G. O. SEWARD, F. VON KÜGELGEN & F. VON BIDDER.

ELECTROLYTIC PRODUCTION OF LIGHT METALS.

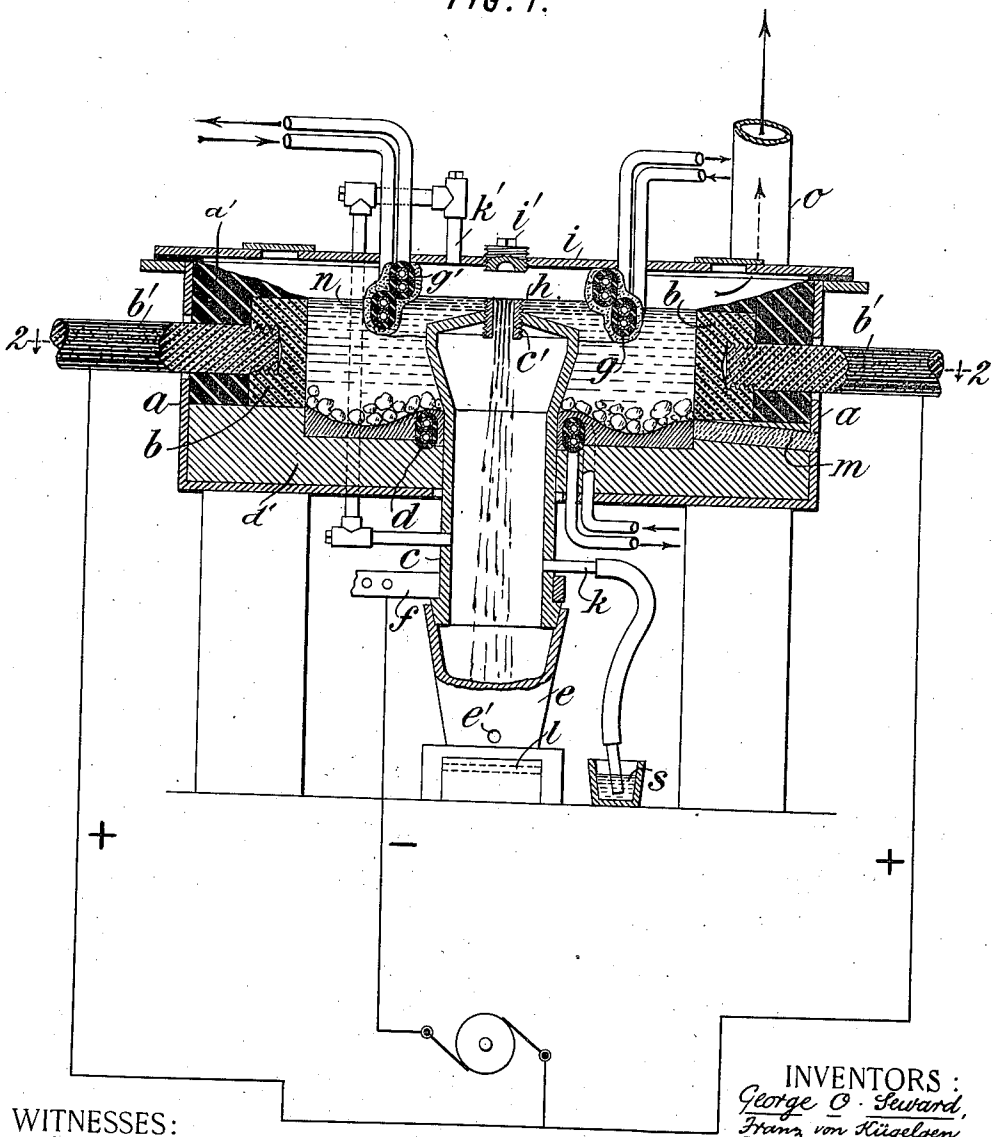
APPLICATION FILED MAY 10, 1909.

1,043,154.

Patented Nov. 5, 1912.

2 SHEETS—SHEET 1.

FIG. 1.



INVENTORS:
George O. Seward,
Franz von Kügelgen,
and Fritz von Bidder,
By Attorneys,
Arthur G. Fraser & Sons

WITNESSES:
Fred White
René Bruine

G. O. SEWARD, F. VON KÜGELGEN & F. VON BIDDER.

ELECTROLYTIC PRODUCTION OF LIGHT METALS.

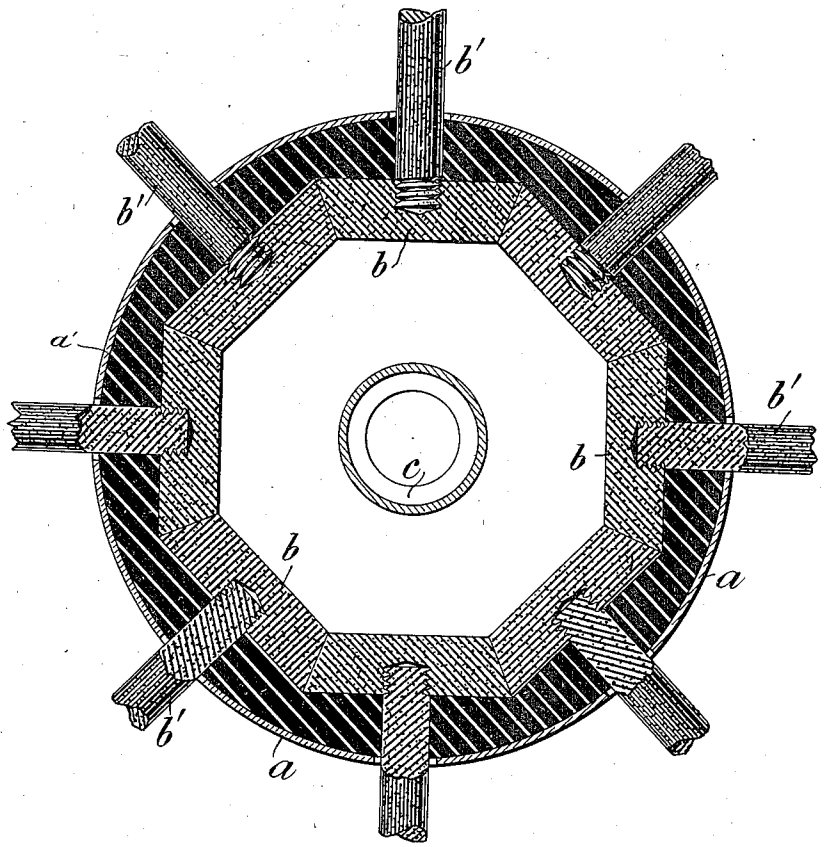
APPLICATION FILED MAY 10, 1909.

1,043,154.

Patented Nov. 5, 1912.

2 SHEETS—SHEET 2.

FIG. 2.



WITNESSES:

Fred Whitt

René Bruine

INVENTORS:

George O. Seward,

Franz von Kügelgen

and Fritz von Bidder,

By Attorneys,

Arthur C. Fraser & Sons

UNITED STATES PATENT OFFICE.

GEORGE O. SEWARD, OF EAST ORANGE, NEW JERSEY, AND FRANZ VON KÜGELGEN AND FRITZ VON BIDDER, OF HOLCOMBS ROCK, VIRGINIA, ASSIGNORS TO VIRGINIA LABORATORY COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

ELECTROLYTIC PRODUCTION OF LIGHT METALS.

1,043,154. Specification of Letters Patent. Patented Nov. 5, 1912.

Application filed May 10, 1909. Serial No. 495,016.

To all whom it may concern:

Be it known that we, GEORGE O. SEWARD, a citizen of the United States, residing at East Orange, in the county of Essex and State of New Jersey, FRANZ VON KÜGELGEN, a subject of the German Emperor, residing at Holcombs Rock, in the county of Bedford and State of Virginia, and FRITZ VON BIDDER, a subject of the Russian Emperor, residing in Holcombs Rock aforesaid, have jointly invented certain new and useful Improvements in Electrolytic Production of Light Metals, of which the following is a specification.

This invention relates in general to the electrolysis of molten salts where the metal or alloy produced is of lower specific gravity than the electrolyte, and specifically to the production of sodium from sodium-chlorid or common salt, the ore of sodium which is found in most abundance and in an almost pure state.

The production of the metal sodium directly by the electrolysis of sodium-chlorid has not, to our knowledge, been accomplished in a commercial way prior to our invention; though many excellent suggestions as to the form of apparatus and much valuable data have been published.

The apparatus is illustrated, in its essential details, by the accompanying drawing, Figure 1 of which is a vertical diametrical section of the furnace, and Fig. 2 is a horizontal section on the line 2—2 in Fig. 1.

Graphite pencils *b'* lead in the current through the sides of the riveted steel case *a* and connect by threaded joints with carbon or graphite plates *b b* which fit together to form a polygonal anode which also serves as the sides of the crucible. This sectional construction of the anode is convenient, but it may be made monolithic if desired.

The space between the anode and the furnace case is filled with a thoroughly tamped agglomerate *a'* of fire-clay, asbestos-fiber, and cement, and the bottom of the crucible *d'* is also conveniently made of this material which is a good insulating lining and which resists the action of the anode gas and of the electrolyte well.

By limiting the height of the anode a protective layer of salt may be maintained over the top, preventing oxidation and disintegration of the carbon.

The cathode *c* is conveniently made of cast-iron. Surrounding the cathode at a point above its entry through the case is a water-cooled coil *d* which serves at once to prevent leakage of electrolyte and limits the activity of the cathode which otherwise would be progressively downward. This coil is embedded in the crucible bottom as shown and also tends to maintain the integrity of the latter by its cooling effect.

A nipple *c'* in the top of the cathode receives the molten metal as its level rises within the sodium-chamber and directs its course so that it will drop clear of the walls of the cathode-cavity and fall into the receiver *e*, from whence it may be tapped at intervals through tap-hole *e'*.

The sodium is collected within the water-cooled and salt-incrusted curtain *g* which dips below the electrolyte and divides the space above it into a "sodium-chamber" and a "chlorin-chamber." *g* is in no sense a "pole cell" as it is kept totally inactive by the layer of chilled salt *n* maintained thereon through the cooling action of the water circulating within the curtain. This curtain is conveniently made of two separate coils of seamless copper tubing which are first covered with a solid insulating material before the layer of chilled salt is applied. Such a preliminary coating will act as an extra insulation in case the layer of salt becomes too thin through irregularities in the run and is conveniently made by closely wrapping two or more layers of strong asbestos twine on the tubes.

The multiple-coil construction of the curtain which is shown in the drawing is a further insurance against activity, as, even in case the upper coil comes in contact with the negatively-charged sodium in the sodium-chamber, the isolation will still be accomplished by the lower coil. The correct determination of the size of this curtain is important as the area of the floating sodium is controlled thereby and, in a measure, the current density at the iron-sodium cathode which is preferably high, for example 10 amperes per sq. inch of total surface of active iron and sodium.

Local heating of the electrolyte between the curtain and the cathode is necessary in order to limit the cooling effect of the former and avoid chilling of the electrolyte and

obstruction of the entrance for the sodium into the sodium-chamber. The function of the cooling medium circulating within the curtain is to maintain an insulating and protective layer of solid salt thereon and its tendency to extend and solidify the electrolyte elsewhere must be checked by the local heating mentioned. Such local heating may be accomplished by maintaining a preponderance of cathodic activity at the upper part of the cathode and thus superheating the electrolyte between the cathode and the curtain. The position of the coil *d* and the size of the curtain and, therefore, of the active floating layer of sodium determine the cathodic activity with a current of given volume. Auxiliary movable iron pieces electrically connected to the negative terminal may be introduced through the cover of the sodium-chamber and into the electrolyte through the floating sodium to give further control of cathodic activity if desired. Local heating may be also accomplished by the use of heating bodies within the sodium-chamber which give control independently of the electrolyzing current. Hollow iron or pressed steel members heated by an internal electric resistance coil or by other than electric means are convenient and, if heated by gas after the manner of gasolene flat-irons or soldering-irons, effect an economy of current and may be used as an auxiliary thereto.

An iron plate *i*, insulated from the furnace case and from the metal of the curtain, covers both the sodium and the chlorin-chamber. The cooling effect of the air, together with a protective deposit of condensed salt-vapor on its under side, keeps the cover *i* from being attacked by the dry chlorin.

An opening through the cover at its center gives access to the sodium-chamber and to the cathode-cavity through the nipple *c'* and is normally closed by the plug *i'*. Other openings through the cover into the chlorin-chamber are provided for feeding in salt and for breaking up salt crusts if any form. The chlorin is drawn out through the stack *o*, a slight suction being preferably maintained.

The crucible may be quickly emptied when desired through the tap-hole *m*.

An approximation to atmospheric pressure is maintained within the cathode-cavity and equilibrium between that and the sodium-chamber by the system of pipes *k* and *k'* and the kerosene seal *s*, whereby the effects of sudden generation of gas or ebullition of the electrolyte are neutralized and any tendency for the cathode nipple to siphon when full of falling sodium overcome. By using tees in the construction of the system of pipes cleaning out is facilitated.

The electrical connections to the cathode and anode are indicated in the drawing and may be made in any convenient manner, preferably so that either direct or alternating current may be used interchangeably. When using alternating current, we can pass it through the electrodes shown or one pole of the current may be iron rods of small cross-section whereby a current of comparatively high voltage and low amperage may be used.

The process.—Alternating current is preferably used in melting and keeping molten the electrolyte at the beginning of a run in order to defer separation of sodium until the level of the electrolyte is so high that it will collect entirely within the sodium-chamber. The curtain is then incrusted with salt by repeatedly ladling on of molten electrolyte or by repeated immersion therein until a sufficiently thick coating has been formed over the preliminary insulating layer. An electrolyte which melts at about 600 degrees C. is preferably used, suitable fluxes being added for this purpose and the electrolysis is conducted at a temperature of between 630 and 670 degrees C. Practically nothing but sodium-chlorid is decomposed, but in a long run slight volatilization and decomposition of the fluxes occur and occasional addition of the same is necessary. After the direct current has replaced the alternating the output is poor until all moisture is eliminated from the lining, etc., and the electrolyte is completely dehydrated. The separation of sodium soon starts however and grows larger and soon the receiver becomes heated up from the overflow of sodium therein which, when using a current of over 3000 amperes, is rapid enough to maintain the metal in a molten state so that it can readily be drawn off through the tap-hole *e'*. By adding some suitable hydrocarbon, such as paraffin, to the ladle before tapping, the sodium is prevented from burning by the covering which is thereby formed. From the tapping ladle the sodium is conveniently poured into large cast-iron caldrons kept hot by small fires and from thence into the molds at convenient times.

The process requires little attention beyond keeping the electrolyte at the proper level and temperature and periodically tapping the sodium from the receiver, but occasionally the appearance of sodium in the chlorin-chamber indicates that the condition of the curtain or of the crucible bottom has become abnormal and corrective methods must be applied.

If the electrolyte gets too hot the layer of salt on the curtain may become too thin to effectively insulate it and it may become active. The cure for this is to reduce the temperature of the electrolyte.

Variations in the thickness of the salt in-

crustation may cause imprisonment of particles of sodium in such a way that a metallic bridge grows downwardly and even into the chlorin-chamber and separation of sodium exterior to the sodium-chamber takes place. By raising the temperature of the electrolyte until the salt-incrustation is melted off the sodium bridges will be released, after which a new coating of salt may be formed on the curtain by cooling the electrolyte to its normal temperature.

It is preferable to replace the direct with alternating current during this operation so as to avoid separation of sodium and hasten the result though not entirely necessary.

The appearance of sodium outside of the curtain may also indicate that accumulated impurities on the crucible bottom have become active and are separating sodium so remote from the cathode that it rises outside the sodium-chamber.

A preliminary refining of the salt, however, renders the accumulation of impurities so slow that the above condition only appears at long intervals. This is conveniently effected by melting the salt in a small electric furnace with a current of comparatively high pressure and low volume. The insoluble impurities settle to the bottom of the melt and the soluble impurities which are less electro-positive than sodium are decomposed (by the current if direct current is used and by bringing sodium into contact with the melt if alternating current is used) and then settle to the bottom. By using the dehydrated and purified salt from the upper part of the melt, practically pure material is obtained for feeding into the electrolysis furnace.

Though our invention is particularly applicable to the production of metals of the alkali group, and specifically to sodium, certain features of it are of great value in the production of alkali-earth metals and of other metals of specific-gravity low enough to float to the surface of the electrolyte employed in their manufacture.

Having described our invention, we now claim as new in the production of a metal from a fused compound thereof of greater specific gravity:

1. Producing metals lighter than their fused salts, by electrolyzing the fused salt of such metal by current between an outer anode and an inner cathode, the anolyte and catholyte being partially separated by a chilled salt-incrusted curtain inclosing the cathode, the latter being of large mass to diminish heating, and approaching the cathode so closely as to form a limited annular zone of electrolyte between, maintaining a pool of produced metal within such curtain to form an extension of the cathode so that a preponderance of cathodic activity takes place in the upper part of the catholyte, and regulating the current density to keep the resistant electrolyte in said zone heated to such fluidity as to facilitate the ascent of produced metal, and to limit the thickness of salt crust on the curtain.

2. Producing metals lighter than their fused salts, by electrolyzing the fused salt of such metal by current between an outer anode and an inner cathode, the anolyte and catholyte being partially separated by a chilled salt-incrusted curtain inclosing the cathode, the cathode being of relatively large mass to avoid heating, and closely approached by the curtain, so that the heat generated in the electrolyte adjacent to the cathode limits the thickness of salt crust on the curtain.

3. Producing metals lighter than their fused salts, by electrolyzing the fused salt of such metal by current between an outer anode and an inner cathode, the anolyte and catholyte being partially separated by a chilled salt-incrusted curtain inclosing the cathode, the space within the curtain being covered over to form a cathode chamber, the produced metal descending from such chamber through a discharge passage, and maintaining atmospheric pressure in this chamber and in the discharge passage, to prevent siphoning of the produced metal.

4. Producing metals lighter than their fused salts, by electrolyzing the fused salt of such metal by current between an outer anode and an inner cathode, the anolyte and catholyte being partially separated by a chilled salt-incrusted curtain inclosing the cathode, the anode being of limited height, and protecting the anode by covering it with the electrolyte.

5. Separating the catholyte from the anolyte by a cooled curtain rendered nonactive first by a layer of solid insulating material and secondly by an outer incrustation of salt maintained solid by the cooling.

6. Separating the catholyte from the anolyte by a cooled curtain rendered nonactive first by a layer of solid infusible insulating material and secondly by an outer incrustation of salt maintained solid by the cooling.

7. Separating the catholyte from the anolyte by a cooled curtain rendered nonactive first by wrapping with asbestos and secondly by an outer incrustation of salt maintained solid by the cooling.

8. Separating the metal at an upwardly projecting cathode, between which and the anode is a cooled salt-incrusted curtain, confining the floating metal within the curtain and in contact with the cathode to form an extension of the latter, the combined cathode having such dimensions as to maintain a preponderance of cathode activity at the

upper part, and consequently maintaining a preponderance of current density in the electrolyte adjacent to the curtain and a consequent localization of heat, and regulating the current so that the cooling action of the curtain is limited to maintaining an insulating layer of salt thereon and prevented from solidifying the electrolyte between the cathode and the curtain.

9. Confining the separated metal by a cooled salt-incrusted curtain comprising upper and lower sections mutually insulated substantially as and for the purpose described.

10. Separating the metal at an upwardly projecting cathode made hollow to form a discharge conduit, confining it within a cooled curtain and maintaining a substantial equilibrium between the atmosphere of the sodium-chamber, cathode-chamber, and exterior to the furnace by the means and for the purpose described.

11. The described electrolytic apparatus, comprising a tubular ring curtain arranged between a central upwardly projecting cathode and an annular anode, the cathode projecting within the curtain and above the electrolyte, and confined within a vertical projection of the curtain, to insure that the produced metal shall ascend within the curtain, the cathode being of relatively large mass, and being closely approached by the curtain.

12. An electrolytic apparatus comprising a tubular ring curtain, a central cathode within it and an anode exterior to it, the space within the curtain being covered over to form a cathode chamber, and the cathode being hollow to form a discharge passage through it, with a connection between the cathode chamber and the discharge passage to equalize the pressures therein.

13. An electrolytic apparatus comprising a tubular ring curtain, a central cathode within it and an anode exterior to it, the space within the curtain being covered over to form a cathode chamber, and the cathode being hollow to form a discharge passage through it, with a connection between the cathode chamber and the discharge passage to equalize the pressures therein, and a seal interposed between said parts and the outer air to maintain them at substantially atmospheric pressure.

In witness whereof, we have hereunto signed our names in the presence of two subscribing witnesses.

GEORGE O. SEWARD.
FRANZ VON KÜGELGEN.
FRITZ VON BIDDER.

Witnesses as to George O. Seward:
D. ANTHONY USINA,
FRED WHITE.

Witnesses as to Franz von Kügelgen and Fritz von Bidder:
J. H. WEBB,
E. F. SCALES, Jr.