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(54) A METHOD OF PRECIPITATING METAL FROM SOLUTION

(71) We, KLOCKNER-HUMBOLDT-DEUTZ AKTIENGESELLSCHAFT of Deutz-Mulheimer-Strasse 111, 5 Koln 80, Federal Republic of Germany, a German Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of precipitating cement metal from a solution with an added precipitating agent.

When precipitating metal in the form of cement metal from a solution of metal with an added non-noble metal as a precipitating agent, substantially the same type of processes, wherein ion exchange takes place between a metal which is more noble and a more base metal in accordance with the electromotive series, always take place in the so-called "cementing" without taking into consideration in detail which metals are concerned.

The concept "cementation" is defined as follows according to the Lexikon der Hüttentechnik von Lüger (Lüger Metallurgical Engineering Dictionary), 4th Edition 1963, Volume 5, Deutche Verlagsanstalt Stuttgart, page 733:

> "Precipitation of the metal from a solution by means of a more base metal. The more base metal has a more negative potential than the metal to be precipitated, it gives positively charged ions in solution, and thus charges itself negatively and discharges all cations with more positive potentials, so effecting separation in metallic form. Thus the potential difference of the various cations under the prevailing conditions is decisive".

During cementation or precipitation processes of various metals basic difficulties occur. The precipitated metal, the so-called cement metal, coats the surfaces of the more base metals used as a precipitating agent and thus hinders or even brings to a standstill the electrochemical reaction, i.e. exchange of ions. Other obstacles to the reaction arise from the fact that either an oxide layer is formed on the surface of the metallic precipitating agent or a coating of fine gas bubbles is formed—brought about by electrolytic processes.

The invention seeks to overcome these known difficulties with all types of metal precipitating processes and may improve both the economics of the process and the yield of metal plus the total efficiency of the process.

According to the invention there is provided a method of precipitating out cement metal from a solution containing ions of metal more noble than zinc in a vibration reactor, which contains the precipitant in the form of elements of zinc metal, whereby these metal elements are agitated at such a frequency and amplitude that the coating of cement metal deposited on the surface of the metal elements is worn away continuously by the motion.

In an advantageous refinement, the invention comprises using the method for zinc hydrometallurgy for the purpose of precipitating metal which is more noble in relation to zinc, for example copper, cadmium, cobalt, nickel, as a cement metal, from a zinc solution using pieces of zinc metal as a precipitating agent.

A vibration mill is thus used to advantage as a precipitating reactor.

In the following the invention and the technological and economic advantage which may be obtained therewith are described and illustrated in greater detail with respect to other processes known to us together with a representative example of application for hydrometallurgy of zinc:

Up to now it has been usual in hydrometallurgy of zinc for the neutral leaching solutions obtained to be freed from foreign metals dissolved therein, for example, Cu, Cd, Co or Ni and for metallic zinc powder to be added solution in agitators and thus for the stated impurities to be precipitated out.

The known method does however have the specific disadvantage among other things that the zinc powder must be produced for example by spraying metallic zinc. Moreover the reaction between the precipitating powder and the leaching solution takes place extremely slowly with a reaction period of up to several hours, particularly because an immunizing layer of zinc oxide is formed on the zinc par-

ticles which decisively inhibits progress of the reaction.

In contrast to this, employing the method of the invention, zinc is provided in the form of pieces as a precipitating agent instead of zinc powder, for example as granular material of 2—10 mm in size added to the leaching solution and that the entire precipitation process is carried out in a vibration mill as a precipitation reactor in order to produce the prescribed intensive shaking motion so that the zinc pieces constantly hit against one another.

As a result of the intensive shaking motion of the zinc pieces and with the invention in a simple and effective manner, the surfaces of the zinc pieces, which form a coating with the deposit of the more noble metal, constantly knock and rub against one another so that their surfaces are scraped clean and remain permanently active for the continuous reaction taking place by means of exchange of ions.

The intensive shaking motion of the precipitating reactor with the metal pieces also causes intensive turbulence in the leaching liquid. As a result intimate mixing of the solid and liquid phase is brought about at the interface. As a result the ion concentration in the region of the surface of the precipitating agent remains considerably greater than in the conventional precipitating method. As a result of this the transfer of material is further accelerated. In addition, hydrogen gas released by the reaction process is emulsified in fine bubbles in the leaching solution and may thus considerably improve the effect as a reducing agent.

Employing the invention, for example in zinc hydrometallurgy, an effect which improves profitability is produced by using cheap waste and intermediate products of zinc, for example waste metal, slags etc. originating from a smelting process, as a precipitating agent instead of expensive zinc powder. Among other things, during smelting and casting of the zinc cathodes gained in electrolysis, waste metals are obtained which only partially comprise metallic zinc. Previously these waste metals had to be dressed by means of segregating the zinc, wherein the segregating residues were passed back to the zinc leaching plant and brought to solution there.

All of these expensive dressing steps are superfluous and may be omitted if, in accordance with the theory of the invention, precipitation is undertaken in a vibrating container, not with expensive zinc powder but with waste metals, waste materials, granulated material or other granular or lumpy parts made of metallic zinc.

As a result of the forced vibration of the precipitating reactor its content achieves such a high energy content that the zinc pieces hit and rub against one another in constant intensive motion. As a result their surfaces are kept free from impurities or passivating, coatings—whether these are oxides, deposit of cement metal or collection of gas bubbles—whereby an accelerated material transfer is ensured as a result of exchange of ions between the metal and the solution.

This leads in the final effect to a considerable shortening of the process and moreover to better utilization of the metallic materials used, the consumption of which is reduced approximately to the stoichiometrical value, but in contrast this consumption may amount to 500% of the stoichiometrical quantity in the conventional precipitating drum.

The technological possibilities and economic advantages arising together with the example from hydrometallurgy of zinc are valid in an analogous manner also for further applications of the principle of the method in practically all desired processes of cementation in the field of hydrometallurgy.

In the following the invention will be described in greater detail together with some examples wherein one example of cementation previously known to us is compared with the one example of a precipitation process in accordance with the invention.

1) An example of a conventional cementation:

When leaching neutrally in zinc metallurgy a neutral leaching solution is obtained which has various quantities of dissolved ions of electrochemically more noble metals such as chiefly Cu; Ni; Co and Cd besides the dissolved zinc oxides.

These foreign metals regarded as impurities in relation to the zinc metal to be obtained must be precipitated out of the leaching solution, as even small concentrations thereof would have an extremely disadvantageous effect on the subsequent electrolysis of the zinc.

Precipitation of these metallic impurities takes place with Zn dust as the said impurities are electrochemically more positive than the cementation agent. Cementation is carried out advisably in stages so that the fractions of the cementate arising are further processed accordingly.

Cementation takes place discontinuously in an agitator vessel wherein the Zn dust is fed in batches. The leaching solution inserted contains: 150 g/l Zn; 500 mg/l Cu; 400 mg/l Cd; 30 mg/l Ni; 20 mg/l Co.

The leaching solution is subjected to the precipitating process in the first stage at 95°C with the addition of Zn dust, $CuSO_4$ and arsenic trioxide, wherein Cu, Co, Ni, and As become cement-like while Cd remains in solution.

The times for both cementation stages amount to approx. 260 minutes. The con-

sumption of Zn dust amounts to 530% of the stoichiometrical theoretical Zn quantity.

Result:

In the purified neutral leaching solution the following residues of impurities are found: Cu 0.1 mg/l, Co 0.2 mg/l, Ni 0.05 mg/l, Cd 0.2 mg/l.

2) An example of cementation according to the invention

Cementation of copper takes place from a zinc leaching solution using granulated zinc as a precipitating agent. The cementation process is carried out in a trial arrangement with the aid of a vibration mill, the rotational speed and amplitude of which may be set variably. A satellite device which may be heated and which is fixed to the vibration mill serves as a reactor having a filling volume of 8.5 dm^3. Filling with cementation agent amount to 65% of the reactor volume=5.5 dm^3, the quantity of leaching solution amounts to 35% of the reactor volume=3 dm^3.

The concentration of dissolved copper amounts to approx. 500 mg/l Cu at the beginning of the reaction.

The treatment temperature is 95°C. Ph value of the leaching solution is 4.

The zinc granulated material as a precipitating agent lies in the grain spectrum 3/10 mm.

Excitation is carried out at an amplitude of 10 mm at 12.5 Hz.

After only 29 seconds of cementation time a final copper concentration of less than 0.1 mg/l Cu is analysed.

Further application of the principle of the method to any other suitable desired processes of cementation in the field of zinc hydrometallurgy fall within the invention.

WHAT WE CLAIM IS:—

1. A method of precipitating out cement metal from a solution containing ions of metals more noble than zinc in a vibration reactor, which contains the precipitant in the form of elements of zinc metal, whereby these metal elements are agitated at such a frequency and amplitude that the coating of cement metal deposited on the surface of the metal elements is worn away continuously by the motion.

2. A method according to Claim 1, when the solution is a cyanide solution containing essentially noble metals.

3. A method of precipitating out cement metals according to Claim 1 and substantially as described herein.

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