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PRODUCTION OF SODIUM

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4 Claims. (Cl. 204—68)

The present invention relates to the production of sodium metal by electrolysis of a fused salt mixture. More particularly it relates to novel salt compositions and a process for the production of sodium by electrolysis of these compositions.

Metallic sodium is usually produced by the electrolysis of sodium chloride in the molten state in a cell containing a steel gauze diaphragm between anode and cathode, the diaphragm serving to reduce recombination of the anode and cathode products as they rise through the electrolyte. In order to obtain an electrolyte of sufficiently low melting point for commercial working, it is usual to add a considerable amount of calcium chloride to the sodium chloride. For example, a bath containing about 60% $CaCl_2$ works in the range 550–600° C., and electrolysis of such a molten mixture yields mainly sodium as the cathode product. Some calcium is, however, also liberated at the cathode so that the cathode product is in effect a solution of the higher-melting calcium in liquid sodium. The presence of this calcium causes serious difficulties in operating the cell. It appears that electrolyte composition variations and/or temperature variations in the anode-cathode gap at times cause an increase in calcium deposition sufficient to exceed the solubility of calcium in sodium, for it is found that solid deposits of calcium occur at the cathode, and these can bridge the gap between cathode and diaphragm, causing short circuits, which result in current efficiency losses and destruction of the diaphragm.

The presence of dissolved calcium in the liquid sodium leaving the cell causes further troubles. As the liquid cools on its way out of the cell, solid calcium precipitates in the exit pipes, and special scrapers have to be operated frequently to prevent blockages. Filtration has to be employed to remove further quantities of calcium from the liquid sodium, and even when this calcium is returned to the system for reaction with the cell electrolyte in order to recover sodium there is some loss of metal from the system, and the current efficiency of sodium production is reduced.

We have now found that the aforementioned difficulties in producing sodium by the electrolysis of a fused salt mixture containing sodium chloride are almost entirely overcome if there is used as the electrolyte a mixture of sodium chloride with the chlorides of the alkaline earth metals calcium, strontium and barium in certain proportions.

According to the present invention, metallic sodium is produced by the electrolysis in the fused state of a salt mixture comprising by weight sodium chloride (NaCl) 28–36%, calcium chloride ($CaCl_2$) 23–35%, strontium chloride ($SrCl_2$) 10–25%, and barium chloride ($BaCl_2$) 13–30%.

We have found that when an electrolyte within this range of compositions is employed in a conventional cell comprising a graphite anode, a steel cathode and a steel gauze diaphragm, little or no solid calcium is precipitated at the cathode and that consequently shorting from cathode to diaphragm does not occur and the life of the diaphragm is increased. The amount of calcium in the liquid sodium leaving the cell is only about 0.07–0.20%

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compared with 1–2% for the conventional sodium chloride/calcium chloride electrolyte, so that deposits of solid calcium in the cell exit pipes and vessels are avoided, with consequent reduction in labour and maintenance costs. Also very much less calcium remains to be removed as sludge from the cooling sodium and returned to the cells. Apart from easing operational difficulties and lowering maintenance costs, the reduction in calcium production brings with it an appreciable improvement in current and energy efficiency. Furthermore, the quaternary electrolytes of the invention permit considerable fluctuations in electrolyte temperature and composition during working without damage to the cell. They become completely solid only at temperatures below about 460° C., whereas the conventional binary mixtures of $CaCl_2/NaCl$ are completely solid at about 507° C., and ternary mixtures which have been proposed devoid of calcium chloride are completely solid at 565–580° C.

To assist in maintaining the quaternary electrolyte completely liquid at all likely operating temperatures we prefer to limit the sodium chloride content to not more than 33% by weight. As shown hereinafter, a commercial cell has been operated successfully with a sodium chloride content up to the limit of 36% by weight, but at this concentration there is a possibility of forming regions of undissolved salt in the electrolyte when the bath is replenished.

The following example illustrates the practice of the invention in commercial sodium cells.

Example 1

An electrolyte of approximate composition by weight NaCl 33%, $CaCl_2$ 30%, $SrCl_2$ 22%, $BaCl_2$ 15% was melted in a substantially conventional Downs cell and electrolysed for the production of sodium over a period of 62 days. The electrolyte was maintained by regular additions of the component salts, and its composition lay in the range NaCl 31–36%, $CaCl_2$ 28–35%, $SrCl_2$ 21–24.5%, $BaCl_2$ 13.6–16.3% throughout the period. The cell operated at a current of 30.6–30.8 ka. with a voltage of 6.68–6.83 volts, in the temperature range 561–579° C., the average energy yield being 116 g. of sodium per kwh. and the average current efficiency being 90.4%.

During one period of 20 days the cell operated at an average voltage of 6.67 volts with an average temperature of 574° C., a current efficiency of 92.4% and an energy yield of 118.9 g. of sodium per kwh. During another period (21 days), when the cell current was 30.8 ka., the voltage was 6.73 volts, the cell temperature was 576° C., with a current efficiency of 92.5% and an energy yield of 117.9 g. of sodium per kwh.

It will be seen that the cell operated at high current efficiency and high energy yield. Operation was trouble free. No calcium deposits were found in the cell exit pipes or the sodium receivers and the average diaphragm life was more than 45% higher than when using a conventional sodium chloride/calcium chloride electrolyte. Analysis of the sodium produced in the cell showed a calcium content of only 0.13% by weight average, together with 400 p.p.m. strontium and less than 5 p.p.m. barium.

Example 2

An electrolyte of approximate composition by weight NaCl 30%, $CaCl_2$ 32%, $SrCl_2$ 15%, $BaCl_2$ 23% was melted in a substantially conventional Downs cell and electrolysed for the production of sodium. The results herein reported were obtained by testing over the first 250 days of the cell's life, but the cell remained in operation thereafter. The electrolyte composition was maintained by addition of the component salts as necessary, and its composition lay in the range NaCl 29–33%, $CaCl_2$

30–34%, $SrCl_2$ 12–15%, $BaCl_2$ 21–24% during the period of the test. The cell operated at a current of 30.0–30.8 ka. with a voltage of 6.3–6.63 volts, in the temperature range of 566–595° C. Over the whole test period of 250 days the cumulative current efficiency was 85.5% on sodium and the cumulative energy yield was 113.9 g. of sodium per kwh. During the first 120 days of operation the efficiencies were even higher, average current efficiency being 88.4% and energy yield 117.4 g. of sodium per kwh., with an average diaphragm life 150% longer than when using a conventional sodium chloride/calcium chloride electrolyte.

No calcium deposits were found in the cell exit pipes or the sodium receivers. Analysis of sodium direct from the cell (without filtration) showed the presence of calcium 0.1%, strontium 0.025% and barium less than 0.0001%.

The electrolyte composition of this example is cheaper in capital cost than that of Example 1, since it contains a smaller proportion of the most expensive strontium salt component.

What we claim is:

1. In a process for the production of metallic sodium containing a minor amount of calcium by electrolyzing a fused salt composition containing sodium chloride and calcium chloride, the improvement for reducing the amount of calcium in the metallic sodium comprising electrolyzing a fused salt composition containing about 28 to 36% by weight sodium chloride, about 23 to 35% by wegiht calcium chloride, about 10 to 25% by weight strontium chloride and about 13 to 30% by weight barium chloride to produce metallic sodium containing less than about 0.20% calcium.

2. A process according to claim **1**, wherein the sodium chloride is present in a proportion not exceeding 33% by weight of the salt composition.

3. A salt composition suitable for the production of metallic sodium containing less than about 0.20% calcium, said composition consisting essentially of a mixture of sodium chloride, calcium chloride, strontium chloride and barium chloride, said mixture having a percent by weight composition comprising a sodium chloride content of about 28 to 36%, a calcium chloride content of about 23 to 35%, a strontium chloride content of about 10 to 25%, and a barium chloride content of about 13 to 30%.

4. A salt composition according to claim **3**, wherein the content of sodium chloride does not exceed 33% by weight of the composition.

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