

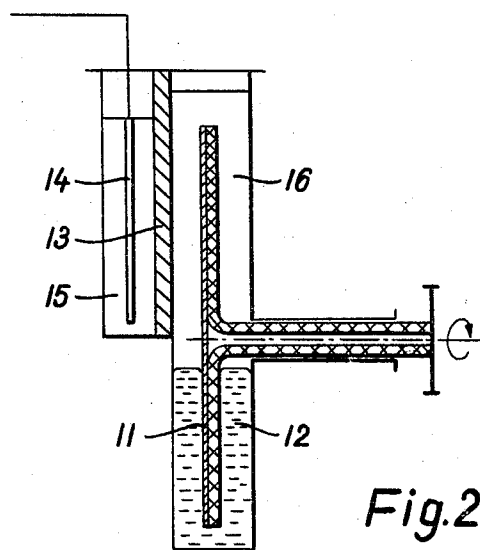
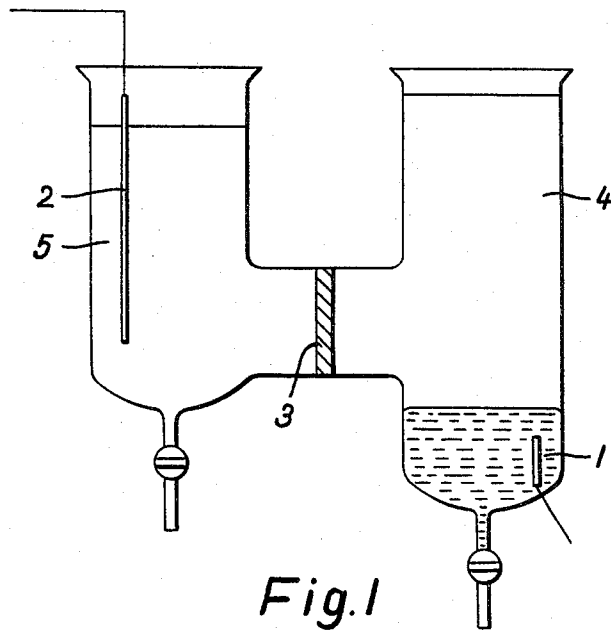
May 7, 1968

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3,382,163

METHOD OF ELECTROLYTIC EXTRACTION OF METALS

Filed July 28, 1964



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METHOD OF ELECTROLYTIC EXTRACTION OF METALS

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Filed July 28, 1964, Ser. No. 385,749

Claims priority, application Austria, Aug. 2, 1963,

A 6,246/63

15 Claims. (Cl. 204—105)

This invention relates to a method of electrolytic extraction of metals.

Various methods are known which use alkali metal sulfides for the refining of ores containing metals capable of forming sulfo-salts, such as the ores of arsenic, antimony, tin, gold, platinum, wolfram, and the like. The extraction of the metals from the solutions thus obtained has been attempted in various ways.

It is known to extract metals, for instance antimony, from the solution of their thio-acid salts by electrolysis. In practice the carrying out of such electrolysis, however, encounters great difficulties due to anodic formation of sulphur or its oxidation products. This decreases the electric current yield and makes regeneration of the electrolyte very difficult. (See Ullmann, "Encyclopädie der technischen Chemie," 3d Ed. Vol. 3, page 818). The dissociation voltage is thereby relatively high.

It is also known to obtain sulfo-salts forming metals by reacting solutions of such sulfo-salts with alkali metal amalgam. The desired metal is thereby obtained either as amalgam or in form of a metal powder which powder, however, frequently contains large amounts of mercury, so that it becomes necessary, for the production of pure metal, to go through further processes for the separation of the mercury. The intimate contact of the metal powder, as it is being formed, with the amalgam frequently leads to an undesired decomposition of the amalgam (particularly in the case of alkali metal amalgam) whereby hydrogen gas is developed which favors the formation of metal hydroxides.

It is accordingly among the principal objects of the invention to avoid the drawbacks of the prior art.

It is an other object of the invention to use an anode of alkali metal amalgam or alkali-earth metal amalgam for the electrolysis of solutions containing sulfo-salts of sulfo-salt forming metals, such as antimony, arsenic, mercury, tin, or the like. In carrying out this electrolysis according to the method of the present invention, sulfo-salts forming metals are electrolytically extracted from the solution of their sulfo-salts by making use of an anode of an alkali metal amalgam or an alkali-earth metal amalgam.

In contrast to the known methods of depositing metals from solutions of their sulfo-salts, the process according to the present invention does not need any additional electromotive force, as the cell made up of metal/solution of sulfo-salt/amalgam, provides a voltage, and the electrolysis may be carried out by putting an external load on the cell or by shunting it. To increase the current density it may, however, be appropriate to apply an additional external voltage for the deposition of the metal.

According to the present invention, a continuous metal deposition may be achieved without the use of any diaphragm, particularly if the sulfo-salt solution shows no tendency to lead to disturbing reactions with the amalgam of the anode.

According to a preferred embodiment of the invention, however, the anode space is separated from the cathode space by a diaphragm in a known manner (see, for instance, German Patent No. 687,388), in order to segregate the sulfo-salt solution from the anode. In such a case, the anode space contains appropriately a solution of an

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alkali metal sulfide or an alkali earth metal sulfide, while the cathode space contains the solution of the sulfo-salt. In this embodiment it is advantageous to maintain, in a known manner, a flow of the electrolyte, preferably a solution of an alkali earth metal sulfide or an alkali metal sulfide, through the diaphragm in the direction towards the cathode. This may, for instance, be done by introducing into the anode space an additional amount of a solution of an alkali earth metal sulfide or an alkali metal sulfide, so as to keep the liquid level in the anode space higher than in the cathode space.

According to a further embodiment of the invention, it is advantageous to carry out the electrolysis in cells having vertically arranged amalgam anodes. In this manner it becomes possible to provide within a small space electrodes with relatively large surfaces, without any need to increase the electric current density to an undesired extent. Vertically arranged electrodes avoid the disturbances that may be brought about by horizontally arranged electrodes caused by metal particles falling off the cathode, or by accumulation of hydrogen on the diaphragm.

Further advantages of the process according to this invention include that no energy or only small amounts of energy need to be provided for the electrolysis and that soluble alkali metal sulfides or alkali earth metal sulfides, respectively, are produced at the anode. If, for instance, a solution of sodium-thioantimonite is electrolyzed in the above described manner, using sodium amalgam as anode and a solution of sodium sulfide as the anode electrolyte, metallic antimony will be deposited on the cathode. The sulfide residue of the sulfo-salt is obtained as sodium sulfide. The latter, together with the soluble sulfide which may have been added at the side of the anode, may be removed from the electrolyte in a relatively simple manner by crystallization.

Thus, one of the important differences between the process of the present invention and the known electrolytic processes of producing metals capable of forming sulfo-salts, is that only one reaction takes place at the anode leading to the formation of alkali metal sulfide or alkali earth metal sulfide, respectively. In distinction from those methods according to which the metal is obtained by reaction with amalgam, the metal produced by the present invention does not come in contact with the mercury, and further steps for the separation of the latter are unnecessary. Furthermore, a contamination of the mercury is safely avoided, so that it may be re-introduced, without special purification, in a cell (for instance, in a chlorine-alkali-cell).

Example 1

100 cubic centimeters of a thioantimonide solution containing 7.7% (percent) antimony are used as the cathode electrolyte, and 100 cubic centimeters of a sodium sulfide solution as the anode electrolyte. The cathode space is separated from the anode space by a diaphragm. A plate of platinum serves in this example as the cathode, and sodium amalgam having a concentration of 0.1 to 0.5% (percent) of sodium, serves as the anode. The cell: antimony (on platinum)/thioantimonite/sodium sulfide/sodium amalgam has an electromotive force of about 1 volt and the electrolysis is put into operation by putting a load on the cell or by shunting it. In order to increase the current density, an additional external voltage is applied, the magnitude of which will depend on the desired electric current intensity and the resistance in ohms of the cell. The antimony metal is obtained with an electric current yield of more than 90% (percent). Calculated on the basis of the consumption of sodium, the yield is from 85 to 90% (percent). Sodium sulfide is obtained as a by-product with the same yield.

Example 2

The arrangement shown in FIG. 1 is used, the amalgam anode 1 being disposed horizontally and the metal cathode 2 and the diaphragm 3 being disposed vertically. The apparatus consists of glass. The diameter of the two vertical containers is about 40 mm., and the height of the said containers is about 100 to 140 mm. The diaphragm has a diameter of 35 mm., the pore size of the diaphragm being 40 to 90 millimicrons. An approximately 10% solution 4 of Na₂S is placed into the compartment above the amalgam anode and the sulfo-salt solution 5 is placed into the compartment of the metal cathode, the said sulfo-salt solution being e.g. a thioantimonite solution comprising about 40 to 90 grams of antimony per liter. The anode 1 consists of sodium amalgam. If the cell is short-circuited via an ampèremeter an electric current starts to flow and metallic antimony is deposited at the cathode.

Example 3

The same arrangement is used as in Example 2, but a solution of thioantimonite comprising about 10 grams of tin per liter is employed as the sulfo-salt solution. Again an electric current will flow through the cell when it is short-circuited. In order to increase the current density, an additional voltage may be applied from outside, and tin will then be deposited at the cathode in good yield.

Example 4

The working conditions are as in Example 3, but a solution of HgS in an alkali metal sulfide is used, so that mercury will be deposited at the cathode.

It is recommendable to keep the liquid level of the alkali metal sulfide solution higher at the anode than in the cathode compartment, so that just a sufficient amount of alkali sulfide solution will flow from the anode to the cathode for preventing the diffusion of sulfo-salt towards the anode. It has been found that the same conditions will prevail if potassium sulfide is used instead of sodium sulfide, and potassium amalgam is employed in the place of sodium amalgam.

Example 5

An electrolysis procedure is performed on a larger scale. For this purpose a vertical amalgam anode according to FIG. 2 is used. A rotatably located iron plate 11, which is provided with a protective insulation on one side, the said iron plate having a diameter of 30 centimeters, dips into the amalgam 12. A metal electrode 14 (copper) is disposed opposite to the said first electrode and separated therefrom by a diaphragm 13. The sulfo-salt solution 15 is placed into the cathode compartment, and the alkali metal sulfide solution 16 is placed into the anode compartment. The liquid level in the anode compartment is correspondingly higher, so as to allow the passage of liquid through the diaphragm in the direction towards the cathode. The rate of flow of electrolyte into the cathode compartment is maintained such that e.g. an average concentration of about 40 to 50 grams of antimony per liter is obtained. In the anode compartment only the solution removed by passage through the diaphragm is replenished by corresponding quantities. The concentration of amalgam is kept at about 0.2%.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with a specific exemplification thereof will suggest various other modifications and applications of the same.

It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific exemplification of the invention described herein.

Having thus described the invention, what I claim as new and desire to be secured by Letters Patent, is as follows:

1. In a method of electrolytic extraction of sulfo-salt forming metals in an electrolytic cell, the steps comprising electrolyzing a solution of the sulfo-salt of said metal and utilizing an anode comprising a member of the group consisting of an alkali metal amalgam and an alkali-earth metal amalgam.

2. In a method according to claim 1, in which the metal of the sulfo-salt is selected from the group consisting of arsenic, antimony, tin, gold, platinum and wolfram.

3. In a method according to claim 1, in which the anode comprises sodium amalgam.

4. In a method according to claim 1, in which the necessary voltage for the electrolysis is provided by putting an external load between the cathode and the amalgam anode.

5. In a method according to claim 1, in which said amalgam anode in said electrolytic cell is arranged vertically.

6. In a method according to claim 1, in which a diaphragm separates the anode space from the cathode space.

7. In a method according to claim 6, in which the anode space comprises the solution of a sulfide selected from the group consisting of alkali metal sulfides and alkali-earth metal sulfides, while the cathode space comprises the solution of the sulfo-salt of the metal to be extracted.

8. In a method according to claim 6, in which the flow of the electrolyte through the diaphragm in the direction towards the cathode is maintained throughout the electrolysis.

9. In a method according to claim 8, in which said constant flow of the electrolyte is achieved by maintaining the liquid level in the anode space higher than in the cathode space.

10. In a method according to claim 1, in which the necessary voltage for the electrolysis is provided by shunting the cell.

11. In a method according to claim 10, in which an additional external voltage is applied to increase the current density.

12. In a method of producing metallic antimony according to claim 7, the steps comprising using sodium amalgam as anode, a solution of sodium sulfide as the anode electrolyte, and a solution of sodium-thioantimonite as the cathode electrolyte.

13. In a method of producing metallic tin according to claim 7, the steps comprising using sodium amalgam as anode, a solution of sodium sulfide as the anode electrolyte, and a solution of sodium-thioantimonite as the cathode electrolyte.

14. In a method of producing metallic antimony according to claim 7, the steps comprising using potassium amalgam as anode, a solution of potassium sulfide as the anode electrolyte, and a solution of potassium-thioantimonite as the cathode electrolyte.

15. In a method of producing metallic tin according to claim 7, the steps comprising using potassium amalgam as anode, a solution of potassium sulfide as the anode electrolyte, and a solution of potassium-thioantimonite as the cathode electrolyte.

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