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(54) Title: SYSTEM FOR THE ELECTROLYTIC PRODUCTION OF SODIUM CHLORATE

(57) Abrégé/Abstract:
The invention relates to a system for the electrolytic production of sodium chlorate starting from a sodium chloride brine buffered with phosphate and having a reduced or zero chromium content. The system comprises electrolytic cells of the undivided type with intercalated cathodes and anodes; in one preferred embodiment, the cathodes consist of steel perforated sheets activated with a Fe-Mo alloy coating.

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(54) Title: SYSTEM FOR THE ELECTROLYTIC PRODUCTION OF SODIUM CHLORATE

(57) Abstract: The invention relates to a system for the electrolytic production of sodium chlorate starting from a sodium chloride brine buffered with phosphate and having a reduced or zero chromium content. The system comprises electrolytic cells of the undivided type with intercalated cathodes and anodes; in one preferred embodiment, the cathodes consist of steel perforated sheets activated with a Fe-Mo alloy coating.

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SYSTEM FOR THE ELECTROLYTIC PRODUCTION OF SODIUM CHLORATE

DESCRIPTION OF THE INVENTION

The present invention relates to a process for the industrial electrolytic production of sodium chlorate, characterised by a high yield and a high electrical efficiency.

The production of chlorates ranks among the most important processes of industrial electrochemistry, since sodium chlorate is the raw matter for the production of sodium perchlorate and chlorite and more importantly of chlorine dioxide, employed for water treatment and for bleaching in the paper industry, as a replacement for chlorine. Sodium chlorate is commonly produced in electrolytic cells of the undivided type starting from a sodium chloride brine at controlled pH, with anodic production of hypochlorite and hypochlorous acid, which quickly disproportionate at the process temperatures (60-90°C) generating chlorate, while hydrogen evolution takes place at the cathode side.

The electrolytic cells for chlorate production can be of the monopolar or of the bipolar type: in the most common case, they consist however of a multiplicity of cathodes and a multiplicity of anodes disposed in a comb-like structure and mutually intercalated.

As regards the construction materials, the anodes generally consist of a titanium substrate activated with suitable catalytic coatings for chlorine evolution, comprising noble metals such as platinum, ruthenium, palladium, iridium or oxides thereof, as such or in admixture with other stabilising oxides for instance as disclosed in US 3,632,498; the cathodes are generally made of a ferrous material, such as for example low carbon steels, and are normally not activated. Some catalytic coatings for hydrogen evolution suitable for ferrous cathodic substrates are in fact known in the art, for instance comprising molybdenum and/or tungsten alloys with iron, cobalt or nickel, as disclosed in GB 992,350 and GB 1,004,380, in the attempt of improving the process voltage and thus decreasing the rather high energy costs; the voltage gain obtained with these types of activation is nevertheless considered too small for justifying the adoption thereof in industrial manufacturing processes.

As regards the details of the chlorate manufacturing process, the electrolyte

initially consisting of a sodium chloride brine is either progressively enriched in chlorate until reaching the required concentration in a batch cycle, or it is at least partially withdrawn at the cell outlet and subjected to a chlorate separation process, while a restoration of sodium chloride concentration is simultaneously carried out in the cell. In both cases, the control of pH is an essential factor to keep the efficiency high, due to the competition between the chlorate generation reaction and the anodic oxygen evolution, and even more between the cathodic hydrogen evolution and the undesirable hypochlorite reduction; the optimum pH interval to maximise the efficiency ranges between 6 and 7, and even more preferably between 6.3 and 6.6. To keep these optimum pH values, it is necessary to buffer the process electrolyte, as will be evident to those skilled in the art; for this purpose, the currently existing plants of chlorate electrolytic industrial production resort to the addition of sensible quantities of dichromate ion (3 to 5 g/l), implying a series of annoying secondary problems. The presence of dichromate (and of chromate in equilibrium therewith) is for instance undesirable in the subsequent chlorine dioxide manufacturing process, and its separation from chlorate by crystallisation is hindered by the very similar solubility. Furthermore, the toxicity of hexavalent chromium increases the treatment cost of process exhausts.

It is an object of the present invention to provide a system for sodium chlorate production with low energy consumption making use of a nil or extremely limited amount of chromium compounds.

This and other objects will be made clear by the following description and examples, which are by no means intended to limit the extent of the invention.

The invention consists of a system for sodium chlorate production comprising electrolytic cells fed with a buffered sodium chloride brine, wherein the buffering agent comprises phosphate ions at a concentration not lower than 1 g/l. By phosphate ion concentration it is hereby intended the sum of the concentrations of all the ionic species derived from phosphoric acid according to their mutual equilibrium in aqueous solutions, for instance comprising $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} anions and optionally the oligomers derived therefrom. According to a preferred embodiment of the invention, the sodium chloride brine of the system of the invention contains chromate and/or dichromate ions at a concentration not higher

than 0.1 g/l; in an even more preferred embodiment, the sodium chloride brine is free of chromium in any form.

In a largely preferred embodiment, the electrolytic cells of the system of the invention are equipped with cathodes consisting of a ferrous matrix, for instance carbon steel, activated with a coating consisting of a molybdenum or tungsten alloy with a metal selected between iron, cobalt and nickel. The inventors have in fact surprisingly noticed that the voltage decrease observed with this type of alloys, which is limited to 100-150 mV with the brines of the prior art at the usual current densities of industrial processes (2.5 - 3 kA/m²) reaches 450-500 mV with the sodium chloride brine added with phosphate ions in accordance with the present invention. The gain in terms of energy efficiency is therefore so high that it largely justifies resorting to cathodes activated with this type of coating, notwithstanding the higher manufacturing costs. The inventors noticed the surprising efficiency of Fe-Mo alloy coatings in a weight ratio comprised between 30:70 and 70:30, but this kind of effect can be observed also with other formulations. Without wishing the present invention to be bound to any particular theory, it might be assumed that the effect of ionic species added to the brine is not only buffering the pH, but also adsorbing to the cathode surfaces creating films which inhibit the decomposition of the generated chlorate or the undesirable cathodic reduction of hypochlorite. The catalytic effect of coatings such as Fe-Mo alloy can be for instance attributable in part to the higher ionic adsorption and to the formation of inhibiting films of higher efficacy, most likely due to their reduced thickness. Such an effect is already sensible with the chromium oxide polymer films generated under the effect of chromate or dichromate adsorption, but it is much more evident in presence of films containing phosphoric species. The cathodic catalytic coating as herein described are preferably applied galvanically, with a thickness preferably comprised between 10 and 50 micrometres.

EXAMPLE 1

A series of cathodes for electrolytic cell was prepared starting from 0.5 mm thick carbon steel perforated sheets; the sheets were degreased in a saturated solution of caustic soda in ethanol for 5 minutes, then etched in 25% by weight HCl for 2 minutes. The samples were then rinsed with distilled water, dried, weighed and

immersed in a bath for Fe-Mo alloy electrodeposition. The bath was prepared by dissolution of 9 g/l $FeCl_3$, 40 g/l Na_2MoO_4, 75 g/l $NaHCO_3$ and 45 g/l $Na_2P_2O_7$ in distilled water, and the deposition was carried out at a constant current density of 100 mA/cm² at a temperature of 60°C, making use of a platinum fine mesh as the counterelectrode, under stirring. The deposition was protracted until obtaining a 20 micrometre thick alloy comprised of 47% by weight molybdenum and 53% by weight iron, as detected by a subsequent EDS test (X-ray energy dispersion spectroscopy).

The so obtained samples were installed in a commercial cell for chlorate production, intercalated in a comb-like fashion with a series of titanium anodes activated with ruthenium and titanium oxides as known in the art, and subjected to a series of electrochemical characterisations as disclosed hereafter. Another cell equivalent to the former was also assembled, the only difference being the cathodes, obtained from the same carbon steel perforated sheet but free of catalytic coating.

EXAMPLE 2

The cells of example 1, one comprising Fe-Mo alloy-coated steel cathodes and the other with non activated cathodes, were employed in a discontinuous sodium chlorate manufacturing process. The feed brine had an initial composition of 300 g/l NaCl added with 3 g/l of $Na_2Cr_2O_7$, as known in the art. The initial feed pH was 6.41. Each of the two cells was operated at a current density of 2.5 kA/m² at a temperature of 61°C, and the test was protracted for 8 hours, until obtaining a chlorate concentration of about 0.8 mol/l. The cell with the activated cathodes worked at a very stable voltage, comprised between 3.01 and 3.02 V, with a 98% efficiency; the cell with the non activated cathodes worked at a voltage comprised between 3.14 and 3.17 V with 97% efficiency. In both cases, the hypochlorite concentration was quickly stabilised at a value of 0.06 mol/l.

EXAMPLE 3

The test of example 2 was repeated with a feed brine having a starting composition of 300 g/l NaCl added with 3 g/l of sodium acid phosphates (as the sum of Na_2HPO_4 and NaH_2PO_4) and 0.1 g/l $Na_2Cr_2O_7$, in accordance with the

invention. The initial feed pH was 6.40. Each of the two cells, equipped with new cathodes, was operated at a current density of 2.5 kA/m² at a temperature comprised between 60 and 61°C, and the test was protracted for 8 hours, until obtaining a chlorate concentration of about 0.8 mol/l.
The cell with the activated cathodes worked at a voltage comprised between 2.86 and 2.87 V, with a 97% efficiency; the cell with the non activated cathodes worked at a voltage comprised between 3.08 and 3.12 V with 91% efficiency. The hypochlorite concentration was quickly stabilised at a value of 0.06 mol/l for the cell with activated cathodes, and of 0.07 mol/l for the cell with non activated cathodes.

EXAMPLE 4
The test of example 2 was repeated with a feed brine having a starting composition of 300 g/l NaCl added with 3 g/l of sodium acid phosphates (as the sum of Na_2HPO_4 and NaH_2PO_4) and free of chromium, in accordance with the invention. The initial feed pH was 6.41. ach of the two cells, equipped with new cathodes, was operated at a current density of 2.5 kA/m² at a temperature of 61°C, and the test was protracted for 8 hours, until obtaining a chlorate concentration of about 0.8 mol/l.
The cell with the activated cathodes worked at a voltage comprised between 2.50 and 2.53 V, with a 94% efficiency; the cell with the non activated cathodes worked at a voltage comprised between 3.16 and 3.17 V with 72% efficiency. The hypochlorite concentration was quickly stabilised at a value of 0.065 mol/l for the cell with activated cathodes, and of 0.076 mol/l for the cell with non activated cathodes.

The examples demonstrate that a downright reduction in the energy consumption of the electrolytic manufacturing process of sodium chlorate starting from sodium chloride is made possible by the system of the invention, meanwhile reducing or eliminating the content of chromium used for buffering the feed solution.
Example 2 shows, as known by those skilled in the art, that the activation of cathodes consisting of a ferrous substrate by means of a molybdenum and iron alloy in combination with a brine of the prior art improves the electrochemical

performances and the process efficiency; the extent of such improvement is nevertheless rather modest.

Example 3 shows that the brine in accordance with the invention, with a significant phosphate content, allows reducing the addition of chromium to minimum levels, maintaining in any case the process efficiency at acceptable levels also making use of non activated cathodes. Moreover, the energy saving obtainable through the use of non activated cathodes is more than interesting, and the efficiency in this case is substantially preserved.

Example 4 shows that the brine totally free of chromium according to a preferred embodiment of the invention, coupled to the use of activated cathodes, allows such a high energy saving that the small efficiency loss of the process can be considered negligible, also in view of the lower cost for the treatment of exhausts permitted by the absence of chromium. The total elimination of chromium on the other hand does not allow the use of non activated cathodes any more, because the process efficiency is lowered to non acceptable levels.

The foregoing description is not intended to limit the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is univocally defined by the appended claims.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements or additives.

CLAIMS

1. System for sodium chlorate production comprising at least one electrolytic cell equipped with a multiplicity of cathodes and a multiplicity of anodes, fed with a sodium chloride brine added with a buffering agent, wherein said buffering agent comprises at least 1 g/l of phosphate ions.

2. The system of claim 1, wherein said cathodes of said electrolytic cell consist of a ferrous matrix provided with a coating consisting of a molybdenum and/or tungsten alloy with at least one metal selected from the group of iron, cobalt and nickel.

3. The system of claim 1 or 2, wherein said feed contains chromate and dichromate ions at a concentration not exceeding 0.1 g/l.

4. The system of claim 1 or 2, wherein said feed is free of chromium.

5. The system of any one of claims 2 to 4, wherein said ferrous matrix of said cathodes is a carbon steel.

6. The system of claim 5, wherein said coating is a galvanic coating containing 30 to 70 % Fe and 30 to 70 % Mo expressed as weight percentage.

7. The system of claim 6, wherein said galvanic coating has a thickness comprised between 10 and 50 micrometres.

8. The system of any one of the previous claims, wherein said electrolytic cell is of the undivided type and said cathodes are disposed in a comp-like fashion intercalated to said anodes.

9. The system of claim 8, wherein said cathodes comprise a ferrous matrix consisting of a perforated sheet.

WT/mm