No. 669,442. Patented Mar. 5, 1901.

H. A. FRASCH.

PROCESS OF RECOVERING AND SEPARATING METALS BY ELECTROLYSIS.

(Application filed Sept. 15, 1900.)

(No Model.)

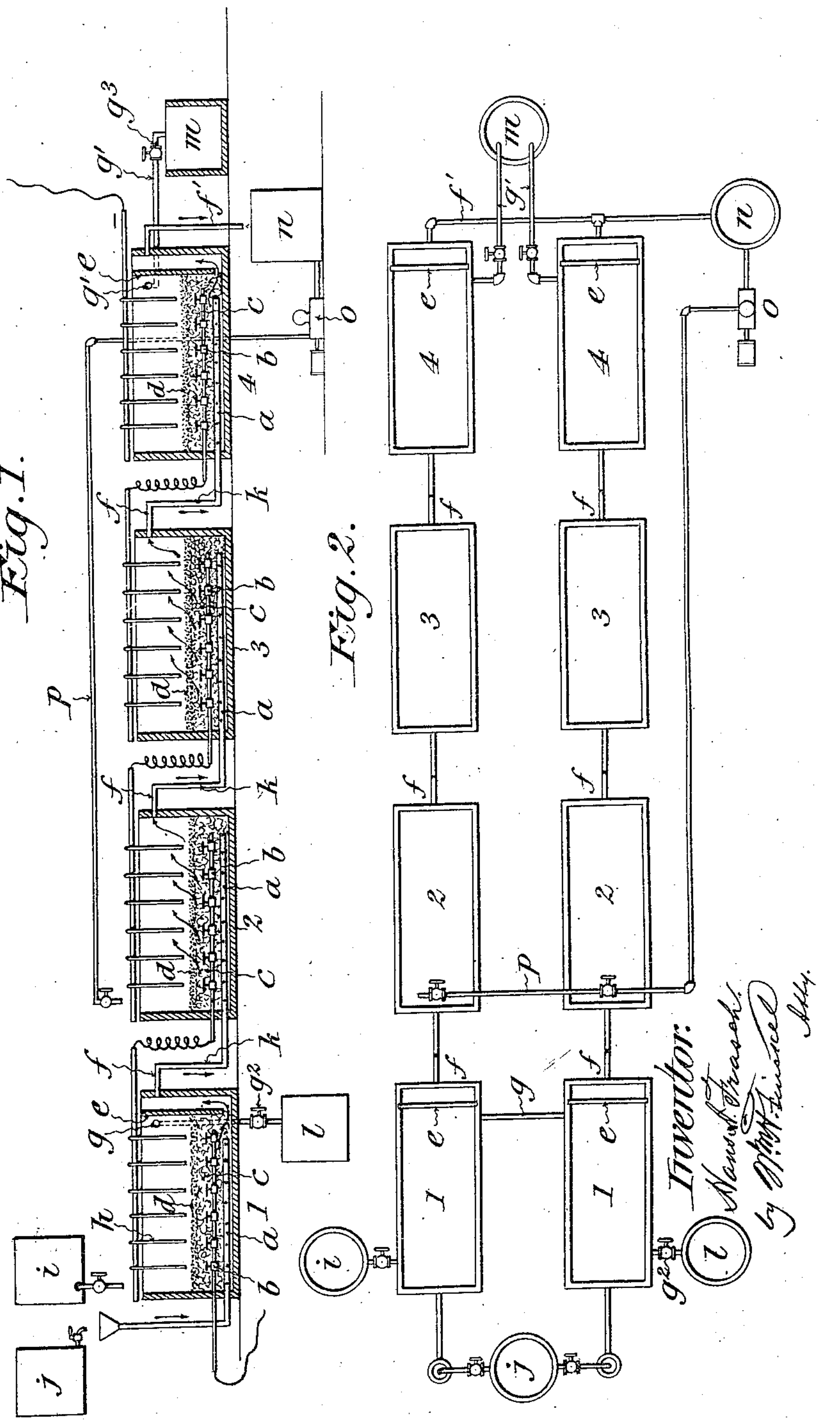

Fig. 1.

Fig. 2.

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PROCESS OF RECOVERING AND SEPARATING METALS BY ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 669,442, dated March 5, 1901.

Application filed September 15, 1900. Serial No. 30,154. (No specimens.)

To all whom it may concern:

Be it known that I, HANS A. FRASCH, a citizen of the United States, residing at Hamilton, in the county of Wentworth and Province of Ontario, Canada, have invented a certain new and useful Improvement in Processes of Recovering and Separating Metals by Electrolysis, of which the following is a full, clear, and exact description.

This invention relates to an electrolytic process of recovering and separating metals from bodies of greater or less complexity, and more especially such as complex ores, matte, slags, &c.

In carrying out my invention I take the body containing the metals to be extracted and whether such body contains only those metals or others and utilize it in the form of an anode as part of an electrolytic bath or a number of baths. The cathode may consist of any usually-employed substance, and I prefer to use a cathode consisting of the same kind of metal as will be deposited upon it.

The object of my invention is to bring the metals represented in the anode in solution and by electrolyzing this solution depositing from it at a given tension of an electric current certain metals upon the cathodes, at the same time resaturating the electrolyte constantly by passing it repeatedly through anodes of the same composition, thereby continuously enriching the electrolyte more and more with such metals as may be present in the anode in comparatively small proportions and which require for deposition an electric current of higher tension, and, finally, by the complete deposition of the metals desired to be removed from the electrolyte a concentrated solution of the remaining metals is obtained, from which the latter may be removed by electrical or chemical means.

My invention is particularly applicable in the treatment of copper-nickel ore or matte. To treat such matte and bring the metals contained therein into solution, I use the matte for anode in an electrolytic bath, in which a solution of a salt of an alkali forms the electrolyte, ordinary carbon or copper cathodes being employed. By electrolysis I obtain caustic soda at the cathode and a solution of the corresponding salts of the metals of which the matte is composed at the anode, while the sulfur contained in the matte remains as residuum in concentrated form. While I prefer to do so, I do not limit myself to producing the solution in this manner, and the solution may be obtained by chemical or any other process. The metallic solution thus obtained I subject to electrolysis in a series of baths, all having matte anodes and cathodes composed, preferably, of copper, the anodes of the baths consisting of disintegrated matte and arranged in such a manner that the metallic solution which forms the electrolyte passes through the body of the anode and through a suitable diaphragm, past the cathodes, and through an overflow onto the anode of the bath next in series, and so on through any desired number of baths. The least electropositive metal represented in the electrolyte—in this instance copper—is deposited at the cathodes in the passage of the electrolyte past the cathodes, care being taken that the tension of the electric current does not greatly exceed the electrochemical requirements for copper, the solvent agent represented in the electrolyte as liberated dissolving a corresponding quantity of fresh metals from the metal-bearing anode of each bath, and by the repeated deposition of copper only and resaturation with the compound metals of the anode the electrolyte becomes more and more saturated with the other metals and impoverished in copper until eventually a point of saturation is reached convenient for the recovery of the metals other than copper. To remove the last quantities of copper yet contained in the electrolyte, the latter in its passage through the bath last in series is not allowed to pass the cathodes, but is brought to circulate through the anode only and below a diaphragm, permitting only enough of the electrolyte to pass through the diaphragm as will insure complete exhaustion of the copper still contained in the electrolyte at the cathodes. The solution derived from the cathode-section of the bath last in series contains then only nickel, iron, and cobalt. The iron is removed from the solution by chemical treatment, and the nickel may be separated from the cobalt by electrolysis or by chemical means.

In the accompanying drawings, illustrating apparatus for practicing my invention, in the two figures of which like parts are similarly designated, Figure 1 is a sectional elevation. Fig. 2 is a diagram of a double battery.

Before proceeding to describe the invention in detail I wish to say that I do not limit my invention to any special form of apparatus or to the character of the material, body, or substance from which the anode is formed, and as to the anode I wish to repeat that it may be of any refractory substances in nature or art—such as ores, mattes, slags, and the like—or complex metallic bodies of other forms, such as concentrates not strictly alloys, and hence in describing and claiming the invention I use the term "ore" and the term "metalliferous body" as including these various substances.

The vessels 1 and 4 at the beginning and end of the series of electrolytic baths are alike and comprise suitable fluid-tight receptacles having in their bottoms perforated pipes a, carbon or other conductors b, suitably wired to a source of electricity, a mass of the metalliferous body c overlying the carbons and constituting an anode, a diaphragm d of granular or equivalent permeable material, such as sand, placed upon the anode, a vertical bridge-wall e across one end of the receptacle and extending from its top nearly to its bottom, an overflow-pipe f at one end, an overflow-pipe g opening from the other side of the bridge-wall, and a cathode h, which may be composed of a series of copper or other plates suitable to receive the selected metal or metals to be deposited. Between these two vessels may be arranged any number of vessels 2 and 3 in all substantial respects like the vessels 1 and 4, excepting that they have no bridge-walls and no overflows, such as those designated g.

A water-tank i may be arranged to supply water to the vessel 1, and the tank j may be arranged to supply the exciting fluid to the pipe a of the same vessel. The pipes a of the succeeding vessels are connected with the outlet of the next preceding vessel by hose or pipes k. The overflow-pipe g of vessel 1 above the diaphragm leads to a tank l, and the pipe g' of vessel 4 leads to a tank m, while the pipe f' of vessel 4 leads to a tank n, which is connected with a pump or other forcing device o, which returns the fluid to any of the vessels, as 2, through pipe p.

The use of a diaphragm may be omitted in such vessels as 2 and 3 if the purity of the copper deposited is not an object.

As an example of one way of carrying out my invention I proceed as follows: I supply tank j with common-salt solution of a preferred strength—say about 20° Baumé—and permit this solution to flow through pipe a into vessel 1, through the anode c and diaphragm d therein, until the solution reaches the overflows f and g, when the valve g^2 of overflow g is closed and the inflow of salt solution is diminished and the salt solution allowed to leave the vessel 1 through overflow f and pass into the second vessel in series. An electric current of the required electrochemical tension is then passed through the vessel 1, and the metallic-chlorid solution formed at the anode of vessel 1 passes below the diaphragm, through overflow f, to the anode of the second vessel, while a limited quantity of water is allowed to flow from tank i to the cathodes of vessel 1 whenever the electrolyte around the cathodes has accumulated enough alkali. This alkaline solution is then withdrawn through overflow g and may be returned to the tank and used over for further concentration, or it may be withdrawn and otherwise used, while the quantity withdrawn is constantly replenished by a corresponding quantity of water or salt brine from tank i. The metallic-chlorid solution from tank 1, passing through overflow f, is delivered to the anode of vessel 2 and passes through the anode and diaphragm d of vessel 2. The electric current is then admitted to vessel 2 at a tension equivalent to the requirements of the metal to be deposited at the cathode—in this instance copper—and a quantity of copper equivalent to the electric current is deposited onto the cathodes of vessel 2, while at the same time a quantity of the complex metals of which the anode is composed is dissolved from the anode and embodied in the electrolyte, so that when the electrolyte leaves vessel 2 by the overflow it contains a larger quantity of metals other than copper than when it entered vessel 2. This operation is repeated successively in any desired number of electrolytic baths constructed similarly to vessel 2, and the electrolyte constantly giving up copper only to the cathodes and dissolving all the time other metals contained in the anode becomes more saturated with those metals in each successive vessel until it has finally reached a concentration which renders it fit for recovery of the metals other than copper. When the electrolyte has reached this point of concentration, it passes through overflow f to the final vessel 4, of which again there may be any desired number. After the vessel 4 has been filled to the overflow g' the bulk of the electrolyte passes through the anode below the diaphragm, leaving this vessel 4 through overflow f'. The valve g^3 in the pipe g' being closed, no circulation through the diaphragm in vessel 4 occurs, and thereby the electrolyte above the diaphragm becomes exhausted of copper, the latter being deposited on the cathode. Valve g^3 of vessel 4 is then opened and a quantity of electrolyte is permitted to flow through pipe g', which causes a corresponding quantity of electrolyte to flow from the anode of vessel 4 through the diaphragm to the cathodes of vessel 4. This quantity is so regulated that the copper contents does not exceed the electrodepositing capacity of the cathodes, so that while the electrolyte coming from the anode and passing through the diaphragm still supplies copper it leaves vessel 4 by overflow *g'* free from copper. So much of the electrolyte as is not allowed to pass through the diaphragm *d* leaves vessel 4 through overflow *f'* and enters receptacle *n* and is returned by pump *o* or other means to vessel 2 or any other of the series in which a like operation is performed. The metallic-chlorid solution leaving vessel 4 through overflow *g'* is then withdrawn from the system and the iron is removed by chemical means, while the nickel, cobalt, and other metals may be separated from each other by ordinary electrolytic or chemical methods.

Having thus described the application of my process to a specific substance, I wish it understood that I do not limit my invention to the use of one class of ores only, but may employ for anodes in a series of baths different kinds of metalliferous bodies—as, for instance, the anodes in vessels 1, 2, and 3 may be composed of copper matte and in vessel 4 the anode may be composed of nickel-bearing iron slag or other metalliferous bodies or the anode in each of the vessels may be of different composition. The electrolyte also may differ between the individual vessels, and it may be withdrawn from any vessel of the series and returned to the same or any other of the vessels, if so desired. That part of the electrolyte supplying the cathode of the vessel 4 for the purpose of exhausting the last quantity of copper instead of passing through the diaphragm, as I prefer to do, may also be taken from the overflow of vessel 3 and directly conducted to the cathode of vessel 4.

If the substance used for anodes contains sulfur, the sulfur is recovered by distillation or other well-known methods from the residuum of the anode after the metals are extracted and forms a valuable by-product.

Having thus described my invention, what I claim is—

1. The method of separating metals from their ores, which consists in providing an electrolytic bath with a permeable anode composed of the ore bearing the metals to be obtained covered with a diaphragm composed of a granular, permeable substance, and circulating through such anode and through the diaphragm to the cathode an electrolyte capable of dissolving the metals, and simultaneously electrodepositing on suitable cathodes the metals to be separated, keeping the other metals in solution, substantially as described.

2. The method of separating by electrolysis metals from their ores, which consists in providing an electrolytic bath with a permeable anode composed of the ore bearing the metals to be obtained, circulating successively through a series of such anodes an electrolyte capable of dissolving the metals contained therein, simultaneously electrodepositing a selected metal on suitable cathodes and thereby continuously removing such metal and enriching the contents of the solution with the other metals, substantially as described.

3. The method of recovering copper and separating nickel and cobalt from matte or ore, by electrolysis, which consists in providing a number of electrolytic baths with permeable anodes composed of the material to be treated, electrolyzing the salt of an alkali in the first of the series of baths and circulating the metal-bearing electrolyte thereby obtained successively through the anodes and past the cathodes of the baths next in series, thereby electrodepositing the copper onto the cathodes of the successive baths and constantly enriching the electrolyte with nickel and cobalt, substantially as described.

4. The method of recovering copper and separating nickel and cobalt from matte or ore, by electrolysis, which consists in providing a number of electrolytic baths with permeable anodes composed of the material to be treated, electrolyzing the salt of an alkali in the first of the series of baths and circulating the metal-bearing electrolyte thereby obtained successively through the anodes and past the cathodes of the baths next in series, thereby electrodepositing the copper onto the cathodes of the successive baths and constantly enriching the electrolyte with nickel and cobalt, and finally circulating the electrolyte past the cathode only of the succeeding bath, thereby depositing the last traces of copper and separating the remaining solution of nickel and cobalt.

5. In the process of separating metals from their ores, by electrolysis, circulating an electrolyte capable of dissolving the metals to be separated, between a soluble anode containing the metals to be extracted and a cathode, and through an intervening diaphragm consisting of a granular substance inert to the electric current and chemical action of the electrolyte, and electrolyzing the solution.

6. In the process of separating metals from their ores, by electrolysis, circulating an electrolyte capable of dissolving the metals successively through the body of a permeable anode bearing the metals to be separated and a diaphragm consisting of a granular substance inert to the electric current and chemical action of the electrolyte and past the cathode, and electrolyzing the solution.

7. The method of exhausting an electrolyte composed of the salts of a number of metals of the individual less-electropositive metals contained therein, by circulating the electrolyte through a permeable anode containing the metals represented in the electrolyte, electrolyzing the solution, passing a portion only of the electrolyte through a diapragm to the cathode and entirely precipitating the metal therefrom and simultaneously drawing off the remaining electrolyte from the anode-compartment.

8. The method of exhausting an electrolyte composed of the salts of a number of metals

of the individual less-electropositive metals contained therein, by circulating the electrolyte in part through a permeable anode on one side of a diaphragm and in part past the cathode on the other side of the diaphragm, thereby exhausting the electrolyte passing the cathode of the less-positive metals and simultaneously enriching the anode fluid with the metals contained in the anode, substantially as described.

9. The method of separating metals from their ores, which consists in providing an electrolytic bath with a permeable anode composed of ore bearing the metals to be obtained and circulating through such anode and through a diaphragm to the cathode an electrolyte capable of dissolving the metals, and simultaneously electrodepositing on suitable cathodes the metals to be separated, keeping the other metals in solution, and finally recovering the sulfur from the residuum of the anode, substantially as described.

In testimony whereof I have hereunto set my hand this 14th day of September, A. D. 1900.

HANS A. FRASCH.

Witnesses:
WM. H. FINCKEL,
C. A. NEALE.