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C. F. CARRIER, Jr.

APPARATUS FOR THE ELECTROLYTIC EXTRACTION OF METALS.

APPLICATION FILED JAN. 30, 1905.

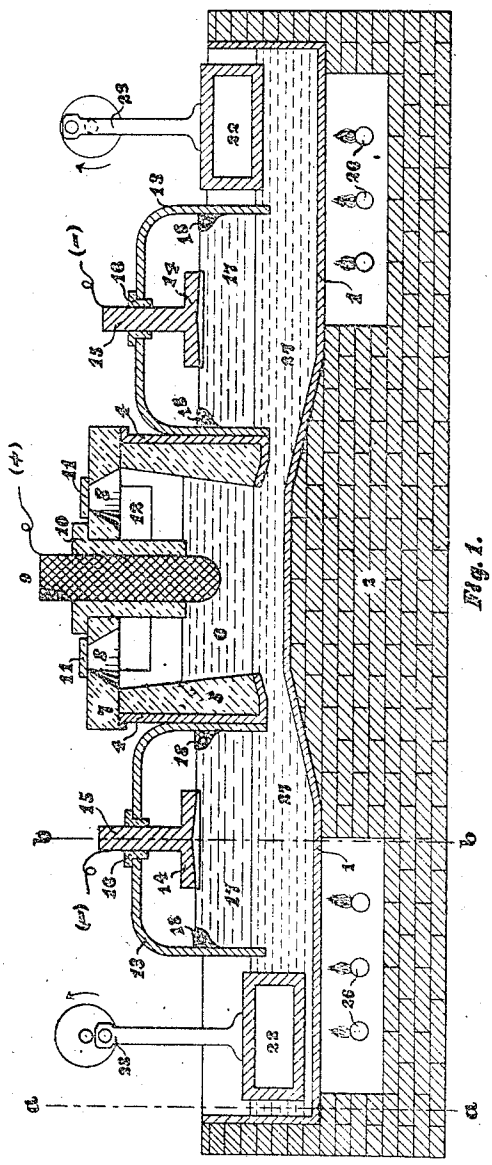


Fig. 1.

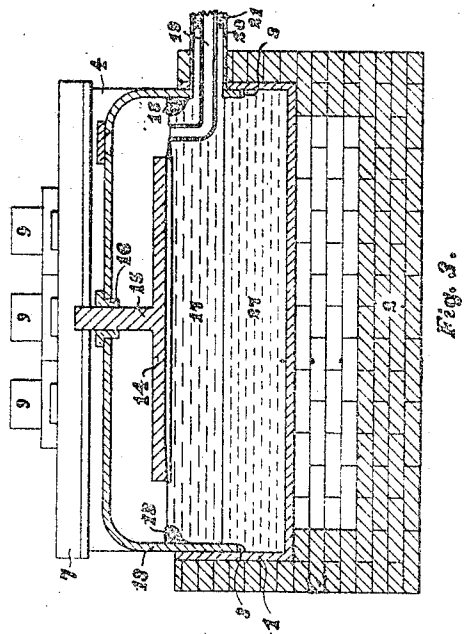


Fig. 3.

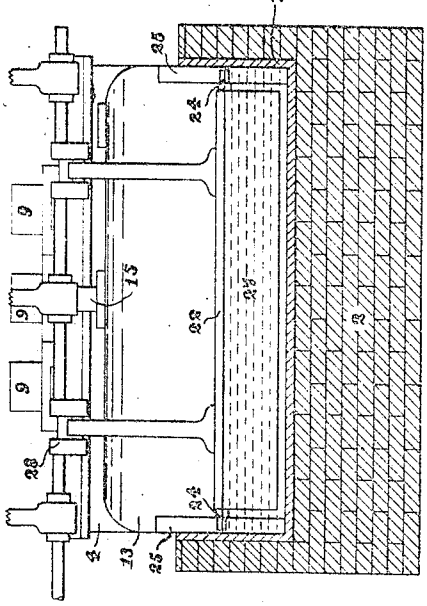


Fig. 2.

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APPARATUS FOR THE ELECTROLYTIC EXTRACTION OF METALS.

No. 830,051. Specification of Letters Patent. Patented Sept. 4, 1906.

Application filed January 30, 1905. Serial No. 243,184.

To all whom it may concern:

Be it known that I, COURTLAND F. CARRIER, Jr., a citizen of the United States, residing at Elmira, in the county of Chemung and State of New York, have invented certain new and useful Improvements in Apparatus for the Electrolytic Extraction of Metals, of which the following is a specification.

My invention relates to improvements in apparatus for carrying on the processes for the electrolytic extraction of metals which are lighter than the electrolytes from which they are separated; and my object is to provide certain novel features in the construction of such apparatus whereby the efficiency and facility of working such processes will be increased and the cost of producing these metals will be diminished.

I attain my object by the arrangement of the several parts of the apparatus, as illustrated in the accompanying drawings, in which—

Figure 1 is a longitudinal vertical section of an electric furnace embodying my improvements, and Figs. 2 and 3 vertical transverse sections of the same on the lines *a a* and *b b* in Fig. 1 looking to the right.

Like numerals designate like parts in the several views.

Referring to the drawings, 1 indicates a large "pan" which is set in a mass of masonry 2. This pan is best made of cast-iron and is preferably of rectangular form. The middle portion of the bottom is raised somewhat above the level of the two end portions, this raised portion extending across the entire width of the pan, forming a shallow portion at the center and depressions of greater depth at each end. The other parts of the furnace up to and including 18 are supported within this pan by means of iron cleats 3, cast with the pan or riveted to the sides or by other suitable means.

Over the raised portion of the pan is located the anode-compartment, which is inclosed by a rectangular frame 4, preferably of cast-iron. This frame is lined with basic material 5, such as magnesia or other material, which will not be attacked by the electrolyte 6 or by the gases given off during the process. The compartment is closed at the top by a cover 7, composed of material similar to the lining. This cover is supplied with feed-holes 8 for replenishing the supply of electrolyte. Openings are also provided for the anodes 9. The most suitable material for the anodes is graphite. To protect the anodes from the action of the gases, they are surrounded by sleeves 10 of the same material as the lining. The feed-holes are covered with small slabs 11 of this same material or of soapstone. The number of anodes used may vary within the limits of practicability, according to the capacity desired, the width of the furnace being increased to accommodate the desired number. At the back of the furnace is located a port 12 for conducting off the gases evolved during the process.

The cathode-compartments are two in number, one being located on each side of the anode-compartment. Each cathode-compartment consists of a rectangular metal box 13, preferably of cast-iron, which is closed upon all sides except the bottom, forming a rectangular "bell." The cathode itself consists of a flat iron plate 14, the lower surface of which is slightly inclined upwardly from the sides toward the center and toward one end. This plate is supported by a heavy lug 15, which is insulated from the bell 13 by a sleeve 16, which may be of porcelain or other suitable material. The electrolyte 17 is only deep enough to touch the entire lower surface of the cathode. Just below the surface of the electrolyte is located a small iron pipe 18, which extends entirely around the compartment. This serves to carry cooling-water, the purpose of which will be explained later. The iron pipe 19 is to carry the liquid metal from the furnace. This pipe is insulated from the pan and carried from the furnace by means of the concentric sleeve 20, which is fastened to the pan. Both pipe and sleeve project several inches from the furnace. At the outer end the space between the pipe and sleeve is filled with a ring 21 of suitable packing material, such as fire-clay.

In the portions of the pan remaining between the cathode-compartments and the ends are located the means of circulating the metal or alloy with which the pan is partially filled. Each consists of a rectangular mass of iron 22, cast hollow, which is caused to move slowly up and down by means of the crank-shafts 23. The two pistons are so regulated that while one is thrust downward the other is drawn upward. In this way the molten metal is caused to flow back and forth across the raised portion of the pan beneath the anode-compartment. At the ends of the pistons are lugs 24, which fit loosely into iron

or steel guides 25 on the sides of the pan and constrain the pistons to move in a vertical plane.

Beneath the ends of the pan are gas-burners 26 for the purpose of heating the apparatus on starting and to keep it hot during any temporary interruption of the current, the passage of which under normal working conditions may supply sufficient heat to keep the contents of the furnace in a molten condition, or they may be used as a continuous source of heat during the action of the process. Where gas is not available, ordinary fire-places may be used instead of the more convenient gas-burners.

The relation of the various parts to one another and their special advantages may be much more clearly understood by considering a concrete example of the working of the apparatus. The metal lighter than the electrolyte from which it is extracted that has the largest commercial demand is sodium, and the cheapest available source is sodium chlorid or common salt. We will therefore consider the production of that metal from salt by means of this improved apparatus. Assuming that the various parts are arranged according to the preceding description, we proceed as follows:

The anode 9 is connected with the positive terminal of a source of electricity and the two cathodes 14 with the negative terminal. The furnace is heated to over 350° centigrade by means of the burners 26. The pan is now filled with a body of molten lead 27, sufficient to form a liquid seal at the bottom of the three electrolytic compartments. Tin, cadmium, or certain alloys of low melting-point may also be used; but lead is the cheapest metal which will perform the desired functions. The cathode-compartments are then filled with molten caustic soda (sodium hydroxid) or other suitable electrolyte to the level of the lower surface of the cathode 14. The caustic soda and lead are readily kept in a molten condition by means of the burners. The anode 9 is lowered until almost in contact with the lead, salt is piled around it, and the current started. The pistons for circulating the lead must also be set in motion. At first the current should not be allowed to pass to the cathodes, but should be conducted away by means of temporary contacts with the pan. If this is not done, the lead will be attacked in the cathode-compartment, for there will not be enough sodium present to protect the lead. The passage of the current from the anode to the lead forms an electric arc which melts the surrounding salt. This requires a temperature of 800° to 900° centigrade. As soon as enough salt is melted to cover the end of the anode the arc will be extinguished; but the passage of a large current through the salt will continue to melt it until the compartment is filled to the required depth with melted salt. More salt must be added later, however, to replace that consumed in the process. During this period a gradually-increasing amount of current may be allowed to pass through the cathode.

The current decomposes the salt, yielding chlorin at the anode and sodium at the surface of the lead, which acts as a "secondary cathode." A distinction must here be made between the primary and secondary electrodes. The anode 9 and the cathodes 14 are the primary anode and cathodes, respectively, while the surface of the lead, which performs in turn the function of intermediate anode and cathode, will hereinafter be known as the "secondary" anode and "secondary" cathode. The primary electrodes will be referred to simply as the "anode" and "cathode," respectively.

The chlorin escapes as a gas and is conveyed away through the port 12. The sodium is absorbed by the molten lead forming an alloy. The advantage of having the sodium set free in this manner rests in the fact that pure sodium would at once be attacked by the electrolyte. The alloy of sodium and lead, however, is attacked to a lesser degree than pure sodium. Therefore by thus absorbing the sodium as rapidly as it is separated by the current the loss by recombination is reduced to a minimum. The alloy is then carried toward the cathode by means of the circulating-pistons. The function of the lead is to act as a bipolar electrode in series with the primary electrodes, its surface, therefore, being negative acting as a cathode nearest the source of positive current and positive acting as an anode nearest the source of negative current. It is, however, possible for the sodium to alloy with the lead, thus being able to pass through the lead, while the electrolytes have not this power. The function of the lead, in brief, is to convey the sodium and the current from the anode to the cathode compartments while holding the electrolytes in their respective compartments.

In the cathode-compartment the current decomposes the caustic soda, liberating sodium at the cathode 14 and hydroxyl ions at the surface of the lead or secondary anode. The affinity between hydroxyl ions and sodium is greater than between hydroxyl ions and lead. Therefore sodium dissolves in preference to lead and the caustic soda is reproduced. It will thus be seen that while caustic soda is constantly decomposed there will be just as much remaining at the end of the process as was supplied in the beginning. Therefore the ultimate source of the sodium is the salt decomposed in the anode-compartment. The caustic soda is then merely a medium for transferring the sodium from the secondary anode to the cathode. The advantage of separating sodium in this manner

rests in the fact that it is liberated in an electrolyte free from the action of the oxidizing substances set free at the anode. This is made possible by the absolute separation of the electrolytes of the anode and cathode compartments by means of the molten lead. The lead thus performs the function of a semipermeable diaphragm, but with greater efficiency than the usual forms of diaphragms, all other forms of which permit portions of the electrolyte, as well as the desired product, to pass through.

The collection of the sodium liberated at the cathode has always been a matter of considerable difficulty in practice. One of the chief objects of this invention is to reduce these difficulties. The sodium collects upon the surface of the electrolyte 17, and therefore has a tendency to form "bridges" between the cathode 14 and the bell 13. In case such a bridge is formed the current is short-circuited between the secondary anode and the cathode, and current thus lost will produce no sodium at the cathode. To prevent this, the small iron pipe 18 is extended entirely around the bell just below the surface of the electrolyte. When cooling-water is passed through this pipe, the portion of electrolyte immediately surrounding the pipe will be solidified. This solid layer is a non-conductor and will prevent stray currents from leaking across from the cathode to the bell, as well as prevent sodium bridges from coming in contact with the iron walls of the bell. The loss due to short circuits and stray currents is thus reduced to a minimum. The most serious source of loss, however, is due to the oxidation of the sodium between the time it is liberated and its formation into ingots. To exclude the atmosphere, use is made of the closed bell 13. This is kept filled with a gas which will not react to any great extent with sodium, such as nitrogen or hydrogen. The sodium as it is liberated moves along the inclined surfaces of the cathodes to the overflow or draw-off pipes 19, whence it is conveyed by iron pipes to a suitable vessel containing melted paraffin, below the surface of which the pipes dip. The sodium sinks to the bottom and can thus be collected without having been exposed to any oxidizing atmosphere at any moment from the time it was liberated till enough has collected to pour into the molds.

The circulating device for the lead is made as simple as possible to avoid the difficulty of making sliding joints, which will remain tight through a great variation of temperature. Instead of a piston as ordinarily constructed use is made of pistons in the form of loosely-fitting floats or plungers, which act merely by displacing a volume of lead equal to the submerged volume of the piston. The lead displaced by the downward movement of one piston is provided for by the simultaneous upward movement of the second. In flowing from one to the other cathode-chamber the lead must pass beneath the anode-chamber and performs the alternate function of secondary cathode and anode, as already described. The lesser depth of the lead where it flows over the raised portion of the pan beneath the anode-compartment causes an increase in the velocity, thus removing the sodium more rapidly from the action of the anode electrolyte. The rate at which the pistons move is governed by the amount of sodium liberated in the anode-chamber (thus on the number of amperes used) and the percentage of sodium which the lead can absorb with maximum efficiency. This percentage varies from four per cent. to six per cent. The lead may also be circulated by other means than the pistons, as shown.

I do not wish to be confined to the production of sodium by my invention, as I may employ the invention for the production of any other metal which is lighter than the electrolyte from which it is separated, nor in the production of sodium do I wish to be confined to the use of pure common salt in the anode-compartment and pure sodium hydroxid in the cathode-compartments, as I may use some other salt or mixture of salts in one or both compartments.

What I claim as new, and desire to secure by Letters Patent, is—

1. An electrolytic apparatus comprising an anode-compartment lined with refractory and non-conducting material, cathode-compartments at opposite sides thereof having interior metallic wall-surfaces, said compartments being supported with downwardly-open ends above a body of molten metal which acts as a seal and also forms part of the electric circuit between the compartments, electrodes in the anode and cathode compartments, and means for producing a flow of the molten metal back and forth between the anode and the cathode compartments.

2. An electrolytic apparatus comprising an anode-compartment, cathode-compartments at opposite sides thereof, a pan containing a molten metal above which the compartments are supported with their downwardly-open ends sealed by said metal, said pan being shallow at the center beneath the anode-compartment and deeper at the ends, means for producing a flow of the molten metal back and forth between the anode and the cathode compartments, and electrodes in the anode and cathode compartments.

3. An electrolytic apparatus comprising a pan resting over a fire-box at each end and having its bottom raised at the center, an anode-compartment supported over the pan with its downwardly-open end above said raised portion, cathode-compartments at opposite sides of the anode-compartment with

their downwardly-open ends above the deeper portion of the pan, a molten metal in the pan sealing the ends of said compartments, and means for producing a flow of the molten metal back and forth between the anode and the cathode compartments.

4. An electrolytic apparatus comprising a pan having its bottom raised in the center, an anode-compartment supported over the pan with its downwardly-open end above said raised portion, cathode-compartments at opposite sides of the anode-compartment with their downwardly-open ends above the deeper portions of the pan, a molten metal in the pan sealing the ends of said compartments, displacement-plungers at each end of the pan adjacent the cathode-compartments, and means for reciprocating said plungers in opposite directions to produce a flow of the molten metal back and forth between the anode and the cathode compartments.

5. An electrolytic apparatus comprising anode and cathode compartments supported with their open ends downward and sealed by a molten metal, displacement-plungers acting upon said body of metal at opposite sides of the compartments, and means for reciprocating said plungers in opposite directions.

6. In an electrolytic apparatus, the combination, with an anode-compartment, of a cathode-compartment comprising a closed metallic bell, said compartments being supported with their open ends downward and sealed by a body of molten metal.

7. In an electrolytic apparatus, a cathode-compartment comprsing a closed bell, an electrolyte contained therein, an electrode having its lower surface in contact with the surface of the electrolyte, said surface of the electrode being inclined upward from the sides to the center and from one end toward the other end, and a draw-off pipe having its orifice at the surface of the electrolyte adjacent the elevated end of the electrode.

In testimony whereof I have affixed my signature in presence of two witnesses.

COURTLAND F. CARRIER, JR.

Witnesses:
M. E. VERBECK,
A. S. DIVEN.