UNITED STATES PATENT OFFICE.

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ELECTROLYTIC DEPOSITION OF COPPER FROM ACID SOLUTIONS.

1,378,145. Specification of Letters Patent. Patented May 17, 1921.

No Drawing. Application filed August 14, 1917. Serial No. 186,192.

To all whom it may concern:

Be it known that I, FRANZ EDWARD STUDT, a subject of the King of Great Britain, and a resident of London, England, have invented certain new and useful Improvements in the Electrolytic Deposition of Copper from Acid Solutions, of which the following is a specification.

This invention relates to improvements in and connected with the electrolytic deposition of copper from acid solutions, and has for its object the provision of a more efficient and economic process than those hitherto proposed for the commercial recovery of copper from acid solutions or electrolytes, when these contain a comparatively large amount of iron.

The invention is particularly applicable to electro-leaching processes in which copper ores are leached by means of acid liquors and the copper subsequently recovered from the liquors by electrolysis, as described in my prior U. S. Patent 1,260,380.

During the electrolysis, I pass into the anode compartment, a slow stream of gas containing SO_2, which gas may be produced as a by-product, by methods described below. This is used as a depolarizer, and the following reactions take place:—

(electrolysis) $CuSO_4=Cu+SO_4$

$SO_4+SO_2+2H_2O=2H_2SO_4$

or

$SO_4+H_2O=H_2SO_4+O$

$O+SO_2+H_2O=H_2SO_4$

or

$$CuSO_4+H_2SO_4+2H_2O+SO_2=Cu+3H_2SO_4$$

The sulfur dioxid, when acting as a depolarizer, thus becomes a source of sulfuric acid for use as a leaching agent in copper extraction from the ores.

It has been found in such processes there is produced an excess of sulfuric acid beyond that required for leaching purposes and my invention mainly consists in utilizing this excess acid as a source of obtaining sulfur dioxid for use in the process. The invention further comprises the decomposition of some of the sulfates which remain in the solution for still further adding to the amount of SO_2 recoverable.

That is to say according to the present invention, I propose to provide some of the sulfur dioxid gas by taking the excess acid liquor from the electrolytic depositing tanks after the copper has been extracted by electrolysis, concentrating it, and then treating it with lump sulfur, carbon or other substance which will decompose the acid, or a mixture of these, for the production of sulfur dioxid gas according to the well-known equations:

$$2H_2SO_4+S=2H_2O+3SO_2$$

or

$$2H_2SO_4+C=2H_2O+CO_2+2SO_2$$

In practical working, the liquor to be treated is run off to the concentration plant, where it passes through a heated series of leaden and acid proof iron pans by which the water is gradually driven off, the concentrated liquor is then treated with lump sulfur, for instance, at a temperature of about 600° F. when the reaction $2H_2SO_4+S=2H_2O+3SO_2$ takes place. The SO_2 obtained is then purified, dried and liquefied according to well known processes.

The amount of new sulfur used in the process is by means of the foregoing very considerably reduced. There is a further advantage due to the fact that about 24% (per centum) of the total SO_2 used can be absorbed by the electrolyte direct by passing the SO_2 gas from the recovery plant through a small absorption tower through which the electrolyte travels on its way from the leaching tanks to the depositing plant.

By means of the foregoing a considerable proportion of the SO_2 required for the electrolytic process can be obtained from what would otherwise be waste liquors and the balance can be obtained from burner gases or by any other suitable process. It may be here mentioned that while I am primarily concerned with the obtaining of SO_2 from the free H_2SO_4 and added sulfur, the total amount of SO_2 obtained may be appreciably increased by the decomposition of some of the sulfates which remain in solution.

The amount of new H_2SO_4 produced in the equation

$$CuSO_4+SO_2+2H_2O=Cu+2H_2SO_4$$
$$(64)\quad(196)$$

shows roughly that for each pound of copper obtained there is 1.5 pound of new H_2SO_4 made from SO_2 by anodic oxidation. Owing, however, to the presence of ferric compounds present in the ore to be leached the resulting ferric sulfate also oxidizes some of the SO_2 to H_2SO_4 while being itself reduced to ferrous sulfate. Hence, in general, when the process is properly carried out, there will be more than $1\frac{1}{2}$ pounds of new H_2SO_4 made per pound of copper produced and experiments indicate that it may be as much as $1\frac{3}{4}$ pounds of new acid per pound of Cu but the exact amount will depend on the type of ore being treated and the particular details of the various operations.

The amount of "irrecoverable or lost acid," *i. e.* that used up by bases, other than copper, in the ore will also vary with the different types and grades of ore but the experimental results seem to show that it will seldom exceed the amount of new acid made and in most cases of ores amenable to successful treatment by this process, will never equal the amount of new acid made so that there will be a continuous excess of this new acid production over and above the amount of "lost acid" consumed in the formation of sulfates other than $CuSO_4$.

The "lost acid" mentioned above goes to form sulfates of the various bases present in the ore other than copper, and it is probable that some of these sulfates can be economically treated for the recovery of their SO_2 according to reaction such as the following:

$$4FeSO_4+S=5SO_2+2F2_2O_3$$
$$2Al(SO_4)_3+3S=9SO_2+2Al_2O_3$$
$$4FeSO_4+C=4SO_2+CO_2+2Fe_2O_3$$
$$2Al_2(SO_4)_3+3C=6SO_2+3CO_2+2Al_2O_3$$

In such case it is probable that the extra SO_2 required when "lost acid" is greater than usual, would be generated from sulfates instead of by burning sulfur and so considerably reduce the total amount of sulfur required for carrying out the electro-leaching process by this method.

It will be seen from the foregoing that I have provided an economic process wherein the sulfur dioxid depolarization is obtained by the direct introduction of pure sulfur dioxid gas into the electrolyte and some of the acid solution formed during electrolysis is subsequently used for leaching and the remainder is used for the production of some or all of the sulfur dioxid gas.

What I claim and desire to secure by Letters Patent is:

1. In the electrolysis of acid copper-sulfate solutions, the cyclic operation of preventing anodic polarization in a copper-depositing cell by introducing an amount of sulfur dioxid into the solution at the anode, capable of forming sulfuric acid in the solution in excess of that required for leaching the ores; utilizing a portion of the so-formed sulfuric acid for leaching copper ore material conveying the solution to said cell, and decomposing another portion of said sulfuric acid by heating the same with a metalloid reducing agent to produce sulfur dioxid and conveying the same to the said cell for use in the first mentioned step of the process, substantially as hereinabove described.

2. A process for the recovery of copper which comprises subjecting an acid leaching solution containing copper to electrolysis, while introducing sulfur dioxid gas directly into the electrolytic vessel in the vicinity of the anode, and subsequently utilizing one part of the acid exit liquor from the electrolytic vessel for leaching copper containing ore material, and utilizing another portion of the said acid exit liquor for the production of sulfur dioxid gas for use in the electrolytic vessel by concentrating the said acid liquor and heating the concentrate with a metalloid reducing agent capable of producing sulfur dioxid therefrom.

3. A process for the recovery of copper which comprises subjecting an acid leaching solution containing dissolved copper and containing sulfates, to electrolysis in the presence of sulfur dioxid introduced directly into the electrolytic vessel in proximity to the anode, and subsequently utilizing one portion of the acid exit liquors from the electrolytic vessel containing sulfates for leaching copper containing ore material and utilizing another portion of said liquors for the production of sulfur dioxid gas for use in the electrolytic vessel, by concentrating said liquor and heating the sulfuric acid and sulfates contained therein with a metalloid reducing agent capable of producing sulfur dioxid.

4. In the process of the above claims, the step of heating the SO_4—containing material with sulfur as the metalloid reducing agent, whereby the sulfur from the SO_4 radical and sulfur of the reducing agent are both converted into sulfur dioxid.

In testimony whereof I affix my signature.

FRANZ EDWARD STUDT.