No. 689,018. Patented Dec. 17, 1901.

W. ORR.

METHOD OF RECOVERING CYANIDS.

(Application filed Mar. 5, 1901.)

(No Model.)

Fig. 1.

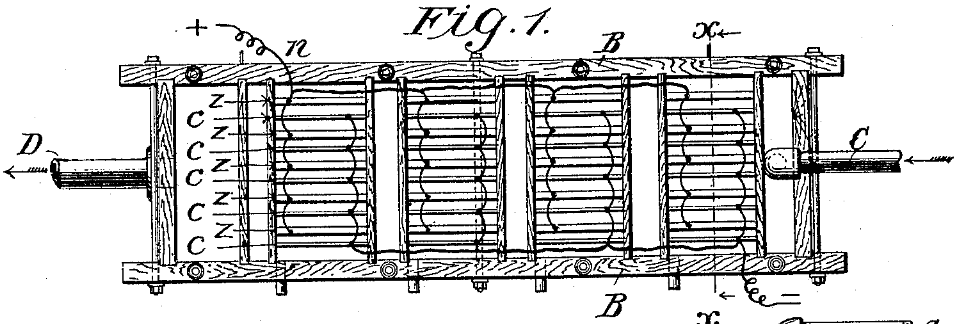


Fig. 2.

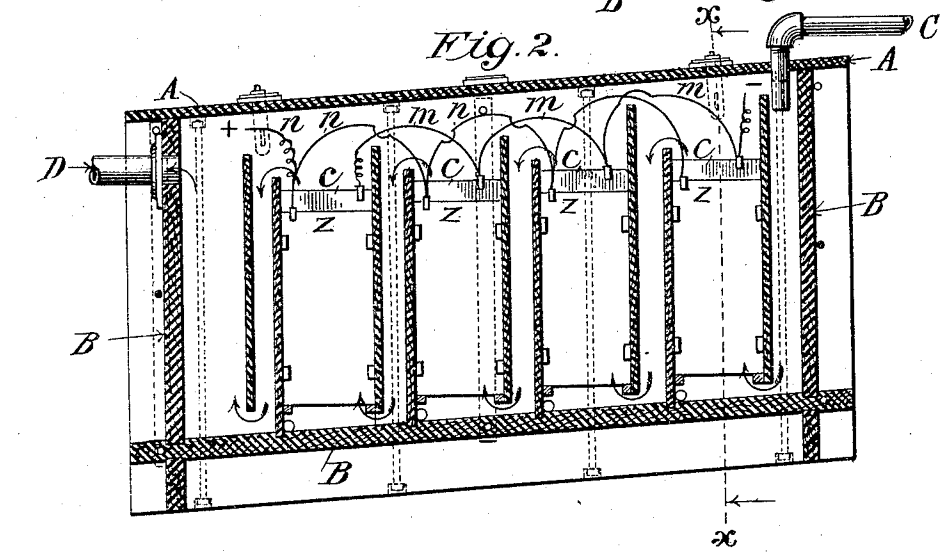
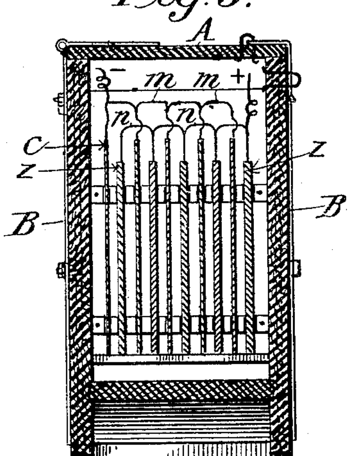


Fig. 3.



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METHOD OF RECOVERING CYANIDS.

SPECIFICATION forming part of Letters Patent No. 689,018, dated December 17, 1901.

Application filed March 5, 1901. Serial No. 49,794. (No specimens.)

To all whom it may concern:

Be it known that I, WILLIAM ORR, a subject of the Queen of Great Britain, residing in Salt Lake City, State of Utah, have invented certain new and useful improvements in methods of and processes for recovering cyanids of potassium or sodium from cyanid solutions fouled by the presence of double cyanids of zinc and copper with the alkali metals, of which the following is a full, clear, concise, and exact description, sufficient to enable persons skilled in the art to which it appertains to use the same.

My present invention relates to the regeneration of those solutions of cyanid which have become, as it is called, "fouled" while being used in the now well-understood process of extracting precious metals from ores or tailings by the formation therein of double cyanids of other than the precious metals—as, for instance, double cyanids of zinc and copper with potassium, sodium, or other alkaline metals. Certain ores and tailings bearing precious metals which it is desired to extract therefrom by the said cyanid process of extraction contain, on the one hand, considerable quantities of copper, which during the application of the said process combine with the cyanid of potassium or sodium employed as the solvent to form a double cyanid of copper and potassium or sodium. On the other hand, the zinc made use of at one stage of the process for the purpose of precipitating the precious metals likewise combines to a considerable extent with the said cyanids of potassium and sodium to form in the solution the double cyanid of zinc and potassium or sodium. In the third place, certain of the ores or tailings treated as aforesaid contain also zinc minerals, the zinc of which also tends in many instances to similarly combine with the said cyanids of the solution to produce an additional quantity of the double cyanid of zinc and potassium or sodium. The presence of these double cyanids in the solution constitutes always an obstacle or disadvantage to the solvent efficiency thereof in its relation to the precious metals, for not only is thereby withdrawn from active use in the solution a considerable proportion of the said cyanids of potassium or sodium, which otherwise would act directly as solvents of the precious metals, but the said double cyanids also constitute an addition of inert matter in the solution unavailable for the purpose of extracting the precious metals and positively injurious in that they proportionately impair the capacity of the solution for absorbing oxygen, the latter element being essential to the solution of the precious metals in the cyanid solution. Besides this, the presence of the copper in the solution interferes to a serious extent in the precipitating of the precious metals when zinc is used as the precipitant, the copper tending to become deposited to a slight extent upon the zinc, thus coating it and preventing the latter from coming into the proper contact with the precious metals held in the solution. For these and other reasons it has long been sought to devise some industrially economical method of removing from the solution the said copper and the said zinc thus held in the double cyanids of those metals with the alkali metals. In solutions thus fouled or infected by the presence of these undesirable compounds it is impossible to precipitate and separate the said zinc therefrom by methods invented by me and applicable to cases in which the ores or tailings are substantially free from copper, because, as I have discovered, the said double cyanids of copper and of zinc with the alkali metals combine together, so as to resist any alkaline hydrate and sulfid treatment.

The object of my present invention, therefore, is to produce a simple, economical, and industrially applicable method or process for removing from the said cyanid solutions employed as aforesaid the said injurious compounds of copper or zinc with alkaline cyanids. I obtain this object by the application of the process which I will now describe, making use therein, among others unnecessary to be specifically described for a full understanding of my invention, of certain apparatus illustrated in the accompanying drawings, in which—

Figure 1 represents a plan or top view (cover A being removed) of my copper-precipitating apparatus; Fig. 2, a central vertical longitudinal section thereof. Fig. 3 is a transverse vertical section taken on the line xx of Fig. 1.

Similar letters in each drawing indicate similar parts.

I provide a box B of any suitable form or construction adapted to the passage therethrough of the solution which it is required to treat by my said process. Within this box I support a series of copper plates $c\ c$, electrically connected with each other by conductors $m\ m$ and with a source of negative electricity. Intermediate between the said copper plates I likewise support a corresponding series of zinc plates $z\ z$, likewise electrically connected together by conductors $n\ n$ and with a source of positive electricity. The said solution containing the said undesirable compounds of zinc and copper is caused to flow through this box in any convenient manner, entering, for instance, by the aperture C and passing out by the aperture D. The solution is thus caused to pass around and between the aforesaid plates, and a current of electricity is simultaneously passed through the latter and the solution, as indicated. The electrical action decomposes the aforesaid compound of copper in the solution and causes the metallic copper to be deposited upon the copper plates or cathodes, while the liberated cyanogen attacks the zinc anodes and combines therewith to produce additional double cyanids of zinc and potassium or sodium in the solution. The solution during its passage through the box, as aforesaid, is thus deprived of its copper, the place of the double cyanid of copper and potassium or sodium being taken by an equivalent of the double cyanid of zinc and potassium or sodium. I next treat in the following manner the said solution so deprived of its copper: I transfer the solution to any convenient and suitable tank or reservoir and retaining it temporarily there, I add thereto a certain amount of alkaline hydrate—for instance, preferably, sodium hydrate, potassium hydrate, calcium hydrate, or barium hydrate or a combination of two or more of these.

In the ordinary course of practice it is not usually required or desirable to release all of the cyanid held up in combination as the double cyanid of zinc and potassium or sodium, the presence of zinc in the solution being much less detrimental than copper to its efficiency for the purpose of extracting the precious metals, and while by the use of my process it is entirely possible, if required, to release all of the cyanid so held up, a moderate proportion thereof is usually all that is required to restore the solution to its original strength. The amount of said hydrate to be added to the solution will depend, therefore, upon the extent to which it is desired to regenerate its solvent strength. For instance, assuming that in a ton of cyanid solution fifty pounds of the cyanid is held up in the form of double cyanid of zinc and potassium and that the solvent efficiency of the solution in relation to that particular extraction of precious metals for which it is employed requires the restoration of eight pounds of free cyanid of potassium. In such a case the amount of hydrate added should be sufficient to secure the disassociation of a sufficient quantity of the double cyanid of zinc and potassium to insure thereafter the complete combination with the zinc of all the sulfid added, as hereinafter described.

The reaction produced by the introduction of the aforesaid hydrates may be exemplified as follows: For instance, where a sodium hydrate is used, illustrating the action of the monovalent alkali metals,

$$ZnCy_2 2KCy+4NaOH+XH_2O= Zn(ONa)_2+2NaCy+2KCy+XH_2O$$

or where calcium hydrate is used, illustrating the action of the divalent alkaline earth metals,

$$ZnCy_2 2KCy+2Ca(OH)_2= ZnOCaO+CaCy_2+2KCy+2H_2O.$$

I find in the ordinary practical application of my invention to mill solutions requiring regeneration to a certain point of efficiency, as aforesaid, that the amount of alkaline hydrate introduced will approximate .1 per cent. or, say, two pounds per ton of solution, this proportion being of course, however, subject to increase should it be required to recover a larger percentage of free cyanid, as likewise in cases in which the solution is found to give an acid reaction. According to the various conditions presented by each case of different ores or tailings bringing into the solution certain elements and ingredients, different alkaline hydrates, including hydrates of one of the alkaline-earth metals, or different combinations of two or more of these may be used with efficiency, depending upon the particular conditions presented by each case, and it is therefore desirable to determine by actual laboratory tests in each instance the particular hydrate or hydrates best adapted for the particular purpose and occasion in hand. Taking, however, the case of a solution from which the copper has been removed, as aforesaid, and which presents no new or extraordinary features—say the average dilute cyanid solution—and which contains at this point in the application of my process, say, fifty pounds per ton of cyanid, held up in the said double cyanid of zinc and potassium and only four pounds remaining of free cyanid of potassium, I find that on its being required to raise the strength of such a solution in said cyanid of potassium to, say, twelve pounds per ton, the desired result can be successfully accomplished through the use of my method by the addition to the said solution of from two to three pounds per ton of the said hydrates, preferably, say, about two pounds of sodium and one pound of calcium hydrate to each ton of the solution. Having added the hydrate to the solution, as aforesaid, I next mix thoroughly, so as to insure as far as possible the disassociation of the double cyanid of zinc and potassium into a zincate and free cyanid of the alkali.

The next step in my process is to introduce into the solution treated as aforesaid an amount of an alkaline sulfid or sulfid of one of the alkaline-earth metals (preferably fused sodium sulfid sixty-five per cent. Na_2S) in amount somewhat less than required to precipitate all the zincate produced, as aforesaid, it being important to insure that no soluble sulfid shall be left unprecipitated in the solution. The effect of the introduction of the sulfid, as aforesaid, is to precipitate the zinc as zinc sulfid, which may afterward be separated in any convenient manner, either by decantation or by filtration through a filter-press. The filtered or supernatant liquor contains the cyanid which was formerly in combination with the zinc and which now appears as free potassium cyanid, rendered again available for further solution of the precious metals or other economic uses. It is of essential importance that the aforesaid hydrate should be added before the introduction of the sulfid and appreciably in advance thereof. Otherwise a complete reaction between the zinc salt and the soluble sulfid will be impossible and the solution correspondingly damaged rather than benefited by the introduction of the latter. The reaction in the solution resulting from the introduction therein, as aforesaid, of the sulfid may be expressed by the following formula:

$$Zn(ONa)_2+2NaCy+2KCy+XH_2O+Na_2S= ZnS(pptd)+2NaCy+2KCy+4NaOH+XH_2O.$$

The amount of soluble sulfid thus introduced will vary in each case according to the requirements within the limitations above described—that is to say, in no case should the amount of the sulfid exceed that required to precipitate all the zincate in the solution, and it is important, therefore, to introduce in every instance less of the soluble sulfid than is required to precipitate all of such zincate.

In cases where two or three pounds per ton of alkaline hydrates have been introduced into the solution, as aforesaid, I have obtained results entirely satisfactory by the subsequent introduction therein, as aforesaid, of from .08 to .1 per cent. of fused sodium sulfid.

Having thus described my invention, what I claim as new, and desire to secure by Letters Patent, is the following, viz:

1. The method of regenerating cyanid solutions which have become "fouled" by the presence of zinc and copper contained in the solution as the double cyanids of zinc and copper with the alkali metals, which consist, first, in passing through the solution from a series of zinc anodes to a corresponding series of metallic cathodes, a current of electricity, next, in introducing into the solution alkaline hydrate, next in introducing into the said solution, so treated, a soluble alkali-metal sulfid, and finally in separating from the solution the resulting zinc-sulfid precipitate substantially as and for the purposes described.

2. The method of regenerating cyanid solutions which have become "fouled" by the presence of zinc and copper contained in the solution as the double cyanids of zinc and copper with the alkali metals, which consists, first in passing through the solution from a series of zinc anodes to a corresponding series of copper cathodes a current of electricity, next in introducing into the solution alkaline hydrate, next in introducing into the said solution, so treated, a soluble alkali-metal sulfid and finally in separating from the solution the resulting zinc-sulfid precipitate, substantially as and for the purposes described.

3. The method of regenerating cyanid solutions which have become "fouled" by the presence of zinc and copper contained in the solution as double cyanids of zinc and copper with the alkali metals which consists first, in passing through the solution from a series of zinc anodes to a corresponding series of copper cathodes a current of electricity, next in introducing into such solution hydrates of sodium and calcium in proportions of about two to one, next introducing into the solution a soluble alkali-metal sulfid and finally removing the resulting zinc-sulfid precipitate, substantially as and for the purposes described.

4. The method of regenerating cyanid solutions which have become fouled by the presence of zinc and copper contained in the solution as double cyanids of zinc and copper with the alkaline metals which consists first, in passing through the solution from a series of zinc anodes to a corresponding series of metallic cathodes a current of electricity, next in introducing into such solution hydrates of sodium and calcium in proportions of about two to one, next introducing into the solution a soluble alkali-metal sulfid and finally removing the resulting zinc-sulfid precipitate, substantially as and for the purposes described.

5. The method of regenerating cyanid solutions which have become fouled by the presence of zinc and copper contained in the solutions as double cyanid of zinc and copper with the alkaline metals which consists first, in passing through the solution from a series of zinc anodes to a corresponding series of metallic cathodes a current of electricity, next in introducing into such solution, alkaline hydrate being hydrate of the monovalent alkali metals and hydrate of the divalent alkali metals in the proportions of about two to one, next introducing into the solution a soluble alkali-metal sulfid and finally removing the resulting zinc-sulfid precipitate, substantially as and for the purposes described.

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