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(54) **METHOD AND DEVICE FOR PRODUCING AN ALKALI METAL HYPOCHLORITE SOLUTION**

(76) Inventors: **Andreas Siemer**, Allmersbach im Tal (DE); **Andreas Schwarz**, Waiblingen (DE); **Norbert Maier**, Weissach im Tal (DE)

Correspondence Address:
HARNESS, DICKEY & PIERCE, P.L.C.
P.O. BOX 828
BLOOMFIELD HILLS, MI 48303 (US)

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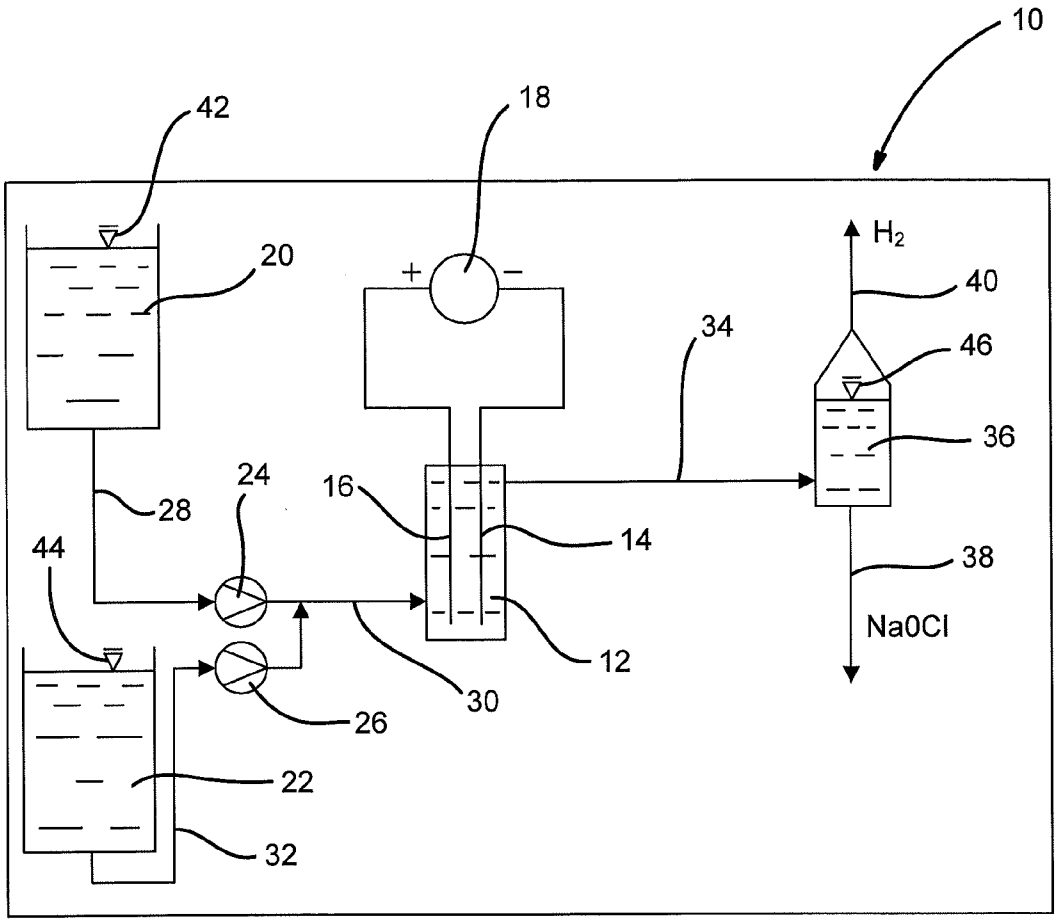
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(57) **ABSTRACT**

The invention provides a method and a device for the production of an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, having at least one non-divided electrolytic cell (**12**), means (**20, 22, 24, 26**) for supplying a brine solution into the electrolytic cell (**12**) at a defined volumetric flow rate and a defined salt concentration, and having an a.c. voltage source (**18**) for the production of current across the electrolytic cell (**12**). The current intensity is adjusted to a fixed value so that the concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l, preferably to 0.6 g/l.



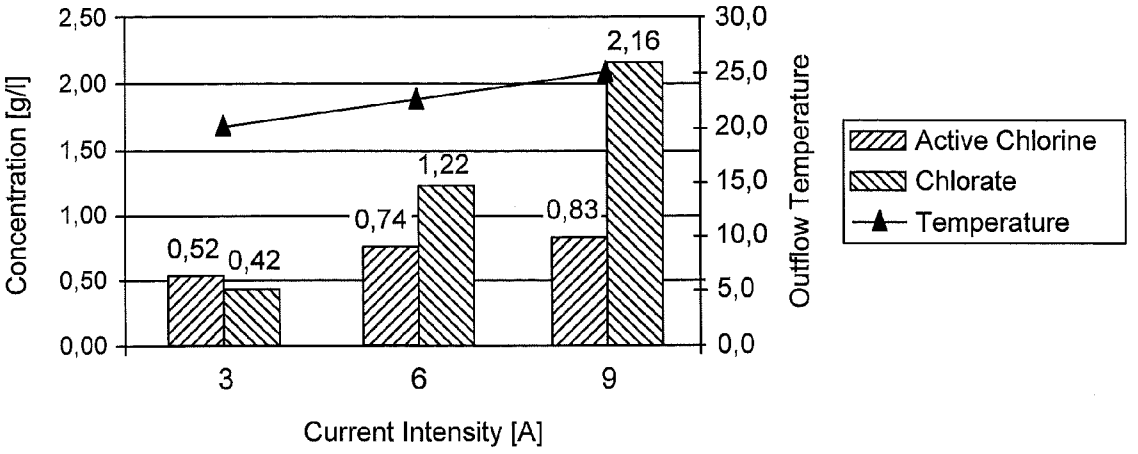

2,50
2,00
1,50
1,00
0,50
0,00
Concentration [g/l]
30,0
25,0
20,0
15,0
10,0
5,0
0,0
Outflow Temperature
0,52
0,42
0,74
1,22
0,83
2,16
3
6
9
Current Intensity [A]
Active Chlorine
Chlorate
Temperature

Fig. 1

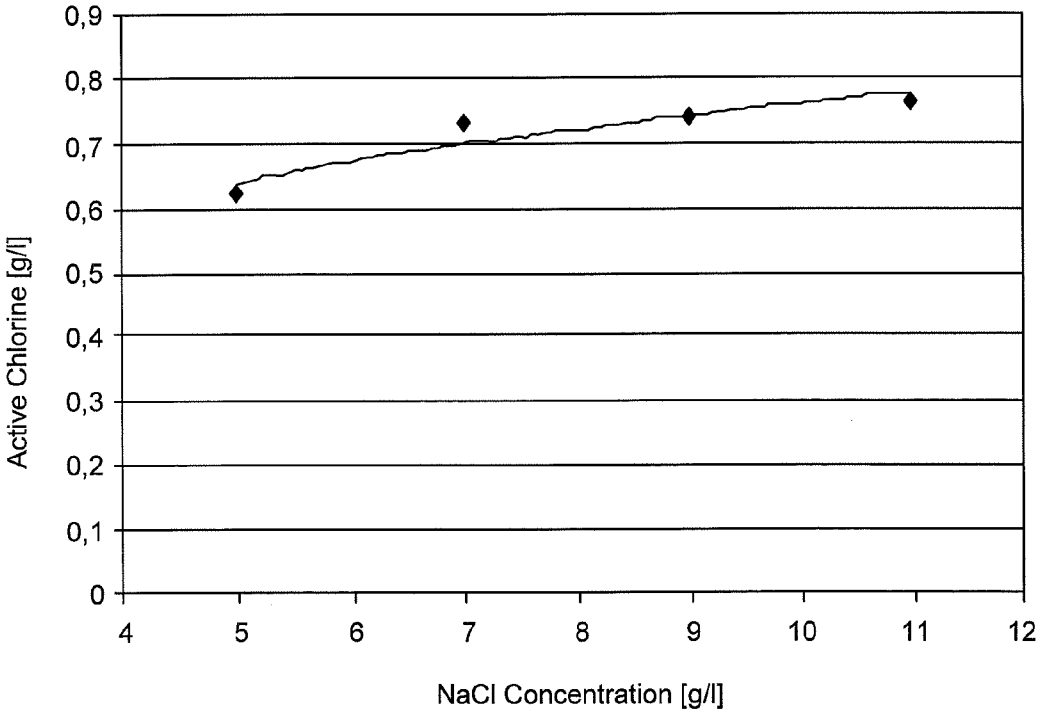

0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Active Chlorine [g/l]
4
5
6
7
8
9
10
11
12
NaCl Concentration [g/l]

Fig. 2

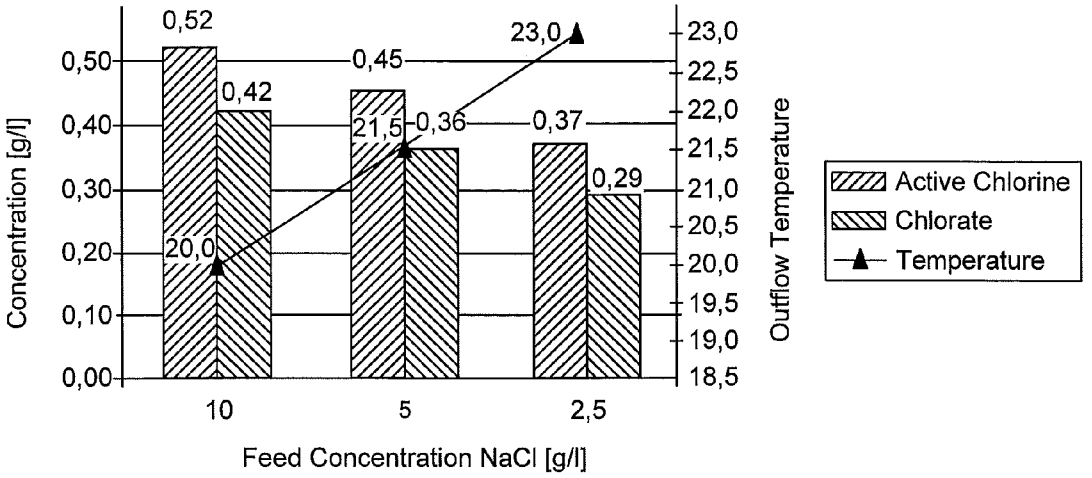

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0,37
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23,0
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0,20
0,10
0,00
23,0
22,5
22,0
21,5
21,0
20,5
20,0
19,5
19,0
18,5
10
5
2,5
Concentration [g/l]
Outflow Temperature
Feed Concentration NaCl [g/l]
Active Chlorine
Chlorate
Temperature

Fig. 3

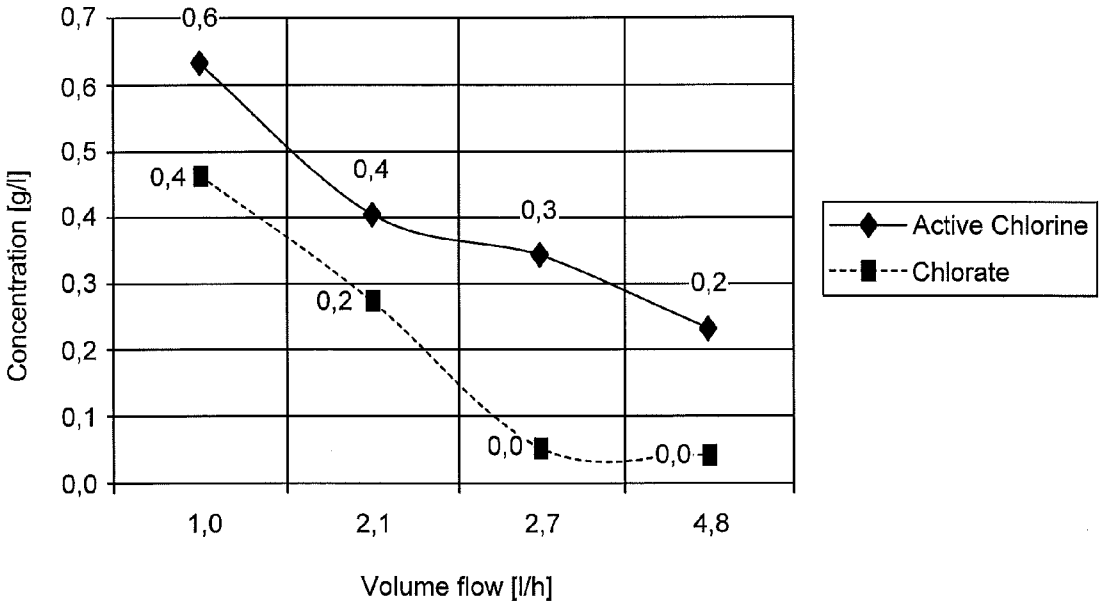

0,6
0,4
0,3
0,2
0,4
0,2
0,0
0,0
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
1,0
2,1
2,7
4,8
Concentration [g/l]
Volume flow [l/h]
Active Chlorine
Chlorate

Fig. 4

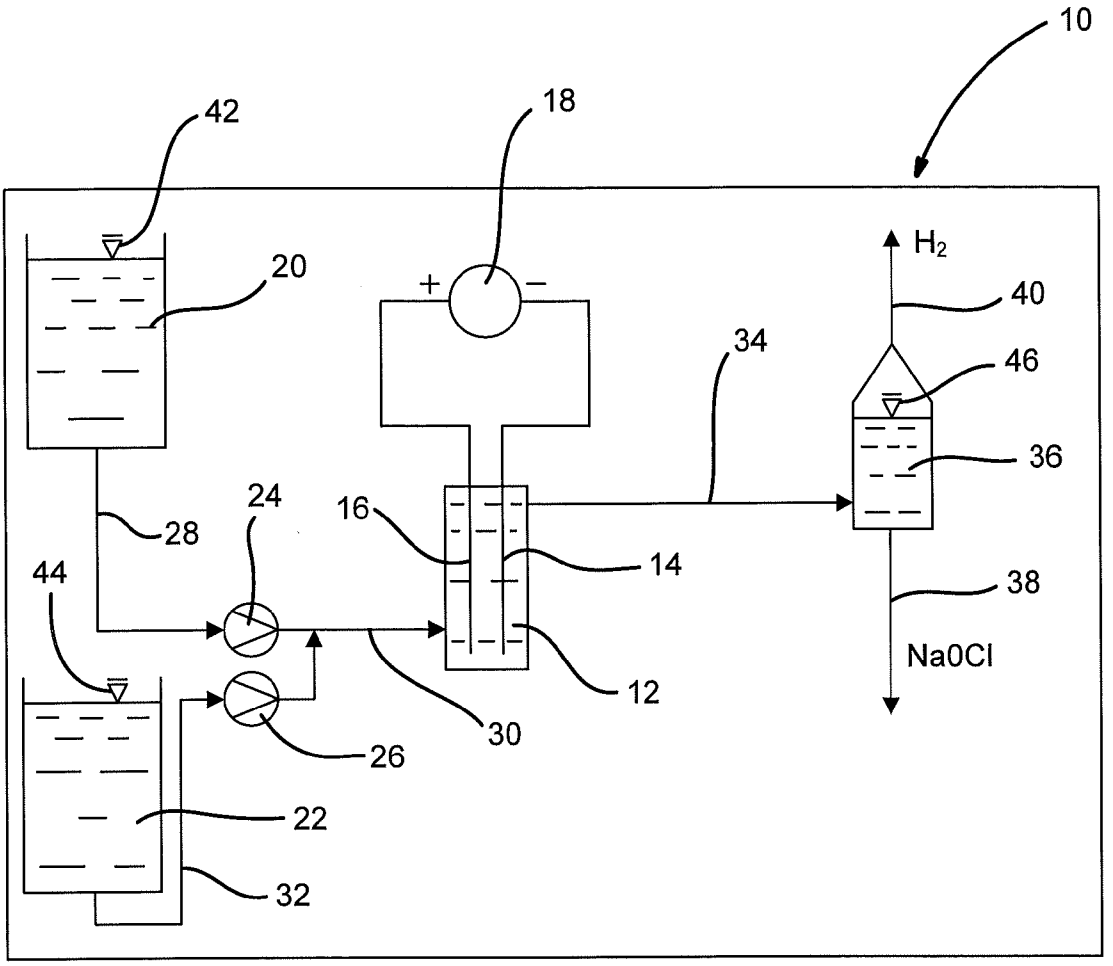


Fig. 5

METHOD AND DEVICE FOR PRODUCING AN ALKALI METAL HYPOCHLORITE SOLUTION

[0001] The present invention relates to a method for producing an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, where a brine solution is supplied to an electrolytic cell at a defined volumetric flow rate and a defined salt concentration. The invention further relates to a device for producing an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution comprising at least one non-divided electrolytic cell, means for supplying the electrolytic cell with a brine solution at a defined volumetric flow rate and a defined salt concentration, and a d.c. voltage source for generation of a current across the electrolytic cell.

[0002] There exists a constant demand for production of sodium hypochlorite solutions which are employed for disinfection of water. While such "chlorination" of water is carried out at an industrial scale, for example in the purification of drinking water by the water supply departments of cities and communities, there is a need for mobile units suitable for the production of sodium hypochlorite solutions on the site, in particular in disaster areas. After filtering and reverse osmosis, purified water is mixed with the sodium hypochlorite solution to prevent renewed germination.

[0003] Mobile systems for the production of sodium hypochlorite solutions by electrolysis of sea water or brine have already been known.

[0004] Such systems are marketed by Wallace & Tiernan GmbH, Günzburg, under the names OSEC-S® and OSEC-B®.

[0005] In the case of these systems, either filtered sea water or saturated brine is supplied into an electrolytic cell using a metering pump. The concentration of the brine is then reduced to approximately 2% by dilution water which likewise is supplied into the electrolytic cell. In the electrolytic cell, sodium hypochlorite solution and hydrogen are produced, and the hydrogen is separated from the sodium hypochlorite solution and is diluted with air to a non-dangerous concentration, using a blower, and is evacuated to the open air. The sodium hypochlorite solution so produced has a concentration of approximately 6 g/l of effective chlorine. The whole process for the production of sodium hypochlorite solution is monitored and controlled by an SPC control with a view to achieving the highest possible yield of chlorine and the least possible amount of waste products.

[0006] The use of an SPC control in combination with corresponding sensors is seen as a problem in such systems as it requires maintenance and supervision. However, this cannot always be guaranteed, in particular when systems of that kind are employed in disaster areas.

[0007] In another system for the production of a sodium hypochlorite solution, known from DE 37 04 955 A1, the brine concentration in the electrolytic cell is measured by evaluation of the voltage at the electrodes and of the flowing current. A signal proportional to the conductivity is then derived from those values and is used for controlling a metering pump for saturated salt solution.

[0008] That system likewise is connected with the beforementioned disadvantages.

[0009] A different system for the production of sodium hypochlorite solution, known from DE 28 06 441 A1, uses an electrolytic cell without a diaphragm that has a ratio of at least 1.5:1 or over between the effective anode area and the effective cathode area in the electrolytic cell. It is intended in this way to improve effective utilization of the sodium hypochlorite and the current yield under stationary flow conditions. According to a variant of that configuration, the electrolytic cell is additionally cooled in order to reduce the quantity of sodium chlorate produced.

[0010] A system of that kind likewise cannot guarantee optimum process control, in particular if it does not use a cooling system in an effort to make the structure as simple as possible.

[0011] It has been further known from U.S. Pat. No. 4,329,215 to use an electrolytic cell for the production of sodium hypochlorite where the anode chamber and the cathode chamber of the electrolytic cell are separated by an ion exchange diaphragm which is permeable to anions, gases and liquids.

[0012] The use of such a diaphragm may reduce the problem of chlorate formation during electrolysis.

[0013] However, such an electrolytic cell is very maintenance-intensive.

[0014] In view of this, it is the object of the invention to provide a method and a device for the production of an alkali metal hypochlorite solution which guarantees a simple, trouble-free and low-maintenance construction and yet allows a sufficiently high concentration of alkali metal hypochlorite solution to be produced.

[0015] This object is achieved by a method for the production of an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, where a brine is supplied into a non-divided electrolytic cell at a defined volumetric flow rate and a defined salt concentration and where the current intensity is adjusted to a fixed value so that the concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l, preferably to a maximum of 1 g/l, more preferably to a maximum of 0.6 g/l.

[0016] The object of the invention is further achieved by a device for the production of an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, having at least one non-divided electrolytic cell, means for supplying a brine solution into the electrolytic cell at a defined volumetric flow rate and a defined salt concentration, and having an a.c. voltage source for the production of current by the electrolytic cell, where the current intensity is adjusted to a fixed value so that the concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l, preferably to a maximum of 1 g/l, more preferably to a maximum of 0.6 g/l.

[0017] The object of the invention is perfectly achieved in this way.

[0018] The use of an undivided electrolytic cell without a diaphragm between anode and cathode, as provided by the invention, guarantees an especially simple and low-maintenance set-up. It has been found according to the invention that production of an alkali metal hypochlorite solution with firmly preset parameters can be operated with advantage if the concentration of chloride obtained in the course of

electrolysis is limited by a preset current intensity. In particular, it has been observed according to the invention that when the current intensity is raised beyond a specific value a less than proportional rise in concentration of active chlorine is obtained while at the same time production of undesirable chlorate as a by-product increases at a more than proportional rate.

[0019] The invention therefore provides that by suitably determining the current intensity it is possible on the one hand to guarantee a favorable concentration of active chlorine in the alkali metal hypochlorite solution produced and, on the other hand, to limit the production of undesirable chlorate to a tolerable amount.

[0020] Generally, it is thus possible to operate the method with preset parameters, without the expense of a special automatic control, in such a favorable way that advantageous continuous operation with little maintenance input is guaranteed.

[0021] According to an advantageous further development of the invention, the current intensity is pre-adjusted to between 2 and 6 amperes, preferably to between 2 and 4.5 amperes, more preferably to between 2.5 and 3.5 amperes.

[0022] One thereby obtains the best possible compromise between the concentration of active chlorine produced and the quantity of undesirable chlorate obtained.

[0023] According to a further embodiment of the invention, a constant salt concentration of the brine is obtained by mixing a saturated brine with water.

[0024] It is possible in this way, in an especially easy fashion, to firmly preset the desired inflow concentration of the brine in the electrolytic cell to a desirable value.

[0025] As a saturated brine mixed with water, preferably with de-ionized water or drinking water, is used as a starting product, it is possible in this way to ensure a suitable concentration of the brine fed into the electrolytic cell, without any additional control input.

[0026] Alternatively, it is also imaginable to use a brine with a given salt concentration that is supplied into the electrolytic cell at a constant feed rate.

[0027] According to an advantageous further development of the invention, the salt concentration of the brine supplied into the electrolytic cell is pre-adjusted to a value of between 2 and 10 g/l, preferably to between 5 and 10 g/l.

[0028] It is possible in this way to guarantee a sufficient yield of chlorine, while the amount of undesirable chlorate obtained will not rise excessively.

[0029] According to another embodiment of the invention, the brine is supplied into the electrolytic cell at a constant volumetric flow rate V that is determined by the formula $V=w\times A$, depending on the effective electrode area A (in m^2), wherein V is the flow velocity, for which a value is selected between 4×10^{-5} m/s and 12×10^{-5} m/s, preferably between 6×10^{-5} m/s and 9×10^{-5} M/s.

[0030] The electrolytic cell is operated in this way with an optimum volumetric flow by which optimum yield is guaranteed as a function of the cell dimensions.

[0031] The DC voltage source according to the invention preferably is designed as constant-current source.

[0032] This permits the current intensity of the electrolytic cell, that has been defined to be optimally suited, to be maintained with particular precision.

[0033] As has been mentioned before, the desired concentration of the brine supplied into the electrolytic cell can be adjusted either by mixing the saturated brine with water or by the use of brine of a specific concentration. For mixing and/or feeding the pre-adjusted brine one preferably uses metering pumps which guarantee a constant mixing ratio or a constant pump rate.

[0034] The electrodes of the electrolytic cell may be made, for example, from a material containing iron, mercury, stainless steel, titanium and/or platinum. Preferably, the electrodes consist of uncoated titanium.

[0035] This has been found to provide good yield and high durability of the electrodes.

[0036] It is understood that the features of the invention mentioned above and those yet to be explained below can be used not only in the respective combination indicated, but also in other combinations or in isolation, without leaving the scope of the invention.

[0037] Further features and advantages of the invention will become apparent from the description that follows of a preferred embodiment of the invention, with reference to the drawing. In the drawings:

[0038] FIG. **1** shows the relationship between current intensity and concentration of active chlorine and/or of chlorate obtained and the outflow temperature in an electrolytic cell according to the invention;

[0039] Fig. shows the relationship between the inflow concentration of a sodium chloride solution fed in and the active chlorine concentration produced;

[0040] FIG. **3** shows the relationship between the inflow concentration of sodium hypochlorite and the concentration of active chlorine and chlorate produced and the outlet temperature;

[0041] FIG. **4** shows the relationship between the volumetric flow employed and the concentration of active chlorine and chlorate produced; and

[0042] FIG. **5** shows a simplified schematic sketch of the device according to the invention.

[0043] The basic structure of a device according to the invention is illustrated in FIG. **5** and is indicated generally by reference numeral **10**.

[0044] The device **10** serves to produce an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, using an electrolytic cell **12**. The electrolytic cell **12** is supplied from a brine tank **20** with a saturated brine that is mixed with water from a water tank **22** before it is supplied into the electrolytic cell **12**. The electrolytic cell **12** is designed as a one-piece cell, not subdivided by a diaphragm, and comprises a housing made from PVDF. The electrodes **14**, **16**, which consist of uncoated titanium, are connected to a DC voltage source **18**, designed as a constant-current source, in order to produce a constant current of 3 amperes at a voltage of approximately 3.5 to 4.5 Volts. In the electrolytic cell, sodium hypochlorite is formed from the aqueous sodium chloride solution during which operation

hydrogen is set free. The outlet of the electrolytic cell is connected with a collection tank **36** via a pipe **34**. The sodium hypochlorite solution produced in this way is carried off through a pipe **38**, while the hydrogen rises to the top and is carried off through an exhaust pipe **40** and is diluted to a non-dangerous concentration. The concentration of the brine supplied into the electrolytic cell **12** is adjusted by metering pumps **24**, **26** each of which produces a constant volumetric flow. The first metering pump **24** draws in saturated brine from the brine tank **20** at a volumetric flow of 42 ml/h. The second metering pump draws in deionized water (or drinking water) from the water tank **22** via a pipe **32** at a volumetric flow of 2.958 l/h. The pressure lines of the two metering pumps **24**, **26** open into the inlet of the electrolytic cell **12** via a common pipe **30**. In the illustrated example, the electrolytic cell **12** is thus supplied with a volumetric flow of 3 l/h of sodium hypochlorite solution the concentration of which is adjusted to a value of approximately 5 g/l by mixing the saturated brine with de-ionized water.

[**0045**] As is further indicated in FIG. **5**, the filling levels of the brine tank **20**, the water tank **22** and the collection tank **36** preferably are monitored by a level monitoring system that may comprise level sensors **42**, **44**, **46** and float switches (not shown), for example.

[**0046**] Now, the operating parameters of the device **10** are adjusted in a fixed way to obtain a yield of sodium hypochlorite in a range desirable for the production of sodium hypochlorite while the amount of undesirable chlorate obtained is simultaneously minimized.

[**0047**] This will be explained in more detail hereafter with reference to FIGS. **1** to **4**.

[**0048**] FIG. **1** shows a diagram of the concentration of active chlorine (sodium hypochlorite, NaOCl) and of chlorate as a function of different current intensities. In addition, the outflow temperature of the electrolytic cell is indicated for a constant inflow temperature of 17° C. The flow rate is 3.5 l/h in the illustrated example, for a sodium chlorite concentration of 10 g/l. All measuring results (including those shown in FIGS. **2** to **4**) relate to an electrolytic cell with an effective electrode area of 140 mm×80 mm and an electrode spacing of 2 mm.

[**0049**] As appears from FIG. **1**, more than proportional amounts of the undesirable by-product chlorate are generated at current intensities of over 3 amperes. Further, it can be clearly seen that the outflow temperature of the product likewise rises as the current intensity increases.

[**0050**] Now, the current intensity is limited according to the invention in such a way that a chlorate concentration in the outflow of less than 1.5 g/l, preferably less than 1.0 g/l, more preferably less than 0.6 g/l or than 0.5 g/l is obtained. This can be achieved using a current intensity that is preferably adjusted to between 2.5 and 3.5 amperes, optimally to 3 amperes.

[**0051**] FIG. **2** illustrates the influence of the NaCl concentration of the inflow on the content of active chlorine in the outflow; the current intensity used in this case was 3 amperes.

[**0052**] It can be seen that starting at an inflow concentration of over 7 g/l the content of active chlorine will continue to rise only insignificantly.

[**0053**] In addition, FIG. **3** shows that as the salt concentration increases, the amount of chloride formed rises above proportion. In FIG. **3**, the concentration of active chlorine and of chlorate in the outflow and the outflow temperature of the electrolytic cell are represented as a function of the NaCl concentration in the inflow (current intensity: 3 A). One therefore has to find a compromise between the yield in chlorine on the one hand and the formation of chlorate, which is to be prevented, on the other hand.

[**0054**] Preferably, the inflow concentration is therefore adjusted to a value of between 2 and 10 g/l, preferably to 5 g/l.

[**0055**] FIG. **4** illustrates the influence of the volumetric flow of the brine solution inflow on the concentration of active chlorine and of chlorate in the outflow, for an NaCl inflow concentration of 10 g/l (current intensity: 3 A).

[**0056**] It was found that with the electrolytic cell used in this case, having an active electrode area of 140 mm×80 mm, at an electrode spacing of 2 mm, the chlorate concentration is clearly reduced for a volumetric flow of 2.77 l/h and above. One therefore uses a volumetric flow of 3 l/h for an electrolytic cell with the before-mentioned dimensions.

[**0057**] The optimum volumetric flow for operation of the electrolytic cell is of course dependent on the geometric dimensions of the cell. In the case of the cell used, the dimensions of the electrode area are 140×80 mm, with a spacing of 2 mm. There exists a functional interdependence between the volumetric flow and the size of the cell as in the case of larger cells the volumetric flow (and the yield) increases proportionally as a function of the ion migration rate.

[**0058**] The volumetric flow V is preferably determined according to the formula $V=w\times A$, as a function of the active electrode area A (in m^2), wherein w is the flow velocity, for which a value is selected between 4×10^{-5} m/s and 12×10^{-5} m/s, preferably between 6×10^{-5} m/s and 9×10^{-5} m/s.

[**0059**] This guarantees optimum operation in the desired range according to FIG. **4**, with minimized formation of chlorate.

[**0060**] It is understood that, accordingly, electrolytic cells of different sizes can be operated in the desired optimum range provided the volumetric flow is adjusted to a corresponding value.

[**0061**] It is further understood that larger units can of course be built up from a plurality of electrolytic cells of any desired size.

[**0062**] The device according to the invention distinguishes itself by an especially simple and reliable construction and operates, even without the use of any automatic control means, in an optimum range in which formation of chlorate is minimized and yet a sufficiently high sodium hypochlorite concentration is obtained.

[**0063**] As the temperature parameter is difficult to influence in practical use and as the temperature influence has been found to be relatively small in the illustrated experiments, temperature has been allowed for only by limiting the current intensity (outflow temperature rises with rising current intensity). One can therefore do without any cooling measures.

[0064] Once stationary conditions were obtained, variations in the concentration of active chlorine were no longer determined, not even after a prolonged operating time of 30 hours. An expensive automatic control system is therefore not needed.

1. A method of producing an alkali metal hypochlorite solution, wherein a brine is supplied into a non-divided electrolytic cell at a preset volumetric flow rate and a specific salt concentration and wherein said electrolytic cell is operated at a current intensity that is preset to a fixed value so that a concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l.

2. The method as defined in claim 1, wherein said current intensity is preset to between 2 and 6 amperes.

3. The method as defined in claim 1, wherein a constant salt concentration of said brine is obtained by mixing a saturated brine with water.

4. The method as defined in claim 1, wherein a brine with a given salt concentration is used as brine solution, that is supplied into the electrolytic cell at a constant feed rate.

5. The method as defined in claim 1, wherein a salt concentration of said brine supplied into the electrolytic cell is preset to a value of between 2 and 10 g/l.

6. The method as defined in claim 1, wherein said brine is supplied into said electrolytic cell at a constant volumetric flow rate V that is determined by the formula V=w×A, depending on the effective electrode area A (in m^2), where V is the flow velocity, for which a value is selected between 4×10^{-5} m/s and 12×10^{-5} m/s.

7. A device for producing an alkali metal hypochlorite solution, comprising at least one non-divided electrolytic cell, means for supplying a brine into said electrolytic cell at a defined volumetric flow rate and a defined salt concentration, and comprising a DC voltage source for the production of current across said electrolytic cell, said DC voltage source operating said electrolytic cell at a preset current intensity so that a concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l.

8. The device as defined in claim 7, wherein said current intensity is preset to between 2 and 6 amperes.

9. The device as defined in claim 8, wherein said DC voltage source is configured as a constant-current source.

10. The device as defined in claim 7, wherein said means for supplying brine comprises a brine tank with saturated brine solution and a water tank with water, each of which are coupled with said electrolytic cell via a metering pump.

11. The device as defined in claim 7, wherein said means for supplying brine comprise a brine tank with brine solution which is coupled with said electrolytic cell via a metering pump.

12. The device as defined in claim 7, wherein a brine solution is supplied into said electrolytic cell at a constant salt concentration which is preset to a value of between 2 and 10 g/l.

13. The device as defined in claim 7, wherein said means for supplying brine into said electrolytic cell is preset to deliver a constant volumetric flow rate V that is determined by the formula V=w×A, depending on an effective electrode area A (in m^2), where V is the flow velocity, for which a value is selected between 4×10^{-5} m/s and 12×10^{-5} m/s.

14. The device as defined in claim 7, wherein said electrolytic cell comprises electrodes that are made from a material selected from the group formed by iron, mercury, stainless steel, titanium and platinum.

15. The device as defined in claim 14, wherein the said electrolytic cell comprises electrodes that consist of uncoated titanium.

16. A device for producing an alkali metal hypochlorite solution, comprising at least one non-divided electrolytic cell, means for supplying a brine into said electrolytic cell at a preset volumetric flow rate and a specific salt concentration, and comprising a DC voltage source for the production of current across the electrolytic cell which is preset to deliver a constant current intensity between 2 and 6 amperes so that the concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l, and wherein said means for supplying brine into said electrolytic cell is preset to deliver a constant salt concentration between 2 and 10 g/l.

17. The device as defined in claim 15, wherein said brine is supplied into the electrolytic cell at a constant volumetric flow rate V that is determined by the formula V=w×A, depending on an effective electrode area A (in m^2), where V is the flow velocity, for which a value is selected between 4×10^{-5} m/s and 12×10^{-5} m/s.

18. The device as defined in claim 16, wherein said current intensity of said electrolytic cell is set to a fixed value so that said concentration of chlorate produced during electrolysis is limited to a maximum of 0.6 g/l.

19. A method of producing an alkali metal hypochlorite solution, wherein a brine is supplied into a non-divided electrolytic cell at a specific volumetric flow rate and a specific salt concentration and wherein said non-divided electrolytic cell is operated at a current intensity that is set to a fixed value between 2 and 6 amperes so that the concentration of chlorate produced during electrolysis is limited to a maximum of 1.5 g/l, and wherein said brine is supplied into said electrolytic cell with a constant salt concentration which is preset to a value of between 2 and 10 g/l.

20. The method of claim 19, wherein said electrolytic cell is operated at a current intensity that is set to a fixed value between 2 and 6 amperes so that the concentration of chlorate produced during electrolysis is limited to a maximum of 0.6 g/l.

* * * * *