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"IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF ELECTROLYTIC CALCIUM METAL"

"COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY, INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Messrs. VEERARAGHAVA ARAVAMUTHAN, Scientist, KUPPUSWAMY VENUGOPALAN, Scientist and THALEPERAMPIL PARAMESWARAN MADHAVAN, Senior Scientific Assistant, all Indian Nationals and working at Central Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF ELECTROLYTIC CALCIUM METAL.

Calcium is extensively used in industry especially as an alloying element. A number of alloys of calcium with aluminium, lead, copper, magnesium etc., are known. Calcium is used as a reducing agent in the production of metals like uranium, thorium, titanium, zirconium and chromium. It is used as a deoxidiser and a desulphurising agent. As a dehydrating agent it is also used in organic chemical industry for dehydrating alcohols and organic solvents. It is employed to separate argon from nitrogen. It is used in the production of nodular cast iron, mechanite castings etc. There are also many other uses for calcium metal.

The production of calcium metal by fused chloride electrolysis has many disadvantages. A high cathodic current density is employed. A water cooling arrangement for the cathode is normally employed and as soon as the metal is formed on the water-cooled cathode, the cathode is raised. Mixtures of calcium chloride with calcium fluoride or potassium chloride are commonly employed as electrolyte. Recently, calcium-chloride-barium chloride mixtures have also been employed with or without the addition of alkali metal chlorides. Because of the high current density employed, high cell voltages are necessary and therefore the energy requirements are high. In addition, as stated already, a water-cooled cathode which is almost a point cathode is employed and the collection of metal has to be done carefully.

These factors have been taken into account and a simple procedure has been evolved for overcoming the difficulties. Not only electric energy requirements have been considerably reduced but also deposition and the removal of calcium metal has been made easy.

It is known that calcium metal and sodium metal lie very close in the electrochemical series. It is also known that calcium and sodium are miscible with each other and form alloys. It is also known that the solubility of the calcium in sodium decreases as temperature decreases. Using these principles, the present invention is made.

According to the present invention, the process for the production of calcium metal by electrolysing calcium chloride in an electrolytic cell is characterised in that 80% calcium chloride (rest being water) is used as a raw material and is fed into the electrolytic cell containing about 90% calcium chloride on anhydrous basis and 5-10% alkali metal chlorides, sodium and/or potassium.

On passing d.c., calcium is liberated at the cathode and chlorine is evolved at the anode.

A high calcium, low sodium alloy is deposited first, instead of directly depositing calcium metal at the cathode.

Thus, a deposit containing about 97% calcium and 3% sodium is first obtained at the cathode which on subsequent reaction with the electrolyte produces calcium metal which floats and reaches the surface of the electrolyte.

By scrapping the cathode, the calcium metal floats on the surface and is removed from the cell by laddling.

The current densities employed, especially the cathode current density, is much lower as compared to the conventional current densities employed (1.5-2 amp/sq. cm.) and therefore a reduction in cell voltage is achieved, e.g., at 10 volts per cell, 26-28 kwh of d.c. are required per kilogram of the metal, and the energy requirement is considerably reduced in high amperage cells.

Electrolysis is conducted at 600°C, whereby the dissolution of calcium metal, unlike in the conventional electrolytic cell, in negligibly small.

This invention includes within its scope, an apparatus for the production of calcium metal by fused chloride electrolysis which comprises a refractory lined mild steel vessel to withstand the action of molten chloride electrolyte, a cathode of stainless steel or mild steel or any other similar material which is submerged in the electrolyte and a rod or plate anode of graphite and/or carbon concentric with the cathode without any gaseous atmosphere above except chlorine and provided with a refractory lined top lid with provision for sucking chlorine whereby the metal is laddled out from the cathode in a solid state.

The electrolytic cell is very simple in construction. It consists of mild steel outer vessel lined inside with fireclay or high alumina bricks. Cathode is of mild steel in the form of plates and the connections are given from the side walls of the electrolytic cell which are suitably insulated. The cell design is such that the shell of the cell can be assembled or dismantled by employing flange like arrangement to fix the face plates. Anodes and cathodes can be very easily fitted into the electrolytic cell. There may be necessity to remove the anode only and therefore a top anode system is employed which allows very easy removal of the anode and its replacement. There is no diaphragm in between the anode and cathode. The electrolyte can be very easily melted within the cell by shorting the anode and cathode with a graphite wedge to start with.

The cell can be operated continuously. The feed material is 80% calcium chloride on anhydrous basis and the remaining 20% as water of hydration.

The process relates to the production of calcium metal by fused chloride electrolysis.

The device is an electrolytic cell which has been simplified as stated already.

Normally, anhydrous calcium chloride is used as a cell feed whereas we employ, as stated already, commercially available 80% calcium chloride, the remaining 20% being water of hydration

In our process, we get a calcium-sodium alloy containing very small percentages of sodium (of the order of 3% sodium) at the cathode which then reacts with the electrolyte (containing on anhydrous basis 95% calcium chloride and about 5% of sodium and/or potassium chloride) to form the calcium metal

The removal of calcium metal is done by simply scrapping the cathode and laddling out the calcium metal This is possible because the calcium metal floats and reaches the electrolyte surface

The process is continuous The current densities and the voltage of operation are low, the energy for the production of calcium metal in comparison with the existing procedures is low

Detailed description of the cell is given below which indicates the novel features mentioned above In the accompanying drawings (1) indicates the mild steel vessel (2) indicates the bolt and nut arrangement (3) represents the refractory lining (4) is cathode lead (5) is mild steel cathode (6) is graphite anode (7) is electrolyte.

The melting of the electrolyte is carried out by placing a wedge of graphite between anode and cathode and filling up the space with a mixture of calcium chloride and sodium chloride and then impressing d c The wedge acts as a resistor The heat generated in the wedge melts the mixture and further feeding of the salt mixture is continued till the required level of the electrolyte is obtained which is about 6″ above the cathode Then the wedge is negotiated with a rod and removed out the cell DC at 10 volts, 500 ampers is impressed The temperature is maintained at about 600°C by varying the current and voltage, if need be Once in an hour or so the cathode is scrapped with rod, when the metal floats up which is laddled out Then fresh calcium chloride is added During this process as metal is formed the electrolyte level lowers and after the metal is removed it is again made up by the fresh addition of calcium chloride

The main advantage of the process is it is a continuous one and requires less electrical energy per kilogram of metal produced

The main difficulty normally encountered in the production of calcium metal is the high solubility of calcium metal in calcium chloride This alkaline earth metal also quickly oxidises when exposed to atmosphere in a hot condition It is rather a cumbersome procedure to employ any inert atmosphere The present invention has taken care of all these factors by employing a suitable electrolyte composition, temperature and also getting the metal deposited just below the electrolyte level so as to prevent the metal from having free access to air However, it allows it to raise upto the electrolyte level The metal is deposited as calcium low sodium alloy The sodium present in the alloy is mostly chlorinated during the upward movement of anodic chlorine The metal is deposited near solid state

WE CLAIM :

1 A process for the production of calcium metal by electrolysing calcium chloride in an electrolytic cell which is characterised in that 80% calcium chloride (rest being water) is used as a raw material and is fed into the electrolytic cell containing about 90% calcium chloride on anhydrous basis and 5-10% alkali metal chlorides sodium and/or potassium

2 A process as claimed in Claim 1 wherein on passing d c , calcium is liberated at the cathode and chlorine is evolved at the anode

3 A process as claimed in Claim 1 or 2 wherein a high calcium, low sodium alloy is deposited first, instead of directly depositing calcium metal at the cathode

4 A process as claimed in Claim 3 wherein a deposit containing about 97% calcium and 3% sodium is first obtained at the cathode which on subsequent reaction with the electrolyte produces calcium metal which floats and reaches the surface of the electrolyte

5 A process as claimed in any of the preceding claims wherein by scrapping the cathode, the calcium metal floats on the surface and is removed from the cell by laddling

6 A process as claimed in any of the preceding claims wherein the current densities employed, especially the cathode current density, is much lower as compared to the conventional current densities employed (1 5 2 amp/sq cm) and therefore a reduction in cell voltage is achieved, e g , at 10 volts per cell, 26-28 kwh of d c are required per kilogram of the metal, and the energy requirement is considerably reduced in high amperage cells

7 A process as claimed in any of the preceding claims wherein electrolysis is conducted at 600°C, whereby the dissolution of calcium metal unlike in the conventional electrolytic cell, in negligibly small

8 An apparatus for the production of calcium metal by fused chloride electrolysis as claimed in any of the preceding claims which comprises a refractory lined mild steel vessel to withstand the action of molten chloride electrolyte, a cathode of stainless steel or mild steel or any other similar material which is submerged in the electrolyte and a rod or plate anode of graphite and/or carbon concentric with the cathode without any gaseous atmosphere above except chlorine and provided with a refractory lined top lid with provision for sucking chlorine whereby the metal is laddled out from the cathode in a solid state

Dated this 23rd day of September, 1967

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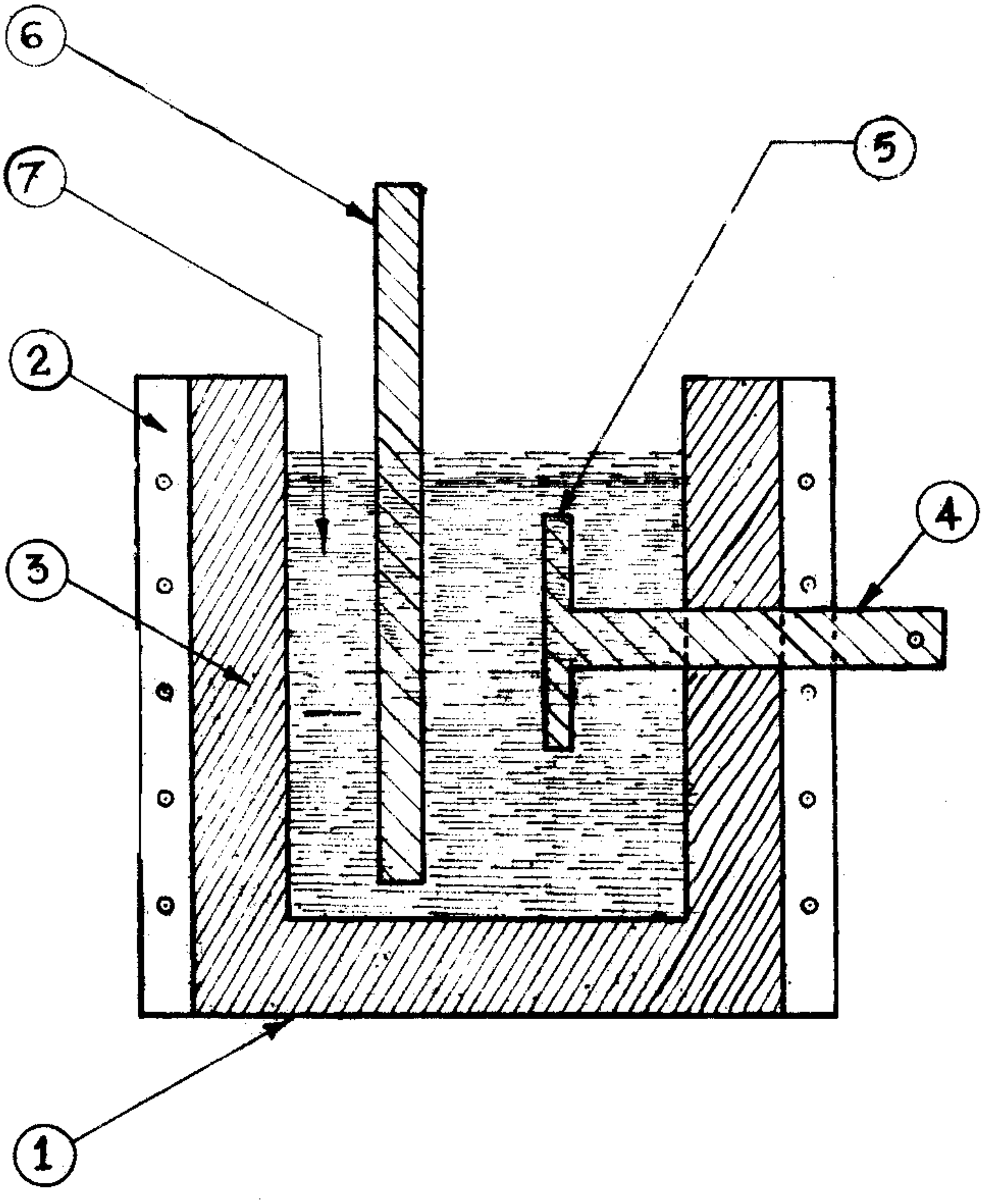

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