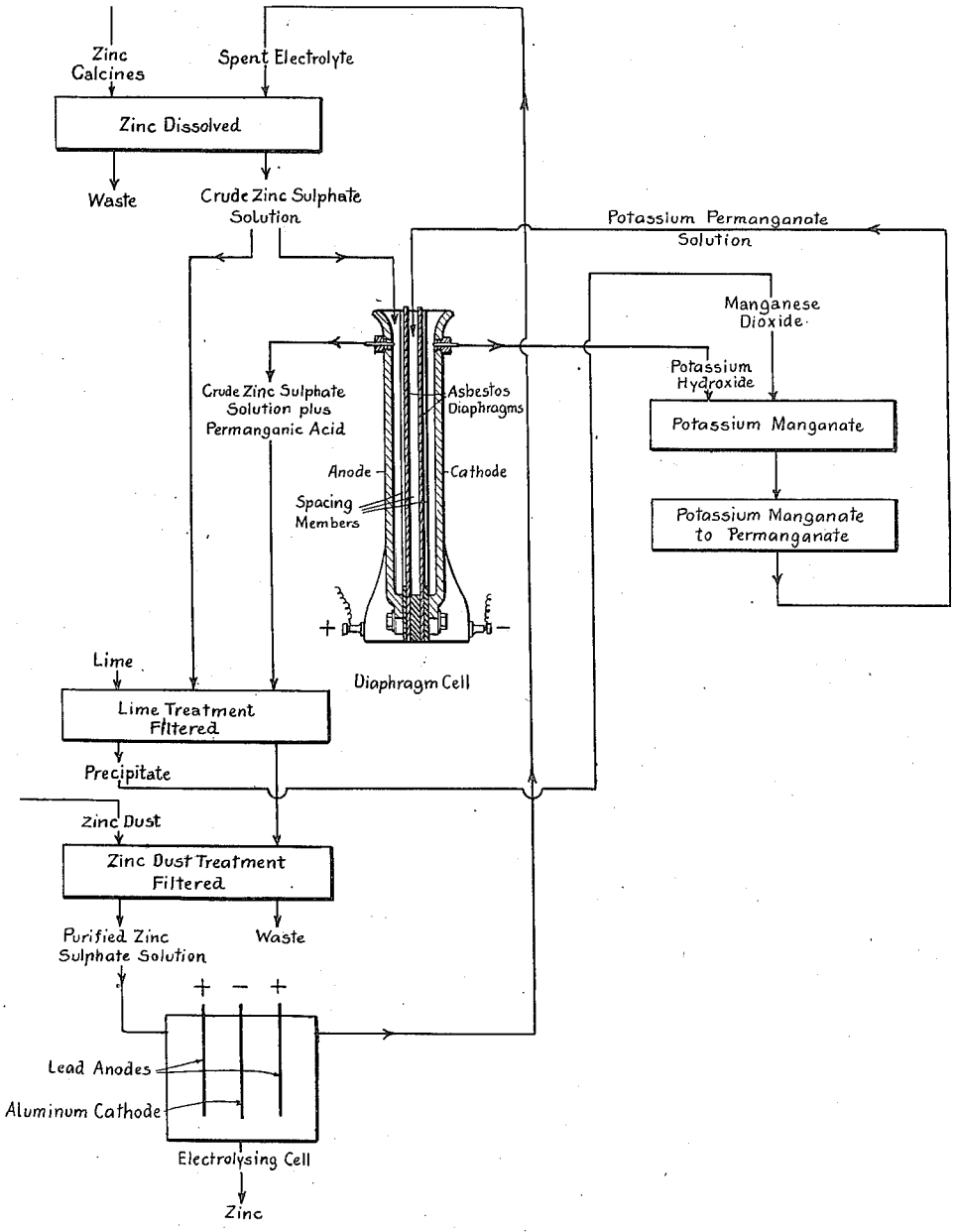
G. H. CLEVENGER.

ELECTROLYTIC PRODUCTION OF ZINC.

APPLICATION FILED MAY 7, 1917.

1,283,077. Patented Oct. 29, 1918.



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ELECTROLYTIC PRODUCTION OF ZINC.

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Application filed May 7, 1917. Serial No. 167,127.

To all whom it may concern:

Be it known that I, GALEN H. CLEVENGER, a citizen of the United States, residing at Palo Alto, in the county of Santa Clara, State of California, have invented certain new and useful Improvements in the Electrolytic Production of Zinc; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the electrolytic production of zinc from zinc sulfate solutions obtained by leaching or extracting zinc ores, concentrates or other zinc containing material.

In the production of zinc sulfate electrolytes, and in the electrodeposition of zinc therefrom, it has heretofore been proposed to remove various impurities which contaminate the zinc deposit or which interfere with the electrodeposition of the zinc.

The present invention relates to the removal of certain very detrimental impurities which even present in small amount seriously interfere with the electrodeposition of zinc from sulfate electrolytes.

I have found that cobalt, even when present in very small amounts, gives continual trouble during electrodeposition of the zinc; and I have also ascertained that methods of purification which are entirely effective for the removal of the usual impurities encountered in connection with other similar ores are inefficient when used with ores containing small amounts of cobalt. The presence of cobalt in the electrolyte is generally indicated by a characteristic pitting of the deposit.

I have also found that the cobalt can be more readily removed when it is in the cobaltic form than when it is in the more stable cobaltous form in which it usually occurs.

In the electrodeposition of zinc from zinc sulfate solutions where lead anodes are used, it is not feasible to use bleaching powder or other halogen oxidizing agent for oxidizing the cobalt, for the reason that chlorin, and, perhaps to a less extent, the other halogens, in solutions of zinc sulfate, causes a rapid disintegration of the lead of the anode which makes it practically impossible to carry out the electrolysis of the zinc sulfate solutions with success.

I have nevertheless found that cobalt can be precipitated from zinc sulfate solutions prior to electrolysis by the addition of a suitable oxidizing agent, such, for example, as a manganate or permanganate. For this purpose sodium or potassium manganate may be used, or potassium, sodium, barium, or calcium permanganates. Permanganic acid can likewise be used, if neutralized with an alkali before or after addition to the solution to be refined.

These reagents do not precipitate cobalt unless manganese be present, and furthermore, they do not precipitate the whole of the cobalt unless the whole of the manganese is precipitated. I have discovered that when manganese is present in such electrolytes and sufficient manganate or permanganate is added to completely precipitate the manganese, cobalt is also completely precipitated. If manganese is not present, it is necessary to add it, as oxidizing agents such as have been mentioned, although they contain manganese, in the absence of a simple salt of manganese do not precipitate cobalt. It is thought that cobalt is thrown down under this particular condition as a manganite. In carrying out the process the solution should be maintained neutral or slightly alkaline in order to bring about the complete precipitation of the manganese. If manganese is not already present in the solution, it may be added in the form of a soluble salt of manganese, preferably the sulfate. Sufficient of the oxidizing agent should be added to precipitate all the manganese. Other oxidizing agents than these above referred to, such as lead peroxid, etc., may be used, either alone or in combination with the manganates or permanganates, for the precipitation of manganese, and with it the cobalt.

The precipitation may be advantageously carried out in the following manner: In practice, if the zinc solution is not neutral, lime, or zinc oxid, (either pure or in the form of calcine), is added until the solution is neutral or slightly alkaline, when a solution of a soluble manganate or permanga-

nate is added until all the manganese is precipitated. The precipitate is separated from the solution by well known methods of settling or filtration. The precipitate may be re-used for the preparation of fresh manganate or permanganate, which may in turn be used for further precipitation of manganese and cobalt. In general a permanganate is preferred to a manganate for manganese and cobalt precipitation, on account of there being less likelihood of the permanganate containing injurious impurities, and also on account of the greater oxidizing power of the permanganate, which results in a higher precipitating efficiency.

A useful modification or embodiment of the process of the invention consists in the generation of permanganic acid in the solution to be refined—so to speak, *in situ*. This may be accomplished, for example, by electrolyzing a solution of potassium permanganate in a double diaphragm cell.

Upon electrolysis permanganic acid is formed in the anode compartment and caustic potash in the cathode compartment. In order to avoid dilution, the permanganic acid is deposited in a portion of the solution to be refined, rather than in water which would later be added to the solution to be refined. A convenient method of doing this is to circulate a portion of the zinc sulfate solution to be refined through the anode compartment. The caustic potash solution discharged from the cathode compartment is used in making potassium manganate, which after conversion into permanganate is again electrolyzed. The process is cyclic, the caustic potash being used repeatedly.

In the accompanying drawing, there is shown a flow sheet diagrammatically representing the various treatment steps in this modification of the invention. The apparatus in which these treatment steps are carried out and the products thereof are diagrammatically indicated on the drawing by appropriate legends, and the lines and arrows indicate the course of travel and the destination of such products. It is believed that the significance of the various diagrams and legends of the drawing will be clearly understood from the following description and that any further specific explanation of the drawing is unnecessary.

All or a portion of the zinc sulfate solution to be refined is circulated through the anode compartment of the diaphragm cell, and there becomes charged with permahganic acid. Caustic alkali may be continuously removed as formed in the cathode side of the cell, and re-used in the preparation of fresh manganate, which, after conversion into permanganate may be in turn again electrolyzed in the special permanganic acid cell. The solution of alkaline permanganate is added to the central compartment of the cell. The zinc solution containing the permanganic acid is neutralized *e. g.* with lime, or if only a portion of the solution has been charged with permanganic acid, this is mixed with the remainder of the untreated solution before neutralization. However, care should be taken to have sufficient permanganic acid present in the solution before neutralization to insure complete precipitation of the manganese. This operation precipitates the manganese and the cobalt, together with portions of certain other impurities, such as copper, etc.

The zinc sulfate electrolyte can be obtained from any naturally or artificially oxidized zinc ore or other zinc-containing material adapted to form a zinc sulfate electrolyte. Where other impurities than cobalt are present, such impurities can be removed when necessary by other well known methods of purification—such, for example, as the zinc dust treatment for the removal of cadmium, copper, lead, bismuth, arsenic, antimony, etc.—as will readily be understood The spent electrolyte may be employed for the solution of fresh zinc values. The strength of the electrolyte and the current used can, of course, be varied or modified in accordance with well known practice.

I claim:—

1. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises precipitating the cobalt by means of an oxidizing agent.

2. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises precipitating the cobalt by means of a manganate or permanganate.

3. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises precipitating the cobalt by means of a permanganate by adding permanganic acid and subsequently neutralizing with an alkali.

4. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises neutralizing the electrolyte and then precipitating the cobalt by means of an oxidizing agent.

5. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises neutralizing the electrolyte and then precipitating the cobalt by means of a manganate or permanganate.

6. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises neutralizing the electrolyte and then precipitating the cobalt by means of a

permanganate by adding permanganic acid and subsequently neutralizing with an alkali.

7. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes, which comprises adding a soluble salt of manganese and precipitating the cobalt by means of an oxidizing agent.

8. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes, which comprises adding a soluble salt of manganese and precipitating the cobalt by means of a manganate or permanganate.

9. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes, which comprises adding a soluble salt of manganese and percipitating the cobalt by means of a permanganate by adding permanganic acid and subsequently neutralizing with an alkali.

10. In the electro-deposition of zinc, the method of removing cobalt from zinc sulfate electrolytes containing manganese, which comprises circulating the electrolyte through the anode compartment of a double diaphragm cell in which a solution of alkaline permanganate is added to the central compartment of the cell.

In testimony whereof I affix my signature.

GALEN HOWELL CLEVENGER.