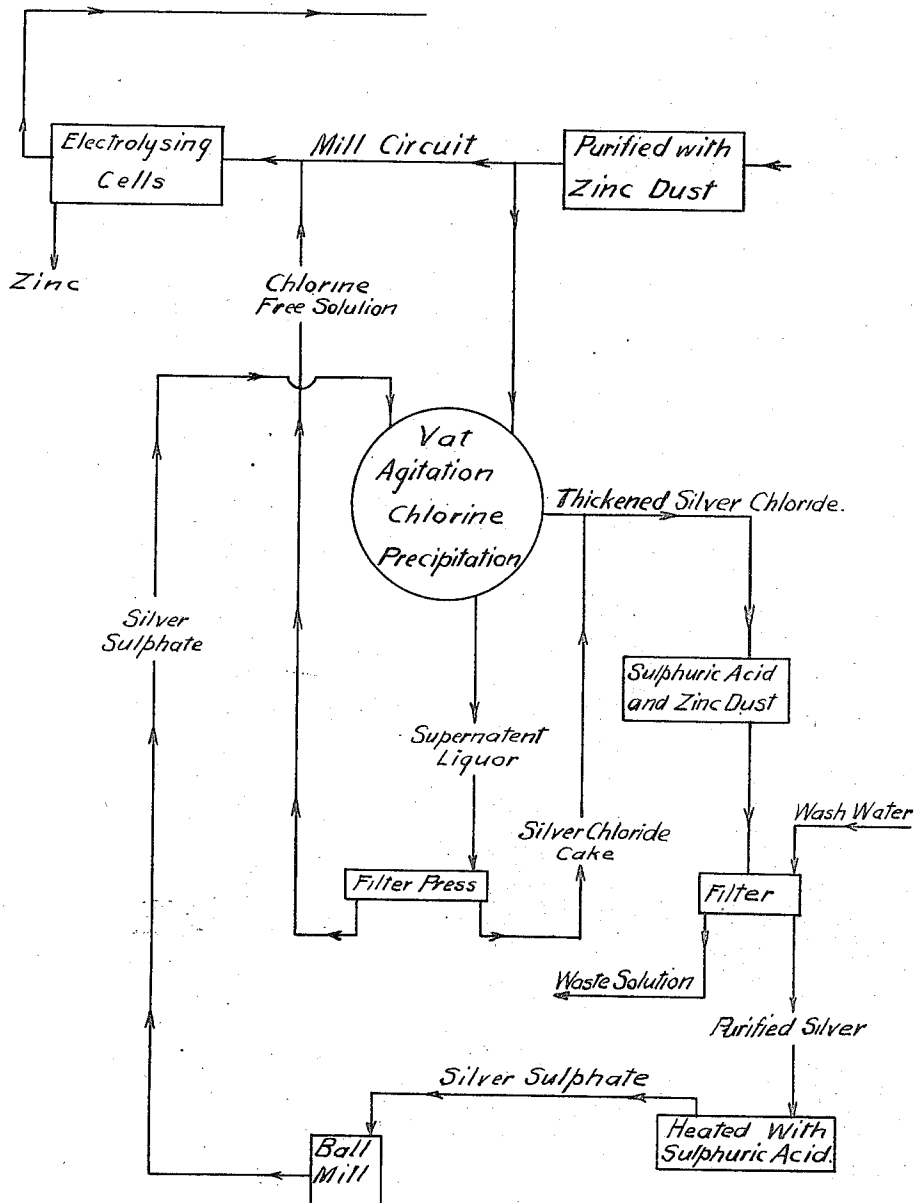


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 RECOVERY OF ZINC BY ELECTROLYSIS.
 APPLICATION FILED MAR. 16, 1920.

1,403,065.

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UNITED STATES PATENT OFFICE.

DAVID AVERY, OF MELBOURNE, VICTORIA, AND ROYALE HILLMAN STEVENS, OF HOBART, TASMANIA, AUSTRALIA, ASSIGNORS TO ELECTROLYTIC ZINC COMPANY OF AUSTRALASIA PROPRIETARY LIMITED, OF MELBOURNE, AUSTRALIA.

RECOVERY OF ZINC BY ELECTROLYSIS.

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Specification of Letters Patent.

Patented Jan. 10, 1922.

Application filed March 16, 1920. Serial No. 366,361.

To all whom it may concern:

Be it known that we, DAVID AVERY, subject of the King of Great Britain, residing at Collins House, 360-366 Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia, by occupation chemical engineer, and ROYALE HILLMAN STEVENS, a citizen of the United States of America, residing at care of Electrolytic Zinc Company of Australasia Proprietary Limited, Risdon, Hobart, in the State of Tasmania, Commonwealth of Australia, by occupation metallurgist, have invented new and useful Improvements in the Recovery of Zinc by Electrolysis, of which the following is a specification.

This invention relates to improvements in the recovery of zinc by electrolysis and refers more especially to the treatment of zinc solutions obtained when the roasted ores or calcines are leached with sulphuric acid (or spent electrolyte) and then subjected to electrolysis for the electro-deposition of zinc therefrom.

In the electrolysis of zinc bearing solutions it is customary to use anodes of lead and cathodes of aluminum, and it has been found that disintegration of corrosion of both these electrodes takes place, requiring frequent renewals and occasioning considerable losses. We have found that this corrosion is chiefly due to the presence of chlorine in the electrolyte which has an injurious effect on both the anodes and cathodes, and that if the chlorine is removed from the solution the amount of corrosion is eliminated or largely reduced and the life of the electrodes is greatly prolonged.

The presence of chlorine may be due to chlorides associated with the ores naturally or introduced during the handling or treatment of the ores.

The object of this invention is to provide certain improvements in the electrolytic treatment of zinc bearing solutions whereby the detrimental effect of chlorine is avoided, more especially in preventing or reducing the corrosion of the lead anodes and the aluminum cathodes in the cells used in such treatment.

We accomplish this object by removing the chlorine from the zinc bearing solution as insoluble silver chloride which is recovered subsequently reconverting the silver

chloride into a soluble silver salt whereby the latter is again available as a chlorine precipitant. In the electrolysis of zinc bearing solutions it is not always practicable to eliminate the whole of the chlorine from the mill circuit and we have found that a small amount of chlorine in the electrolyte may in some cases be permitted without serious effects, for example, when the electrolyte contains glue in solution and when the lead anodes are coated with a manganese dioxide deposit or scale, an amount of chlorine up to 50 milligrams per litre may be present without serious corrosion of electrodes occurring; but when electrolysis is being carried on without the addition of glue or similar substances and/or when the anodes are not coated with a deposit of manganese dioxide corrosion takes place more readily and the chlorine in the electrolyte should be eliminated as completely as possible.

The single figure of the accompanying drawings illustrates by means of a conventional flow sheet the novel features of the invention. This flow-sheet will be clearly understood from the following description.

In carrying this invention into effect one method of preventing the accumulation of chlorine in the electrolyte beyond a certain predetermined point is by withdrawing a certain quantity of solution from the circuit from time to time removing the chlorine from this portion of the solution by treatment with a soluble salt of silver and returning the purified solution to the circuit. The silver chloride formed is collected, reduced to metallic silver and reconverted into a soluble salt for re-use in subsequent operations. The quantity of solution which it will be necessary to treat for the removal of chlorine during any given period, can be determined by consideration of the amount of chlorine which is present in the solution at the beginning of the period, the amount of chlorine which would be introduced during the period and the amount of chlorine to which it is desired to reduce to the total contents of the electrolyte.

We prefer to effect the removal of the chlorine after the purification of the solution with zinc dust. In applying this invention to the procedure in zinc electrolysis the predetermined quantity of solution is

diverted from the mill circuit preferably in convenient charges and introduced into a suitable vat in which silver chloride is to be precipitated. A sample of the solution is taken and titrated with acid, the basicity of the solution determined and calculated in terms of sulphuric acid. The required quantity of sulphuric acid is then added to the charge to render it slightly acid. Finely powdered silver sulphate is then added to the solution in quantity sufficient to remove the bulk of the chlorine present preferably leaving however 2 or 3 milligrams of chlorine per litre in solution.

The mixture is now agitated until the reaction is complete which will be in about one hour, mill solution is then added until the charge is rendered neutral or slightly basic whereby the silver chloride is coagulated a result which is hastened by continuing the agitation. The precipitate is now allowed to settle and the supernatant liquor is filtered through a chamber type filter press (preferably wooden) the clear solution is then treated with a small amount of zinc dust and again filtered to remove any traces of silver that remain in solution thereby obtaining a chlorine depleted solution which is returned to the mill circuit the chlorine content of which will be reduced thereby to the desired amount. This solution with low chlorine content is passed into the cells and the zinc recovered by electrolysis. It will be found that corrosion of electrodes is by this procedure substantially reduced.

Several charges of solution can be treated consecutively in the precipitation vat in the manner indicated above without removing the silver chloride which settles and accumulates as each additional charge is treated. When sufficient silver chloride has accumulated in this way, it is mixed, after decanting the clear solution from the last charge, with the remaining bottom solution and pumped into a small tank to which is also added the cake of silver chloride obtained in the wooden filter press. To this sulphuric acid and zinc dust are added and the whole agitated to reduce the silver chloride to metallic silver. The quantity of zinc dust added should be sufficient to reduce the whole of the silver present which is assumed to be equal to the amount of silver used in the form of sulphate during the process of chlorine precipitation, whereas the amount of sulphuric acid added should be sufficient to leave the solution slightly acid after the action is complete. It is necessary to have this slight excess of sulphuric acid present otherwise zinc dust would probably remain with and contaminate the reduced silver, on the other hand, care should be taken not to allow the solution to become too acid. When the reaction is thought to be complete the silver precipitate is tested for

unreduced chloride by filtering off a little of the precipitate, treating it on the filter with ammonium hydroxide, collecting the filtrate and acidifying it with nitric acid. A white precipitate is formed if unreduced silver chloride is present. When all the silver chloride is reduced the precipitate of metallic silver is agitated for some time, care being taken to keep the solution slightly acid throughout, to ensure the removal of any excess zinc dust. The tank or vat is then discharged into a flat bottomed filter, the solution removed by the aid of a vacuum pump and the precipitate finally washed with water until free from chlorides.

The silver is then removed dried weighed and introduced into a converting pan where pure sulphuric acid is added in calculated amount to convert the whole of the silver into the sulphate. The mixture is heated until the temperature reaches 250° C. or 300° C. and is stirred, occasionally at first but more constantly towards the end of the operation so as to obtain the silver sulphate in the form of a granular mass. This is removed and ground to a fine powder in a Ball mill using flint pebbles. It is then ready for reuse as a chlorine precipitant in subsequent purification operations.

We claim—

1. In the recovery of zinc by electrolysis from a zinc bearing solution containing chlorine, the step of removing chlorine to the desired extent from the zinc-bearing solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis of the solution.

2. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of removing chlorine to the desired extent from the zinc bearing solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis, and electrolyzing the resulting solution with anodes of lead and cathodes of aluminium.

3. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the step of treating the zinc-bearing solution with a silver compound and thereby removing chlorine to the desired extent from the solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis.

4. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the step of treating the zinc-bearing solution with silver sulfate and thereby removing chlorine to the desired extent from the solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis.

5. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of treating the zinc-bearing

ing solution with a silver compound and thereby removing chlorine by precipitation to the desired extent from the solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis, and converting the precipitated silver chloride removed from the solution into metallic silver.

6. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of treating the zinc-bearing solution with a soluble silver compound and thereby removing chlorine by precipitation to the desired extent from the solution prior to electrolysis for the purpose of reducing the corrosion of the electrodes during the electrolysis, and converting the precipitated silver chloride removed from the solution into the soluble silver compound which is then available for the removal of a further quantity of chlorine from zinc-bearing solutions.

7. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of deflecting a portion of the zinc-bearing solution and removing chlorine therefrom to the desired extent and passing the substantially chlorine-free solution back into the remaining zinc-bearing solution, whereby the latter solution has its chlorine content reduced to the extent desired before electrolysis.

8. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of deflecting a portion of the zinc-bearing solution and removing chlorine therefrom to the desired extent by

precipitation with a soluble silver compound, and passing the chlorine depleted solution back into the zinc-bearing solution whereby the latter solution has its chlorine content reduced to the extent desired before electrolysis.

9. In the recovery of zinc by electrolysis from a zinc-bearing solution containing chlorine, the steps of deflecting a portion of the zinc-bearing solution and removing chlorine therefrom to the desired extent by rendering the solution slightly acid and then adding silver sulfate, after which the solution is rendered basic to coagulate the precipitated silver chloride, removing the silver chloride from the solution, reducing the silver chloride to metallic silver, and heating the metallic silver with the calculated amount of sulfuric acid to form silver sulfate which is then available for removing chlorine from a further quantity of solution, the chlorine depleted solution being returned to the zinc-bearing solution whereby the chlorine content of the latter is reduced to the extent desired before electrolysis.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

DAVID AVERY.

ROYALE HILLMAN STEVENS.

Witnesses for David Avery:

V. G. ANDERSON,

M. R. CULLEN.

Witnesses for Royale Hillman Stevens:

ALLAN MCINTYRE,

V. S. CHAMBERS.