W. E. GREENAWALT.

ELECTROLYTIC PROCESS.

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1,340,826. **Patented May 18, 1920.**

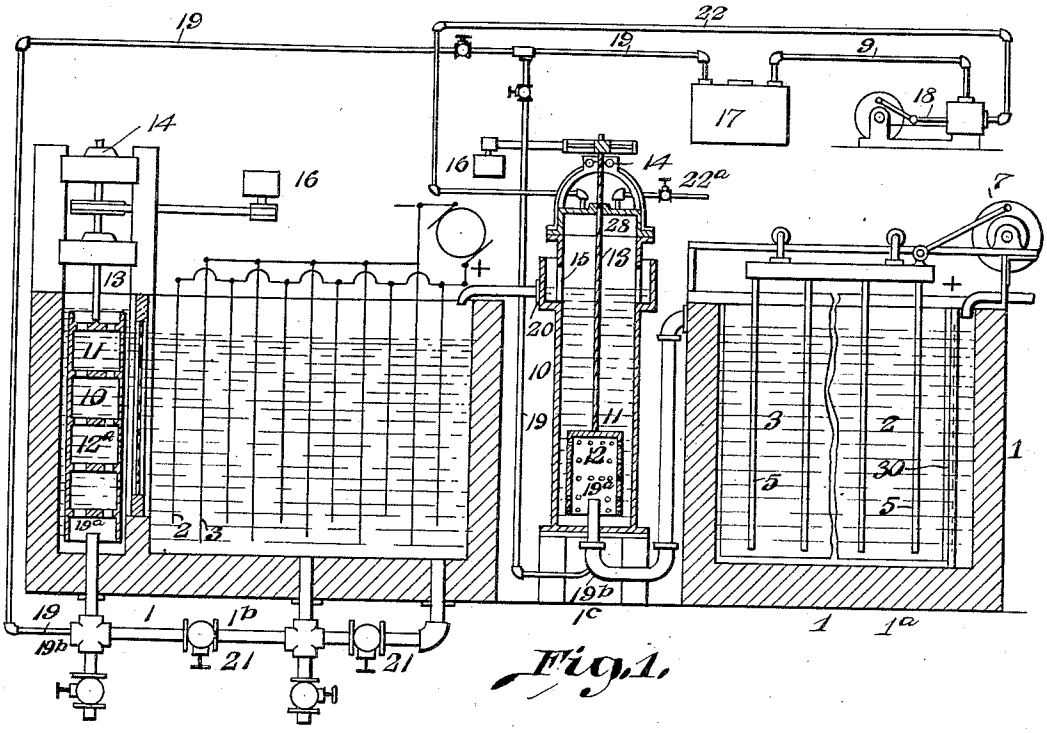


Fig. 1.

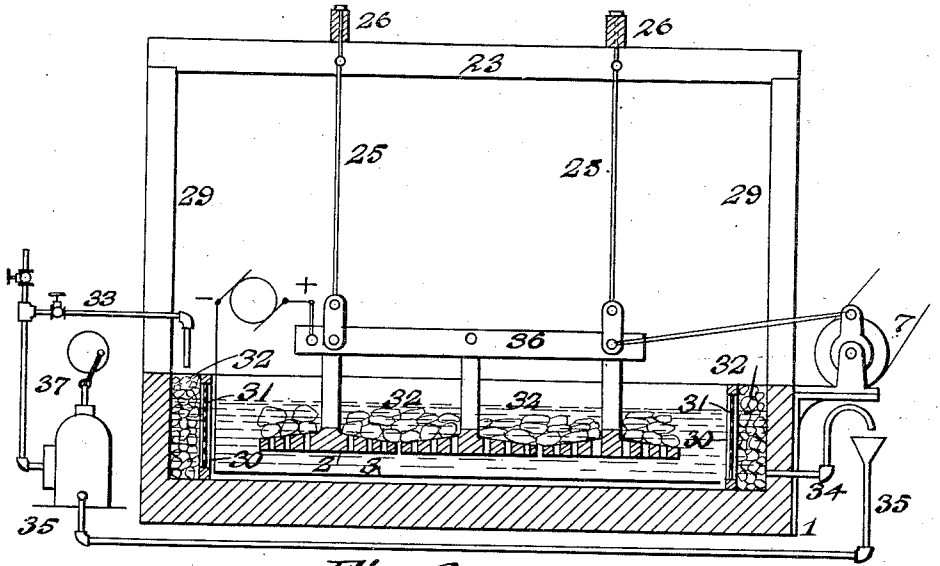


Fig. 2.

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UNITED STATES PATENT OFFICE.

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ELECTROLYTIC PROCESS.

1,340,826. Specification of Letters Patent. Patented May 18, 1920.

Original application filed February 24, 1914, Serial No. 820,496. Divided and this application filed March 13, 1915. Serial No. 15,583.

To all whom it may concern:

Be it known that I, WILLIAM E. GREENAWALT, a citizen of the United States, residing in the city and county of Denver and State of Colorado, have invented certain new and useful Improvements in Electrolytic Processes, of which the following is a specification.

The invention has for its more immediate object the maintaining of the variable valent elements in an impure electrolyte at their lowest valency, and thus, to a very large extent, increasing the cathode efficiency.

This process application may be considered a division of my pending application, Serial No. 820,496, filed February 24, 1914, and, like that application, will be described more particularly to the electrolysis of impure copper sulfate solution, although it is not intended to limit it to this use.

In the electrolysis of impure copper solutions, as for example those obtained in leaching copper ores, there is always present iron sulfate, which injuriously affects the operation. Ferrous sulfate in the electrolyte is not particularly harmful, but the ferric sulfate is highly detrimental.

If a solution of copper sulfate, containing ferrous sulfate is electrolyzed, copper is deposited at the cathode while sulfuric acid and ferric sulfate are produced at the anode, as represented by the following equations;

1. $CuSO_4+H_2O=Cu+H_2SO_4+O$
2. $CuSO_4+2FeSO_4=Cu+Fe_2(SO_4)_3$

The ferric sulfate, finding its way back to the cathode, combines with the deposited copper and is again reduced to the ferrous condition, thus representing a loss of efficiency, as represented by the equation;

3. $Cu+Fe_2(SO_4)_3=CuSO_4+2FeSO_4$

If, however, the ferric sulfate can be reduced at the expense of a comparatively cheap reducing agent, such as hydrogen sulfid, copper sulfid, or perhaps even iron sulfid, then acid is regenerated, and the iron in the electrolyte loses its ability to combine with the deposited copper, as shown by the equations;

4. $Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$
5. $Fe_2(SO_4)_3+CuS=2FeSO_4+CuSO_4+S$
6. $Fe_2(SO_4)_3+FeS=3FeSO_4+S$
7. $FeS+H_2SO_4=FeSO_4+H_2S$.

Ordinarily the reducing agents will be confined to hydrogen sulfid and copper sulfid, as shown by equations 4 and 5. The iron sulfid, if used, may react with the acid to form hydrogen sulfid, as shown by equation 7, and the hydrogen sulfid may then react with the ferric sulfate as shown by equation 4, or the reduction may take place as shown by equation 6.

The sulfid reducing agent may be derived and applied in various ways. If hydrogen sulfid is used, the hydrogen sulfid is readily produced by reacting on iron matte with sulfuric acid. If copper sulfid is used, it is preferably obtained by precipitating copper from its sulfate or chlorid solutions, with hydrogen sulfid and applying the resulting copper sulfid to the electrolyte. Copper matte, preferably high in copper and low in iron, can effectively be used, or, if native chalcocite is available, that may be used.

Ordinarily hydrogen sulfid will be used as the reducing agent and applied in excess so that copper sulfid will be precipitated, and the copper sulfid will then act as the reducing agent. Preferably also, the copper sulfid should be very finely divided so that agitation will keep it suspended in the electrolyte, and thus give the maximum effect. Copper matte may be used in large pieces, but it is preferably finely ground before applying. In any event, the copper sulfid or matte would not be used as an electrode, but simply as a reducing agent, to reduce and maintain reduced, the injurious variable compounds in the electrolyte.

Referring to the accompanying drawing, Figure 1 represents a longitudinal section of a preferred apparatus for carrying out the process when either hydrogen sulfid or finely divided copper sulfid, or both, are made the reducing agents. Fig. 2 is a

modified arrangement if copper sulfid or matte is to be used in large pieces, or in bulk form.

In the figures, 1 represents a tank containing the electrolyte, which may be presumed to be copper sulfate solution as obtained from leaching copper ores, and necessarily containing soluble salts of iron. 2 are the anodes and 3 the cathodes. 4 is a frame having stirring bars 5, interposed between the electrodes, if it is desired to stir the electrolyte. This frame reciprocates, as a whole, and is suspended from the track 6 by the rollers 8 and is moved by the mechanism 7.

10 represents a mechanism, taken as a whole, by means of which the gas, say hydrogen sulfid, is brought into a minute state of subdivision, or atomized, in contact with the electrolyte, and consists preferably of a tube, hood, or cylinder, 11, having perforations 12, in its periphery, or in disks 12^a, suspended in the solution, or electrolyte, by the shaft 13, from the ball bearings 14. This cylinder, or hood, is made to revolve at a high speed, driven by the motor 16.

The gas is preferably produced in the hydrogen sulfid generator 17, from iron sulfid and dilute sulfuric acid, and, by means of the compressor 18, is forced, with air, through the pipe 19, and into the atomizer 10, and into the revolving cylinder 11 through the stationary nozzle 19^a.

It is desirable to maintain a circulation of the electrolyte. It may also be desirable to agitate the electrolyte. The idea is to bring a large volume of the solution in contact with the gas for the reduction of the variable valent salts, and then bring a large volume of the reduced solution in contact with the electrodes, and to prevent, as far as possible, the variable valent elements from being oxidized to the higher valencies. To accomplish this, it is preferred to apply the hydrogen sulfid in excess of that required to reduce the variable valent salts, so that some copper sulfid will be precipitated, according to the well known equation:

$$8.\ CuSO_4+H_2S=CuS+H_2SO_4$$

This precipitated copper sulfid will then, in turn, act as a reducing agent for the variable valent salts, as shown by equation 5. The copper sulfid so obtained is finely divided, easily agitated and kept in suspension, and thus offers the maximum effect, as a reducing agent.

The agitation and circulation of the electrolyte is effectively accomplished by forcing the gas, preferably from a stationary pipe 19, into an inverted perforated cylinder or hood 11, while the cylinder is in rapid rotation. The gas, escaping from the nozzle 19^a, is trapped by the hood or cylinder, and, as the pressure accumulates, it forces its way out of the perforations 12. As the cylinder and perforations are revolving at a high speed, the gas is distributed in exceedingly small subdivisions, or atomized, in contact with the solution. By regulating the speed of rotation, the amount and dilution of the gas, and the volume of the electrolyte, the variable valent salts may be readily reduced without chemically precipitating any more copper sulfid than is desired, with the hydrogen sulfid.

The air and gas ascending through the apparatus 10, acts as an air lift and raises the level of the solution in the atomizer above the level of the electrolyte in the tank, proper, from which it is flowing, and thus permits of its being circulated, as shown at 1^b, or of its being introduced into the next tank, as shown at 1^a. In either case the amount of ferric sulfate in the electrolyte may be kept so low as to be quite harmless.

The space in the upper portion of the atomizer 10 is inclosed, as shown by 28, so as to collect the excess gas, should there be any, which may then be conducted outside of the building, but it is preferably returned to the gasometer 17, through the pipe 22, and again enriched in hydrogen sulfid, thus avoiding any waste of gas, while at the same time it is prevented from becoming a nuisance, as it would be if allowed to escape indiscriminately.

In Fig. 2, instead of using hydrogen sulfid, or copper sulfid precipitated with hydrogen sulfid, matte, or fused copper sulfid may be used, and introduced into the electrolyte. This may be effectively accomplished by circulating the electrolyte through the matte or by moving the matte through the electrolyte. The result, in either case is much the same. The perforated anodes 2, are suspended from a bar 36, and from flexible suspenders 25, and oscillated by the mechanism 7. The matte, 32, or fused copper sulfid, is placed on top of the anodes and moves through the electrolyte, with the anodes. The action is further promoted by having chambers 31 at the ends of the electrolyzer filled with matte, or copper sulfid, 32, through which the electrolyte is circulated to and from the electrodes. The filter 30, prevents precipitate and insoluble matter from the matte from getting to the electrodes. The electrolyte, flowing out of the cell through the pipe 34, is delivered to the pipe 35, and to the pump 37, and returned to the cell through the pipe 33. In this way the electrolyte may be circulated indefinitely, while the oscillating anodes serve to agitate it.

It will be noted that neither in Fig. 1, nor Fig. 2 is the matte or copper sulfid electrically connected with the electrodes, nor is it

directly electrolyzed, but is used primarily to maintain the variable valent salts at their lowest valency in the electrolysis of the copper solutions.

The preferred method of operating the process, however, is to apply the copper sulfid in a finely divided condition, in the atomizer 10, where it is agitated and remains in suspension, and thus gives the maximum effect. The sulfid is prevented from getting to the electrodes by means of the filter 15, and 30, so that while the electrolyte is agitated with the copper sulfid, the clear electrolyte only passes to the electrodes, while the copper sulfid remains behind until it is used up. The air and gas pipe 19, connecting with the solution pipes 21, induces an effective circulation, and thus the ferric salts may be kept at any minimum standard by regulating the circulation of the electrolyte, and the circulation of the electrolyte is best governed by the air and gas supplied to the atomizer. The solution may be alternately passed through the electrolyzers and the reducers, as shown in Fig. 1, especially if the solution is high in copper and high in iron, to make successive reductions advisable.

The action of the hydrogen sulfid under the conditions used in this process is positive so that none of it is likely to remain unconsumed, and hence it may be used with perfect safety, but should any escape, it is taken care of by the hood 28.

In treating copper ores, there are usually a lot of dilute solutions resulting from washing the ore; such solutions are preferably precipitated with hydrogen sulfid, and the copper sulfid precipitate used in the atomizer 10, as the reducing agent; in which case, little, if any hydrogen sulfid need be applied. Similarly, extremely foul solutions may be precipitated with hydrogen sulfid and the precipitate used in the atomizer. In either case the precipitate is dissolved in the act of reducing the ferric salts, and goes into solution as copper sulfate, and in going to the electrodes it is decomposed into pure copper and sulfuric acid. From this it will be seen that in an extraction plant, all the copper may be obtained as the pure electrolytic metal. The copper sulfid will go into solution according to equation 2, and on electrolysis of the resulting copper sulfate, pure electrolytic metal will be deposited, and sulfuric acid regenerated, according to equation 1.

It is evident that, due to the energetic action of the sulfid reducing agent, practically all the iron is maintained in the ferrous condition, and thus the ferrous iron, in being re-oxidized at the anodes, to the ferric condition, acts as a depolarizer, and hence tends to reduce the electromotive force required for the electrolysis. There is a compensation, therefore, for any expense attached to the sulfid reducing agent, both in the sulfuric acid regenerated and in the diminished electromotive force.

The elemental sulfur, as formed by equations 4, 5, and 6, may be removed from the electrolyte, from time to time. This is best done by withdrawing the solution from the electrolyzer, filtering, or settling, the insoluble matter from the electrolyte, and then distilling the sulfur from the insoluble matter. The sulfur may in this way be made a valuable by-product. If the elemental sulfur is not desired it may be burned off as sulfur dioxid, but on the whole the sulfur is best used in the production of hydrogen sulfid.

If hydrogen sulfid is not introduced into the atomizer 10, it will still be desirable to introduce the air to act as an air lift and agitator, and also to assist in circulating the electrolyte.

By regulating the circulation of the electrolyte, it is easy to regulate the amount of ferric salts in the electrolyte, and as a small amount of ferric salts is not particularly harmful, the process can easily be maintained under effective working conditions.

If iron sulfid is used as the reducing agent, hydrogen and hydrogen sulfid will be liberated by the acid solution, and will act to reduce the ferric salts. If preferred, either of these gases may be used separately for the reduction, or either gas may be used in connection with copper sulfid.

I claim:

1. In the electrolysis of impure copper solutions the process which consists in precipitating copper sulfid from copper solutions, with hydrogen sulfid, and applying the copper sulfid precipitate to the electrolyte as a reducing agent.

2. In the electrolysis of impure copper solutions the process which consists in precipitating copper sulfid from copper solutions, with hydrogen sulfid, applying the copper sulfid precipitate to the electrolyte as a reducing agent, and agitating the electrolyte in the presence of the precipitate.

3. In the electrolysis of copper solutions obtained from leaching ores and containing salts of the variable valent elements, the process which consists in applying finely divided copper sulfid to the electrolyte as a reducing agent, agitating the electrolyte in the presence of the finely divided copper sulfid, separating the remaining sulfid and the resulting liberated sulfur from the electrolyte, returning the electrolyte to the electrodes, and then when the electrolyte is sufficiently impoverished in copper returning it to the ore.

4. In the electrolysis of copper solutions containing salts of the variable valent elements, the process which consists in reduc-

ing the variable valent salts to their lowest valency with hydrogen sulfid, and then maintaining them reduced with copper sulfid.

5. In the electrolysis of copper solutions containing salts of the variable valent elements, the process which consists in applying copper sulfid to the electrolyte as a reducing agent, said copper sulfid not being electrically connected with either electrode.

6. In the electrolysis of copper solutions obtained from leaching ores and containing salts of iron, the process which consist in segregating a portion of the electrolyte out of contact with the electrodes, applying copper sulfid to the segregated electrolyte, agitating the segregated electrolyte in the presence of the copper sulfid, separating the excess of copper sulfid and the resulting liberated sulfur from the segregated electrolyte, and repeating the cycle of deposition and reduction if necessary, and then when the electrolyte is sufficiently impoverished in copper returning it to the ore.

7. In the electrolysis of a solution of a metal salt of a polybasic acid obtained from leaching ores and containing salts of the variable valent elements, the process which consists in applying a reducing gas to the solution to reduce the salts of the variable valent elements from a higher to a lower valency, and then continuing the reduction of the higher valency salts formed by the electrolysis by means of concentrated copper sulfid, and then when the solution is sufficiently impoverished in the metal being deposited and regenerated in acid returning the solution to the ore.

8. In the electrolysis of copper sulfate solutions obtained from leaching ores and containing salts of iron, the process which consists in applying copper sulfid to the electrolyte in a finely divided condition to reduce the ferric sulfate formed by the electrolysis to the ferrous sulfate so that the solution is returned to the ore in the ferrous condition.

9. In the electrolysis of copper solutions obtained from leaching ores and containing salts of the variable valent elements, the process which consists in applying a sulfid reducing agent to the electrolyte to reduce and maintain reduced the variable valent elements at their lowest valency during electrolysis, so that the solution may be returned to the ore in a reduced condition.

10. In the electrolysis of copper solutions obtained from leaching copper ores and containing salts of the variable valent elements, the process which consists in applying finely divided copper sulfid to the electrolyte as a reducing agent, agitating the electrolyte in the presence of the finely divided copper sulfid so that the variable valent salts are in a substantially reduced condition when the solvent is again applied to the ore.

11. In the electrolysis of impure copper solutions obtained from leaching copper ores and containing salts of the variable valent elements, the process which consists in reducing the variable valent salts from their higher to their lower valencies produced in the electrolysis, with an insoluble compound capable of reacting with the variable valent elements but incapable of reacting with the regenerated acid, so that the solution may be returned to the ore in a reduced condition.

12. A process which consists in leaching ores of copper with an acid solution to dissolve the copper, subjecting the resulting impure copper solution containing salts of the variable valent elements to the action of electrolysis to deposit the copper, maintaining the variable valent elements at their lowest valency by means of copper sulfid, and then returning the solution to the ore in substantially a reduced condition.

13. A process which consists in treating ores of copper with an acid sulfate solution, subjecting the resulting copper sulfate solution containing salts of iron to the action of electrolysis to deposit the copper and regenerate the solvent, maintaining the iron salts in the solution in substantially the ferrous condition by the action of copper sulfid not electrically connected with either electrode, and then returning the regenerated solution to the ore with the iron in substantially the ferrous condition.

14. A process which consists in treating ores of copper with an acid sulfate solution to dissolve the copper from the ore, subjecting the resulting copper sulfate solution containing salts of iron to the action of electrolysis to deposit the copper and regenerate the solvent, applying copper sulfid to the electrolyte to reduce the ferric iron produced by the electrolysis to the ferrous condition, and then returning the regenerated acid sulfate solution to the ore with the iron in substantially the ferrous condition.

15. In the electrolysis of a solution of a salt of a polybasic acid containing salts of the variable valent elements, the process which consists in introducing into the solution a precipitated sulfid reagent capable of reducing the salts of the variable valent elements from a higher to a lower valency.

16. In the electrolysis of a solution of a salt of a polybasic acid obtained from leaching ores of metals and containing salts of the variable valent elements, the process which consists in precipitating copper from its solutions with hydrogen sulfid, and applying the copper sulfid precipitate to the electrolyte to reduce the higher valency salts formed by the electrolysis to a lower valency.

17. In the electrolysis of a solution of a metal salt of a polybasic acid obtained from leaching ores and containing salts of the variable valent elements, the process which

consists in reducing the higher valency salts formed by the electrolysis to a lower valency by means of copper sulfid, and then when the solution is sufficiently impoverished in metal returning the solution to the ore.

18. In the electrolysis of a solution of a metal salt of a polybasic acid obtained from leaching ores and containing salts of the variable valent elements, the process which consists in repeatedly reducing the higher valency salts formed by the electrolysis to a lower valency by means of copper sulfid, and then when the solution is sufficiently impoverished in metal values and regenerated in acid returning the solution to the ore.

19. In the electrolysis of a solution of a metal salt of a polybasic acid obtained from leaching ores and containing salts of the variable valent elements, the process which consists in reducing the higher valency salts formed by the electrolysis to a lower valency by means of concentrated copper sulfid, and then when the solution is sufficiently impoverished in the metals being deposited and regenerated in acid returning the solution to the ore.

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Witnesses:
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