Aug. 9, 1966 G. MARULLO ETAL 3,265,606

ELECTROLYTIC CELL FOR PREPARATION OF ALLOYS OF LEAD WITH ALKALINE METALS

Filed March 26, 1962 2 Sheets-Sheet 1

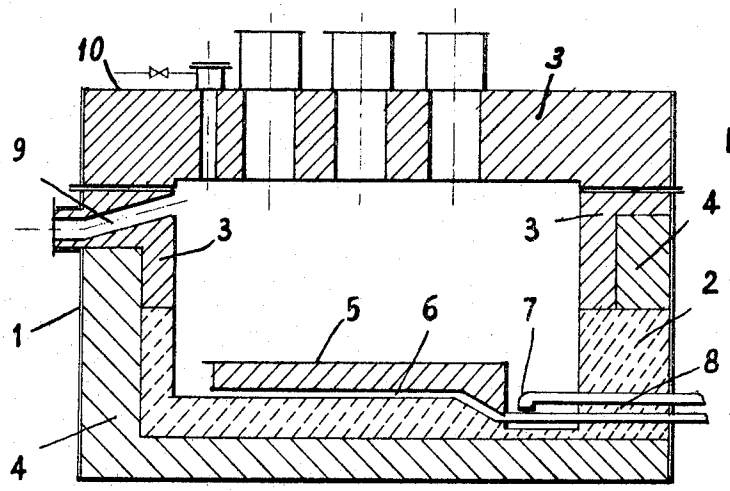
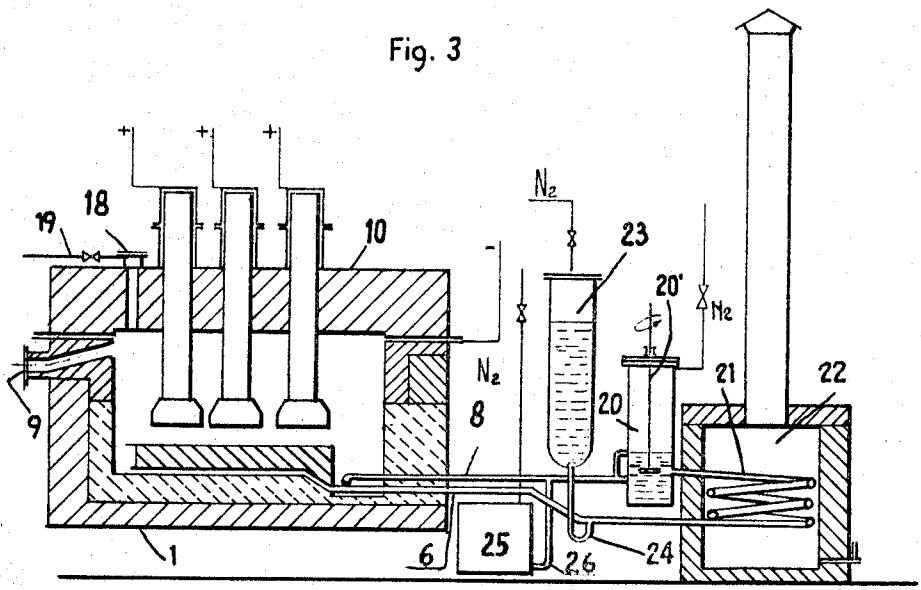


Fig. 1

Fig. 3



INVENTOR.

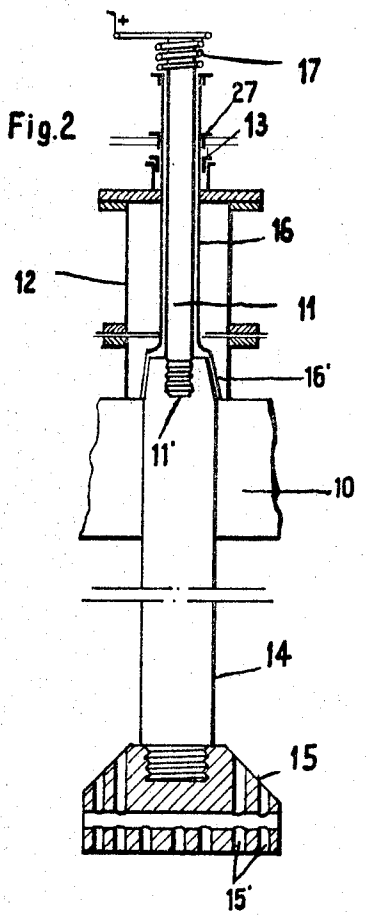
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ELECTROLYTIC CELL FOR PREPARATION OF ALLOYS OF LEAD WITH ALKALINE METALS

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Fig.2



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3,265,606

ELECTROLYTIC CELL FOR PREPARATION OF ALLOYS OF LEAD WITH ALKALINE METALS

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Claims priority, application Italy, Mar. 29, 1961, 5,610/61
11 Claims. (Cl. 204—245)

The present invention relates to a method of electrolysis and an electrolytic cell for preparing alloys of lead with alkaline metals. It particularly relates to a cell in which is carried out electrolytic decomposition of a molten alkaline chloride or mixture of alkaline chlorides.

In such cell the cathode consists of molten lead or a molten alloy of lead with alkaline metals, the anode being made of graphite. The cathodic alloy being heavier than the electrolyte occupies the bottom of the cell, the electrolyte floating thereon. The anodes are immersed in the electrolyte at a suitable distance from the cathode surface. The metal ions discharged at the cathode form an alloy with the latter, the chlorine freed at the anode being recovered as a gas.

For example, the cell is employed to prepare the ternary alloy 89% Pb, 10% Na and 1% K. This alloy is used directly in the production of tetraethyl lead.

The electrolytic cells heretofore used or known for the preparation of these alloys do not give technologically satisfactory results. An important cause of the failure is to be found in the fact that the cell is insufficiently gas-tight. This results in the re-entrance of air into the cell, and the pollution of the gaseous anodic product, chlorine, the recovery of which is thus made more difficult. Due to the high temperature, the air also causes a substantial attack on the graphite anode, with the formation of CO_2. This combustion of the graphite also causes crumbling of the anode, with the formation of graphite powder which is deposited onto the cathode surface, thus preventing the cation from being absorbed by the alloy.

The presence of graphite powder, in addition to chlorine, in the gaseous atmosphere of the cell, is also very harmful due to attack upon the refractory material lining the inside of the cell. Insoluble slags are formed which deposit on the cathode surface, thus hindering the electrolysis.

Consequently, among the causes of the unsatisfactory results is the use of a refractory material not suitable as inner lining of the cell.

The cells heretofore known or used for electrolysis of halides, on a cathode of molten material, had an inner lining of magnesium-containing refractory material, or an inner lining of a silicon-aluminum-containing refractory material. Our tests demonstrated that the magnesium-containing refractory is considerably attacked by chlorine, whereas it withstands very well molten alloys of alkaline metals. The tests also showed that the silicon-aluminum-containing refractory has good resistance to chlorine and poor resistance to the molten alloys of alkaline metals which act as cathodes. Both refractory materials have good resistance to the molten electrolyte.

If a non-resistant refractory material is used, slags form, accumulating on the cathode surface. Such slag accumulation prevents the regular passage of current, causing a substantial increase in the electrolysis voltage, resulting in overheating the bath and loss in respect to current and energy.

Finally, marked inconveniences occur in operation of the known cells, due to the lack of adequate means for assuring the homogeneity of the cathodic alloy, and the control of its temperature. The homogenization of the cathode alloy is essential in order to keep the cathode surface from becoming too rich in alkaline metal. In such case not all of the electrolyzed alkaline metal combines with the cathode. A part of the metal surfaces combines again with chlorine, thus damaging the anodes and lowering the yields.

The control of temperature is necessary in order to prevent solidification of the electrolyte in case of too low a temperature, or to prevent excessive corrosion of the materials when the temperature is too high.

In some of the prior cells, control of the temperature of the alloy was carried out by heating it through the metal bottom of the cell. This method was very inconvenient, due mainly to mechanical deformation of the metal body taking place at the high temperatures needed to keep the bath in the molten state.

The devices used to agitate the cathodic alloy, in the prior cells, were of the electromagnetic or mechanical type. The former has limited effectiveness for operation of long duration. The mechanical type requires a complicated sealing system for the mobile parts, and is subject to corrosion of the parts in contact with the electrolyte. Absence of or insufficient circulation of the alloy causes an accumulation of slags in the electrolysis zone, lowering the yields.

An object of the present invention is to provide an improved electrolytic cell which avoids the aforementioned disadvantages and difficulties.

The cell, which is under low pressure, is sealed by flanges provided with gaskets for the cover-to-cell connection, and by stuffing boxes for the anode holders hanging from the cover.

For the inner lining of the cell, two types of refractory material are employed. A silica-alumina material is used for the part in contact with the molten electrolyte and the anodic gas, and a magnesia material for the part in contact with the alloy.

The circulation of the cathodic alloy and its thermal conditioning is carried out by means of a pump and a heat exchanger, placed outside the cell. This outside pumping system is made of a metallic material resistant to the attack of the alloy at high temperature, with the advantage that the means for charging and discharging the products can be connected thereto, as will be explained below.

The system we employ for circulating the cathodic alloy also serves to entrain, to one end of the cell, the slags, if any, formed in a zone left intentionally free of anodes.

However, it is noted that the amount of slag is in any event negligible, due to the use of suitable refractory materials, and to the purity of the products introduced into the cell.

The accompanying drawing is not intended to limit the invention. It serves to illustrate a preferred embodiment of the new electrolytic cell. This cell is employed to produce an 89% lead-10% sodium-1% potassium alloy, by electrolysis of a mixture of 55% NaCl and 45% KCl, with high current yields and over a long period of time, without need for disassembling the cell for the purpose of maintenance and scorifying.

FIG. 1 is a longitudinal section of the cell; FIG. 2 illustrates details of the connection between the power nipple, i.e. the current carrier, and the anodes, and for their upward movement; FIG. 3 is a view of the entire system, details of the anode and its connections being omitted for simplification. The same reference numbers indicate the same parts in the different figures.

An iron-plate body **1** in the form of a rectangular parallelepipedon, dimensions 1200 x 2600 x 1000 mm., having a side reinforcement and mounted on a set of iron beams (not shown), is lined inside with two types of refractory material. One type is a compact refractory material **2**, containing about 90% of MgO, lining the bottom of the cell and wall over or up to half the height of the electrolyte. Refractory **2** is never in contact with chlorine. On the remaining part of the inner surface of the cell, i.e., in the zone in contact with the electrolyte and with chlorine, the refractory lining consists of a very compact silica-alumina material **3** containing 30% Al_2O_3. The inner lining of the cell cover consists of the same refractory material **3**.

Between the inner lining and the metal body, a refractory material **4** having high insulating property is interposed, to assure a uniform temperature lower than 100° C. in all the outer body, so as to avoid attack by chlorine.

All of the aforementioned inner lining material was applied with limited and minimum use of a binder, to reduce the possible formation of impurities which can deposit on the cathode surface.

The inner bottom of the cell is lined with a stainless steel sheet **5** fixed to or held in a grooving in or on the side wall, but which can freely expand when hot. The purpose of this sheet is to prevent the non-cemented brickworks forming the bottom of the cell from being removed by buoyancy, i.e., hydrostatic thrust of the alloy.

Beneath the plane of the inner bottom wall of the cell, is a stainless steel pipe **6** having a section sufficiently wide (110 x 60 mm.) passing through the cell over its entire length and connected, outside the cell, with the pressure side of the circulation system for the cathodic alloy.

On the part opposite the outlet of the said pipe, and inside the cell, there is a trap or sump **7** in which is immersed a pipe **8** having the same section as pipe **6**, for collecting the alloy. Pipe **8** is connected to the suction side of the circulation system of the cathodic alloy.

This precaution makes it possible to prevent the electrolyte from being drawn into the circulation system, which could cause stoppage of the pipes due to solidification of the salt.

The side wall of the cell has an opening **9** through which gas produced at the anode is discharged. The gas passes successively into a cooling chamber and through a fiberglass filter, not shown in the figure, which detains any solid impurity, essentially electrolyte. The gas can then be recovered.

The upper part of the cell is closed by an iron sheet forming a cover **10** flanged onto the cell body and provided with an inner lining of silica-alumina refractory material **3**, containing 30% of Al_2O_3.

The anodes (FIG. 2) consist of a graphite stem **14** having 150 mm. diameter connected with a graphite head **15**, having a square section of 450 x 450 mm. provided with holes **15'** having a diameter of 20 mm. uniformly distributed and occupying a surface corresponding to about 10% of the total anodic surface. The holes permit a regular flow of the anodic gas therethrough.

The three anodes shown are of compact electrographite, and are suspended from cover **10** by nipples (FIG. 2), which are electrically insulated in respect to the cover. The height of the anodes can be regulated by a screw (not shown). The anodes pass through three holes in the inner lining of the cover.

The anode stem **14** has a smaller cross section than that of the head, to reduce heat loss along the stem. It is not convenient to further reduce the section, so as not to unduly increase the potential drop.

The current carrying nipple of each anode comprises a stem **11** and a jacket **16**. The stem **11** is made partly of nickel, or of other metallic material resistant to chlorine at high temperature, for the portion in contact with the gaseous atmosphere of the cell, and partly of iron, for the outer portion. Stem **11** is cooled with water circulated inside the jacket, and is screwed to the graphite stem at **11'**.

Jacket **16** comprises a nickel cylinder whose lower part has the shape of a truncated cone. The truncated-cone cap **16'** is spring-pressed upon the correspondingly shaped upper part of the graphite stem **14**. A perfect graphite-to-metal electric contact is assured by the spring shown at **17**, being mounted about the upper end of stem **11**, upon the flange of the upper end of jacket **16**.

Each anode is supported by an Inconel dome **12** lying on the cover **10** and electrically insulated from it.

A perfect gas seal of the power connection is assured by a stuffing box indicated at **13**, between jacket **16** and dome **12**, and by a rubber ring of the O-ring type (not shown in the figures) between jacket **16** and stem **11**. The cell is sealed in respect to gases, under low pressures, by asbestos gaskets (not shown) for the flanges of cover **10**, and also of dome **12**. On the cover is a valve or gate **18** (FIG. 3) used for charging the molten electrolyte, and also a valved conduit **19** for controlling the measuring pressure. In addition, the cover can be provided with one or more glass windows, not shown in the figures, which can serve for control of temperature by an optical pyrometer.

The useful anodic surface of the cell described is about 5,500 cm.^{2}, the cathodic surface being about 11,000 cm.^{2}. The higher cathodic surface, as compared with the anodic surface, is due to the fact that the corresponding part or zone of the alloy suction trap **7** is kept free of anodes. This precaution was found very useful during operation of the cell. Due to the circulation of the alloy, there is an accumulation of all the impurities, particularly in said trap **7** zone. Even if present in minimized amounts, the impurities deposit onto the surface of said alloy.

The impurities are reduced to a minimum by suitable selection of the refractory materials lining of the cell, and by use of very pure starting materials, and also by feeding them in molten state.

The circulation of the cathodic alloy is carried out by mechanical immersion pump **20** having a rotary shaft **20'** pivoted on bearings outside the body containing the molten alloy. The shaft **20'** and its stuffing box are cooled by water. The steel body containing the molten alloy is kept under an inert atmosphere. The stuffing box has a double seal with interposed nitrogen pressure.

On the pressure side of the pump **20** is a heat exchanger comprising a steel coil **21** immersed in a small furnace **22** which can be heated by a flame, or cooled by an air stream. The coil **21** can also be heated electrically by low-voltage alternate current passing through the entire outer alloy circulation system.

The temperature of the cathodic alloy can thus be regulated with absolute accuracy. As a result, or as a function of this temperature control, it is also possible to carry out the automatic control of the electrical operating conditions by regulating the interpolar distance, employing the usual vertical anode movement system.

The lead feeding is carried out batchwise by means of the melting pot **23** kept under nitrogen inert atmosphere. The melting pot is a 50-liter iron cylinder, which is electrically heated, and is connected to the pressure side of the pump **20** by pipe **24** which is heated to a temperature above the melting point of lead.

The molten lead is fed into the cell by gravity, the bottom of the melting pot being placed at a height such that, at the end of charging, there is on said bottom a head of 100 to 150 mm., which is sufficient to prevent slags, if any are present, from entering the cell.

Batchwise discharge of the alloy is carried out into a 75-liter tank **25** connected through pipe **26** to the inlet of pump **20**. Pipe **26** is heated to a temperature higher than the melting point of the alloy. During discharge of the

alloy, also carried out by gravity, collecting tank 25 is kept under an inert gas.

The electrolyte consisting of very pure salts, free of oxygen-containing compounds in particular, is fed batchwise, in molten state, to the cell through gate 18 (FIG. 3). Best results are obtained by feeding the electrolyte in the molten state after decantation. In this manner it is possible to remove completely all traces of humidity and all infusible impurities contained in the salts. The melting pot for the salts, not shown in the figure, is made of refractory materials since it has been ascertained that ordinary metallic materials undergo considerable corrosion caused by the molten salts used in the process, resulting in the introduction of impurities which can damage the electrolysis.

Heating is carried out by means of graphite electrodes (not shown) which are arranged sideways on the bottom of the melting pot and are always immersed in the molten salt. These heating electrodes are fed with an alternate current of variable voltage. As an alternative for industrial operation, provision is made for flame heating in a reverberatory furnace.

The following is one example of operation of the cell:

The electrolyte consisted of a mixture of 55% NaCl and 45% KCl, and was at a temperature of 710° C. The cathodic alloy contained 9.8% Na and 1% K and occupied the bottom of the cell for a height of 8 cm. Its temperature was 700° C.

375 kg. of molten lead and 111 kg. of a molten mixture of NaCl and KCl, containing 7.4% of KCl, were charged.

The electrolysis was carried out at 1.7 a./cm.^{2}, corresponding to a total of 9200 amperes, with a voltage of 5.5 volts. After 6 hours and a feeding of 55,000 ampere hours, the level of the cathodic alloy was 14 cm. from the bottom; 410 kg. of an alloy having an Na content of 10% and a K content of 1.05% were discharged.

A production of 43.5 kg. of lead-alkaline metal was obtained, being a current yield of about 92%, based upon the sodium.

The power consumption per kg. of metal produced was about 7 kilowatt hours.

We claim:

1. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a dependent carbon anode structure extending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, a lower portion of the cell structure providing a trap into which molten lead flows, the trap being in a locality free of any anode, being removed laterally from the lower end of the carbon anode, the trap having a bottom wall which is below the level of that zone of the bottom wall of the cell opposite the anode, so as to accumulate in the trap such slags as may form, downwardly opening substantially horizontal conduit means for removing molten lead alloy and accumulated slag from said trap at a level thereof below the level of the bottom wall zone opposite the anode, so that sucking out of alkaline halide electrolyte together with the alloy is minimized.

2. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a plurality of carbon anodes extending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anodes, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anodes, a lower portion of the cell structure providing a trap into which molten lead flows, the trap being in a locality free of any anodes, being removed laterally from the lower end of the carbon anodes, the trap having a bottom wall which is below the level of that zone of the bottom wall of the cell opposite the anodes, so as to accumulate in the trap such slags as may form, downwardly opening substantially horizontal conduit means for removing molten lead alloy from said trap at a level thereof below the level of the bottom wall zone opposite the anodes, so that sucking out of alkaline halide electrolyte together with the alloy is minimized.

3. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a carbon anode structure depending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, a lower portion of the cell structure providing a trap into which molten lead flows, the trap being in a locality free of any anode, being removed laterally from the lower end of the carbon anode, the trap having a bottom wall which is below the level of that zone of the bottom wall of the cell opposite the anode, so as to catch in the trap such slags as may form, downwardly opening substantially horizontal conduit means for removing molten lead alloy and for maintaining circulation of the molten lead alloy in the cell, comprising pump means located outside the cell, outflow conduit means communicating between the suction intake thereof and with said trap at a level thereof below the level of the bottom wall zone opposite the anode, so as to suck molten lead alloy therefrom, and so that sucking out of alkaline halide electrolyte together with the alloy is minimized, return flow conduit means communicating between the pressure side of said suction means and a zone of said cell removed from said trap on the opposite side of the anode, so as to promote movement of the slags lead and lead alloy along the bottom wall of the cell.

4. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a carbon anode structure depending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell being adapted to retain a body of molten lead in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, a lower portion of the cell structure providing a trap into which molten lead flows, the trap being in a locality free of any anode, being removed laterally from the lower end of the carbon anode, the trap having a bottom wall which is below the level of that zone of the bottom wall of the

cell opposite the anode, so as to catch in the trap such slags as may form, downwardly opening substantially horizontal conduit means for removing molten lead alloy and for maintaining circulation of the molten lead alloy in the cell, comprising pump means located outside the cell, outflow conduit means communicating between the suction intake of said pump means and with said trap at a level thereof below the level of the bottom wall zone opposite the anode, so as to suck molten lead alloy therefrom, and so that sucking out of alkaline halide electrolyte together with the alloy is minimized, heat exchanging means for controlling the temperature of the molten lead alloy before it is returned to the cell, return flow conduit means communicating between the pressure side of said pump means and into a zone of said cell removed from said trap, so as to promote movement of the lead and lead alloy in the cell.

5. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode; comprising an electrolysis cell having a bottom wall, side walls and a top wall defining a single chamber, a carbon anode structure extending into the cell through said top wall to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis and an inlet for molten alkaline halide electrolyte, the cell being adapted to retain a body of molten lead in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, a lower portion of the cell structure providing a trap into which molten lead flows, for segregation of a part of the molten lead and lead alloy, the trap being in a locality free of any anode, being removed laterally from the lower end of the carbon anode, the trap having a bottom wall which is below the level of that zone of the bottom wall of the cell opposite the anode, so as to catch in the trap such slags as may from, means for removing molten lead alloy and for maintaining circulation of the molten lead alloy in the cell, comprising suction means located outside the cell, downwardly opening substantially horizontal outflow conduit means communicating between the suction intake thereof and with said trap at a level thereof below the level of the bottom wall zone opposite the anode, so as to suck molten lead alloy therefrom, and so that sucking out of alkaline halide electrolyte together with the alloy is minimized, heat exchanging means for controlling the temperature of the molten lead alloy before it is returned to the cell, return flow conduit means communicating between the pressure side of said suction means and a zone of said cell removed from said trap on the opposite side of the anode, so as to promote circulation of the lead and lead alloy along the bottom wall of the cell, a melting pot for lead located outside the cell and having gravity feed connection to said return flow conduit means.

6. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a dependent carbon anode structure extending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, a lower portion of the cell structure providing a trap into which molten lead flows, the trap being in a locality free of any anode, being removed laterally from the lower end of the carbon anode, the trap having a bottom wall which is below the level of that zone of the bottom wall of the cell opposite the anode, so as to accumulate in the trap such slags as may form, means for removing molten lead alloy and accumulated slag from said trap at a level thereof below the level of the bottom wall zone opposite the anode, so that sucking out of alkaline halide electrolyte together with the alloy is minimized, the cell having an inner lining of a compact magnesium oxide refractory in its lower portion in contact with the alloy and the supernatant electrolyte, and an inner lining of a compact alumina-aluminum silicate refractory in its upper part in contact with the halogen generated in the process and with the electrolyte.

7. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, a carbon anode structure depending into the cell from said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, the cell having an inner lining of a compact magnesium oxide refractory in its lower portion in contact with the alloy and the supernatant electrolyte, and an inner lining of a compact alumina-aluminum silicate refractory in its upper part in contact with the halogen generated in the process and with the electrolyte.

8. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall, a cover and side walls defining a single chamber, the cell having an inner lining of a compact magnesium oxide refractory in its lower portion in contact with the alloy and the supernatant electrolyte, and an inner lining of a compact alumina-aluminum silicate refractory in its upper part in contact with the halogen generated in the process and with the electrolyte, at least one carbon anode structure extending into the cell through said cover to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode, the anode being of graphite and comprising an upper stem portion and a lower head portion, the head portion having a cross-sectional diameter larger than the stem portion, the head portion having a plurality of passageways extending therein from a lower surface of the head to an upper surface of the head, permitting upward flow therethrough of halogen gases formed in the process.

9. An electrolysis furnace apparatus for preparing an alloy of lead and an alkaline metal by electrolysis of a molten alkaline halide electrolyte in contact with and between a molten lead cathode and a carbon anode, comprising an electrolysis cell having a bottom wall and side walls and a top wall defining a single chamber, a carbon anode structure depending into the cell from said top wall to a point removed from the bottom wall, electric current feeding means connected to the anode, the cell having an outlet for gases formed in the electrolysis and inlet means for molten electrolyte, the cell being adapted to retain a body of molten lead and molten lead alloy in its lower part, on said bottom wall, and being adapted so that in operation the molten lead and lead alloy provide a cathode below the lower end of the carbon anode and

electrically communicating therewith via molten electrolyte, the anode being of graphite and having an upper stem portion of graphite, the graphite stem portion having an upper tapering connector portion, a metallic jacket in the form of a sleeve extending downwardly through said top wall, a stuffing box, gas sealing means between the top wall and the sleeve, screw means permitting raising and lowering of the sleeve, the sleeve having at its lower end a flaring connector portion which seats upon the upper tapering connector portion of the graphite stem, spring means for forcing the two connector portions together, an electric current feeding nipple comprising a metal stem extending in the sleeve and screw-threadedly connected to the upper end portion of the graphite stem.

10. An electrolysis furnace apparatus, comprising a single chambered cell, the cell having a top wall, a cathode in the cell, a carbonaceous anode extending into the cell, the anode having an upper carbonaceous stem portion which is provided with an upper tapering connector portion, a metallic jacket in the form of a sleeve extending downwardly, a stuffing box, gas sealing means between the top wall and the sleeve, screw means permitting raising and lowering of the sleeve, the sleeve having at its lower end a flaring connector portion which seats upon the upper tapering connector portion of the carbonaceous stem, spring means for forcing the two connector portions together, an electric current feeding nipple comprising a metal stem extending in the sleeve and screw-threadedly connected to the upper end portion of the carbonaceous stem.

11. In a single chambered electrolysis cell for making an alloy of a heavy metal with an alkaline metal by electrolysis of supernatant molten alkaline halide electrolyte

in contact with molten heavy metal and with a carbonaceous anode, the molten alloy and molten heavy metal forming the cathode below the molten electrolyte and below the anode; the improvement comprising a recirculating system (for the molten cathode alloy, comprising a downwardly opening substantially horizontal conduit means and a pump) for withdrawing molten cathode alloy from the single chambered cell from below the electrolyte, and for returning molten cathode alloy, the points of withdrawal and of return being laterally removed from each other within said chamber so as to cause flow of molten lead alloy along the cell bottom below the anode.

References Cited by the Examiner

UNITED STATES PATENTS

995,476	6/1911	McNitt	204—71
1,628,050	5/1927	Krans et al.	204—71
1,849,749	3/1932	McIntyre	204—245
2,431,723	12/1947	Yerkes	204—71
2,742,418	4/1956	Padgitt	204—71
2,850,443	9/1958	Atterton	204—71
2,920,022	1/1960	Resnick	204—71
2,944,949	7/1960	Leech	204—245
2,944,955	7/1960	Fentress	204—245
3,037,928	6/1962	Hass et al.	204—286
3,085,969	4/1963	Motock	204—247
3,104,213	9/1963	Szechtman	204—245

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