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JOHN J. GREBE AND RAY H. BOUNDY, OF MIDLAND, MICHIGAN, ASSIGNORS TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN

ELECTROLYTIC PRODUCTION OF ALKALI AND ALKALINE EARTH METALS

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The present invention relates to the production of alkali and alkaline earth metals, particularly to the production of metallic sodium or metallic calcium, by the electrolysis of a fused bath of the corresponding halide.

Although theoretically the electrolysis of a fused chloride should permit production of the metal at a relatively high current efficiency, as compared with the electrolysis of a fused hydroxide as, for example, in the case of sodium, yet in practice the expected high current efficiencies have not been realized, and in the present commercial processes of the character in hand the current efficiency may fall as low as 25% or lower.

In our experience with the electrolysis of a fused sodium chloride bath, as well as with a fused calcium chloride bath, initial current efficiencies of high value were obtained, which, however, rapidly decreased with continued operation, and in fact, although metal was formed copiously at first, its formation in some cases ceased entirely after a short period. Thise phenomenon was found to be caused by the presence in the bath of dissolved oxides of the metal being formed by the electrolysis, such oxides resulting from the action of oxygen of the air which entered the cell with the raw material feed or through leakage, or otherwise. We have discovered that the deleterious effect of oxygen may be overcome by adding to the bath a substance capable of uniting with the oxides present therein to form insoluble compounds which are precipitated and thereby rendered inert. By means of our improved method a current efficiency as high as 65 per cent. or more may be regularly attained.

To the accomplishment of the foregoing and related ends the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth but one of the various ways in which the principle of the invention may be carried out.

During the operation of an electrolytic cell for the production of sodium, calcium or other alkali or alkaline earth metals from their fused halides, the action of the oxygen of the air which may enter with the feed of raw material, by leakage or otherwise, results in the production of oxides of the corresponding metals. Such oxides are soluble in the fused bath, wherein they tend to accumulate as the electrolysis proceeds. We have not determined precisely the nature of the influence exerted by the dissolved oxides whereby the yield of metal is adversely affected, but there seems to be a cyclic oxidation and reduction which dissipates a part of the electrical energy supplied to the cell. Such action is also aided, apparently, by the rapid diffusion of the several components of the bath at the operating temperature, which would be about 800° C., for example, in the electrolysis of fused sodium chloride. Unless the aforesaid oxides are removed, the cumulative effect of their increasing concentration in the bath may eventually consume the greater part of the electrical energy without a corresponding yield of the desired product.

The oxides of the alkali and alkaline earth metals are basic in character, and we have found that at the temperature of the fused electrolyte they will unite readily with oxides of acidic character, such as alumina, silica, or boric acid, forming thereby aluminates, silicates, or borates, respectively, which are insoluble in the bath. In fact, the acidic compound employed need not be the oxide, but may equally well be the element itself, or a salt thereof, such as a chloride or sulphate, which may be converted to the oxide by reacting with a portion of the basic oxides in the bath and may thereupon react with a further portion of basic oxide to form the insoluble precipitate. For example, we have found that aluminum oxide will completely precipitate any sodium oxide or per-oxide that may be present in a fused sodium chloride bath employed for the electrolytic production of metallic sodium, forming an insoluble sodium aluminate which is precipitated out. The same result is obtained, however, if, instead of the oxide, metallic aluminum or aluminum chloride be used. Working in this way, we have found that a continuous production of the desired metal is achieved at a satisfactory current efficiency,

whereas, operating the same cell without employing a deoxidizer as herein disclosed, the current efficiency will steadily diminish and may finally be reduced approximately to zero by reason of the accumulation of dissolved oxide in the bath.

Since in practice great practical difficulties are connected with any attempt to prevent entirely the entrance of oxygen into the cell, our invention constitutes a valuable improvement in the art of electrolyzing a fused salt bath for the production of metals such as sodium, calcium, or the like, of the alkali or alkaline earth metal groups, concisely designated hereinafter as alkali-forming metals, wherein the action of oxygen affects the yield unfavorably. Our improved method may be applied with advantage to any type of electrolytic cell adapted to the process in hand, thereby counteracting the harmful effect of any oxygen which may enter, as well as making less necessary the costly and burdensome devices for rendering the cell air-tight.

Incidentally, the elimination of dissolved oxygen compounds from the bath minimizes the consumption of oxidizable carbon or graphite electrodes, which are best adapted for use in a fused salt bath.

In practice we have found it convenient to add the deoxidizer in the form of aluminum oxide along with the feed to the cell. The quantity to be added may vary within rather wide limits, dependant upon operating conditions, and the extent to which the design of the cell permits exclusion of air. However in general from one to two per cent. of the weight of raw material fed will be sufficient under good operating conditions. It is best to maintain a slight excess of deoxidizer, which is itself insoluble in the bath and does not cause disturbances, while at the same time it is capable of removing completely every trace of basic oxides dissolved therein. The sediment or sludge which collects at the bottom of the cell is removed from time to time by dipping, or by other suitable means.

We do not limit ourselves, however, to the manner of adding a deoxidizer nor to the particular compound employed for the purpose, provided it is a compound of the aforementioned character, nor to a definitely predetermined amount thereof to be added. We further point out that metallic aluminum, aluminum chloride and other salts of aluminum are effective, as well as aluminum oxide, and likewise silica, boric acid or other oxides of acidic character.

In the following claims it is understood that the expression "an agent providing an oxide of acidic character" includes such element itself, or a compound thereof, and specifically that "an agent containing aluminum" includes metallic aluminum, or a compound thereof.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. A method of the character described, which comprises electrolyzing a fused bath containing chiefly a halide of an alkali-forming metal, together with a minor component of at least one of the following:—a metal or compound of a metal capable of forming a metallic oxide of acidic character and further capable of reacting with the metal to be produced or with an oxide thereof to form a compound insoluble in said bath.

2. A method of the character described, which comprises electroyzing a fused bath containing chiefly a halide of sodium, together with a minor component of at least one of the following, to wit:—a metal or compound of a metal capable of forming a metallic oxide of acidic character and further capable of reacting with the metal to be produced or with an oxide thereof to form a compound insoluble in said bath.

3. A method of the character described, which comprises electrolyzing a fused bath containing chiefly a halide of an alkali-forming metal, together with a minor component of at least one of the following aluminum or aluminum oxide.

4. A method of producing metallic sodium, which comprises electrolyzing a bath of the fused chloride thereof in the presence of an agent providing an oxide of acidic character.

5. In the electrolytic production of metallic sodium from a bath of fused chloride thereof, the method of deoxidizing said chloride which consists in adding thereto an oxide of acidic character.

6. In the electrolytic production of metallic sodium from a bath of fused chloride thereof, the method of deoxidizing said chloride which consists in adding thereto aluminum oxide.

7. The method of making an alkali-forming metal which comprises electrolyzing a bath of the fused chloride thereof while continuously maintaining said bath substantially free from oxides of said alkali-forming metal by adding thereto aluminum oxide.

8. The method of making metallic sodium which comprises electrolyzing a bath of fused chloride thereof while continuously maintaining said bath substantially free from oxides of sodium by adding thereto aluminum oxide.

9. The method of deoxidizing a fused halide of an alkali-forming metal containing oxide of such metal dissolved therein, which consists in precipitating said oxide as an insoluble compound with an oxide of acidic character.

10. The method of making an alkali-form-

ing metal, which comprises electrolyzing a bath of fused chloride thereof while continuously maintaining said bath substantially free from dissolved oxides by adding thereto an agent containing aluminum.

11. The method of deoxidizing a fused halide of an alkali-forming metal containing oxide of such metal dissolved therein, which consists in precipitating said oxide as an insoluble compound with aluminum oxide.

12. The method of producing an alkali forming metal, which comprises electrolyzing a bath of a fused chloride thereof, replenishing said bath by adding fresh chloride thereto, and maintaining said bath substantially free from oxygen by continuously adding aluminum oxide thereto in admixture with said fresh chloride.

Signed by us this 28th day of June, 1928.

JOHN J. GREBE.
RAY H. BOUNDY.