to precipitate the metals contained, and returning and circulating the catholyte after precipitation of the metal through the anode compartment to expel objectionable anions and to oxidize and saturate the solution with chlorine.

6. In the electrolysis with insoluble anodes of solutions which contain substances (anions) of a kind which tend to cause disintegration of said anodes, a method of operation which consists in separating the anodes from the catholyte by permeable diaphragms and maintaining a circulation through the anode compartment so formed

a solution of a kind which will not attack the anodes.

7. In the electrolysis with insoluble lead anodes of cyanide solutions which contain substances (anions) of a kind which tend to cause disintegration of the said anode, a method of operation which consists in separating the anodes from the catholyte by permeable diaphragms, and maintaining a circulation through the anode compartment so formed of a solution containing a large excess of sulphate ions.

8. In the electrolysis with insoluble anodes of chloride solutions which contain substances (anions) of a kind which tend to cause disintegration of the anodes, a method of treatment which consists in removing from the solution before it comes in contact with the anodes the anions which cause disintegration of the anodes.

9. In the electrolysis with insoluble anodes of solutions which tend to cause disintegration of the anodes, a method of operation which consists in enclosing the anodes with a porous partition and feeding to the compartment so formed, concurrently with the progress of electrolysis, a solution containing the salt of a metal which will form a deposit of an oxide on the anode surface and protect it against corrosion.

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