# Amount of Table Salt When Making Sodium Hypochlorite and Temperature to Product Performance Effect Study

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### Abstract

The article deals with the dependence of the product yield of the process on the concentration and temperature of the starting material in the process conducted in an electrolyzer with vertically mounted graphite electrodes in the flow mode. To prevent side processes in the installation, only graphite electrodes are used. The article also provides the theoretical basis for the formation of sodium hypochlorite.

**Keywords:** *drinking water, sodium chloride, electrolysis plant, hypochlorite, graphite electrodes, free active chlorine, sodium cations, chloride anions.* 

### INTRODUCTION

In 1785, the Swedish chemist Carl Wilhelm Scheele [1] and in 1787 the French chemist Claude Louis Bertolle [2] discovered that a solution of chlorine gas in the water had the property of bleaching natural fabrics. [3, 4].

## $Cl_2 + H_2O \leftrightarrow HCl + HOCl$ (1)

In 1778, on the banks of the Seine River in Paris, a company called Societé Javel began producing bleach by dissolving chlorine gas in water. Since this product was unstable, from 1787 chlorine was passed through a solution of potassium carbonate to produce a product called "javel water", which had strong bleaching properties and was stable.

$$Cl_2 + 2K_2CO_3 + H_2O \rightarrow KCl + KOCl + 2KHCO_3$$
(2)

French pharmacist Antoine Labarrack replaces potash with caustic soda (sodium hydroxide) and produces the cheaper sodium hypochlorite "Labarrack water" for bleaching and disinfection. This process is carried out in a cold solution:

$$Cl_{2} + 2NaOH + H_{2}O \rightarrow NaCl + NaOCl + H_{2}O$$
(3)

Even though the disinfecting properties of hypochlorites were discovered in the first half of the 19th century, their practical use began only at the end of the century. The first water treatment system was established in Hamburg in 1893 [5]. The first drinking water treatment plant appeared in Jersey City, America in 1908 [6].

Chlorination of drinking water was first enforced by adding chlorinated lime to water in 1910 during cholera epidemics in Kronstadt, Russia, and typhoid fever in Nizhny Novgorod. Treatment of water with gaseous chlorine was carried out in 1917 at the Leningrad water treatment station [7, 8]. Sodium hypochlorite - chlorine and sodium oxide, chemical formula - NaOCl - sodium salt of chloric acid. Historical names of this saltwater solution are "javel water" or "labarrack water".

Sodium hypochlorite is very unstable in the free form and is usually used as a relatively stable colourless crystalline substance pentahydrate NaOCl·5N2O or as aqueous solutions with a strong chlorine odour. Its elemental composition is Na (sodium) (30.9%), Cl (chlorine) 47.6%), and O (oxygen) (21.5%). The molecular mass of NaClO is -74.44 and it is very soluble in water. 53.4 g of sodium hypochlorite dissolves in 100 g of water at 20  $^{\circ}$ C (or 130 g dissolves in 100 g of water at 50  $^{\circ}$ C). The solubility of NaClO is given in the table below.

|     | Temperature, °C   | 10     | 0      | 10     | 20     | 25     | 30     | 50     |  |  |
|-----|---|--------|--------|--------|--------|--------|--------|--------|--|--|
|     | Solubility, %   | 26     | 29.5   | 38     | 53.4   | 82     | 100    | 130    |  |  |
| Tab | Table 2. Densities of NaClO aqueous solutions at 18 °C [9]. |        |        |        |        |        |        |        |  |  |
|     | Quantity, %   | 1      | 2      | 4      | 6      | 8      | 10     | 14     |  |  |
|     | Density, G/L  | 1005.3 | 1012.1 | 1025.8 | 1039.7 | 1053.8 | 1068.1 | 1097.7 |  |  |
|     | Quantity, %   | 18     | 22     | 26     | 30     | 34     | 38     | 40     |  |  |
|     | Density, G/L  | 1128.8 | 1161.4 | 1195.3 | 1230.7 | 1268.0 | 1308.5 | 1328.5 |  |  |

Table 1. Solubility of NaClO in water

 Table 3. Freezing temperatures of NaClO aqueous solutions [10]

| Quantity, %                 | 0,8   | 2     | 4     | 6     | 8      | 10     | 12     | 15,6   |
|-----------------------------|-------|-------|-------|-------|--------|--------|--------|--------|
| Freezing temperature,<br>°C | - 1.0 | - 2.2 | - 4.4 | - 7.5 | - 10.0 | - 13.9 | - 19.4 | - 29.7 |

Values of thermodynamic quantities of sodium hypochlorite in infinitely dilute aqueous solution [11]:

• standard enthalpy of formation,  $\Delta$ Ho298: - 350.4 kDj/mol;

• standard Gibbs energy, ΔGo298: – 298,7 kDj/mol;

Concentrated aqueous solutions of sodium hypochlorite are unstable under normal conditions, and their amount in solution decreases over time (at a rate of 0.08 to 0.1% per day). Its decomposition rate is actively influenced by sunlight, heavy metal cations and alkali metal chlorides. However, the presence of magnesium or calcium sulfate, boric acid, silicates, etc. in the solution reduces the rate of decomposition of hypochlorite. The stability of solutions with a strong (pH value > 11) [12] alkaline environment is considered longer.

Three crystalline hydrates of sodium hypochlorite have been identified:

□ monohydrate NaOCl·H2O – very unstable, decomposes at 60°C, explodes at higher temperatures [12],

□ crystalline hydrate NaOCl·2.5 H2O – It is more stable than the monohydrate and liquefies at 57.5  $^{\circ}$ C [12],

Dentahydrate NaOCl·5 H2O – stable form [13], consists of white or light green rhombic crystals (a = 0.808 nm, b = 1.606 nm, c = 0.533 nm, Z = 4). This salt is not hygroscopic, but it dissolves well in water. It rapidly decomposes in the air and turns into a liquid state [12]. The liquid temperature of sodium hypochlorite: 18 - 24.4 °C [13]. It decomposes when heated to 30-50 °C [14].

When choosing a chlorine disinfectant compound, attention is paid to the active chlorine-retaining substances in its composition. Active chlorine refers to the amount of chlorine that actively reacts with the main parts of the cells of microorganisms and other additives in water [15, 16].

When an aqueous solution of table salt is electrolyzed in a device with a steel cathode and a graphite anode, it is possible to obtain gaseous chlorine, hydrogen and caustic sodium under certain conditions. Chlorine and oxygen gases can be expected to evolve when a direct current is passed through an aqueous solution of sodium chloride:

$$2HO^{-} - 2\overline{e} \rightarrow \frac{1}{2}O_{2}\uparrow + H_{2}O \quad or \quad 2Cl^{-} - 2\overline{e} \rightarrow Cl_{2}\uparrow$$
(4)

HO – – The oxidation potential of anions is +0.41 B, and the oxidation potential of chlorine anions is +1.36 B. A saturated aqueous solution of table salt in a neutral environment contains  $1 \cdot 10^{-7}$  g-equiv/l of hydroxyl anions. The equilibrium oxidation potential of hydroxyl ions  $\varphi ar=0.82$  is equal to B and the amount of chlorine anions in this solution is 4.6 g-eq/l, its equilibrium oxidation potential  $\varphi ar=1.32$ . It is considered equal to B.

According to these data, it would be correct to release oxygen gas at the anode first, and chlorine gas to release when the amount of hydroxyl ions in the solution is too low. However, since the overstrain of oxygen is higher than that of chlorine in graphite, which is the anode material, chlorine gases are released first in the graphite anode. So, in the anode, chlorine anions give up their electron and become oxidized to chlorine atoms, and two atoms combine to form chlorine gas and move upward from the solution:

 $2Cl^{-} - 2\overline{e} \rightarrow Cl_{2} \uparrow \quad (5)$ 

The smallest value of the equilibrium oxidation potential of chlorine is observed in a saturated solution of table salt. Accordingly, it is recommended to use a saturated solution (310–315 g/l) in the stream to increase chlorine output.

At the cathode, the hydrogen cations in the solution are reduced and released as a gas:

$$2H^+ + 2\overline{e} \to H_2 \uparrow \qquad (6)$$

Since sodium chloride salt consists of strong alkali and strong acid residues, when dissolved

in water, it immediately dissociates into sodium cation and chlorine anion, both of which split water molecules to form hydrogen cation and hydroxyl anion. So, sodium and hydrogen cations neutralize chlorine and hydroxyl anions in this solution. When the polarized anodes and cathodes are lowered into the solution, chlorine gas is emitted from the anode and hydrogen gas from the cathode, leaving undissociated water molecules and hydroxyl anions with dissociated sodium cations in the solution. The remaining sodium cation in the solution breaks up an equivalent amount of water molecules. Therefore, the electrolysis process can continue until the amount of sodium chloride salt in the solution is exhausted. What kind of products are obtained as a result of this process depends on the conditions created, the material of the anode and cathode, the length of the electrodes, and the degree of separation of the resulting products from other compounds and raw materials in the reaction mixture.

Analysing the processes that occur when an aqueous solution of sodium chloride is electrolyzed, it has been confirmed in practice that hydrogen gases are produced at the cathode, not sodium metal. When any metal salt dissolves in water, it dissociates into a metal cation and an acid residue. Water molecules that do not contain other substances do not dissociate under normal conditions, that is, water molecules are not separated into ions. So, when table salt is dissolved in water, it breaks down into Na+ cation and Cl- anion. The resulting sodium cation breaks down water molecules according to the following reaction

$$NaCl + H_2O \rightarrow Na^+ + Cl^- + H^+ + HO^-$$
(7)

From this reaction, it can be seen that the ions of strong hydrochloric acid and strong caustic sodium neutralize each other in the solution. When the anode and cathode are lowered into this solution and a direct current is passed, the reason for the release of hydrogen at the cathode is that the reduction potential of hydrogen cations at the cathode is much smaller than the reduction potential of sodium at the cathode [17]:

$$Na^{+} + e^{-} = Na \qquad E = -2,71B$$
  

$$H_{2}O + 2e^{-} = H_{2} + 2HO^{-} \qquad E = -0,83B . \qquad (8)$$
  

$$2Cl^{-} - 2e^{-} = \uparrow Cl_{2} \qquad E = -1,36B$$

From these values, it can be seen that a smaller voltage is required for the hydrogen cation to accept an electron, and a larger voltage is required for the sodium cation to accept an electron. So, if hydrogen is released from the solution at the cathode and chlorine at the anode, sodium cations and hydroxyl anions remain in the solution. At the same time, gaseous chlorine with hydroxyl ions forms chloric active acid HOCl, and sodium cation splits a new water molecule to form hydrogen cation and hydroxyl anions. Instead of hydrogen in chloric active acid, the sodium cation is exchanged and sodium hypochlorite is formed in the solution. The process of electrolysis of an aqueous solution of sodium chloride in a device with a vertical electrode, without a barrier, is as follows [18].

Fig.1. In a vertical electrode, unobstructed device appearance of salt solution electrolysis



# Fig.2. Diagram of a laboratory apparatus for salt electrolysis.



### Practical part

A continuous-mode cellular electrolyzer with a vertically installed graphite electrode was assembled and research was conducted in 6 different amounts of table salt solutions at 4 different temperatures. In this device, both electrodes are made of graphite. In this case, the dimensions of the working surface of the electrode were 2.0 cm wide and 7.0 cm long, the distance between the electrodes was 1.1 cm, and the working surface of the electrodes was 0.14 dm2. A 500 ml saline solution is fed into the process through a hose from a dropper funnel placed 50 cm above the device (see image below). The resulting sodium hypochlorite flows through a hose to a product collector flask placed 50 cm below the device. During the process, the hydrogen gases generated at the cathode are vented into the air using a chimney cabinet.

At the beginning of the study, the temperature dependence of the process was studied. The rate of electrolyte passing through the device was kept between 50 and 55 mL/min by holding the separatory funnel tap in a certain position. The dependence of the process on the temperature based on the information in the available literature is about  $8A/dm^2$  current density and the amount of table salt is 1n. (5.85%) was taken. The hydrogen indicator of the electrolyte before the process was rN = 6.89. The results of research at this stage are presented in table 4 below.

Temperature measurement during the process was carried out in mercury glass thermometers manufactured based on GOST 215-73. The electrolysis process was carried out in the German GUNT Geratebau GmbH CE-105 rectifier. In this case, the mode of keeping the current constant was used. The hydrogen index of the obtained solutions was measured in a Bante 210 rN meter.

The presence of sodium hypochlorite was determined by decolorizing an aqueous solution of methyl orange indicator under the influence of active chlorine. A 0.005% solution of methyl orange and a 1 N solution of hydrochloric acid were used.

The amount of hypochlorite in the product is determined by determining the active chlorine. In this case, the amount of active chlorine is extracted from the potassium iodide solution by iodometry using active chlorine and determined by titration with a solution of sodium thiosulfate of known normality in the starch indicator.

| Fig. 3. A | ctive chlo | orine conten | t temperature |
|-----------|------------|--------------|---------------|
|-----------|------------|--------------|---------------|



| N⁰ | Temperature,<br>°C | Time spent<br>min. | $V_{Na_2S_2O_3},ml$ | Amount of active chlorine, g/l | rN    |
|----|--------------------|--------------------|---------------------|--------------------------------|-------|
| 1  | 10                 | 9,40               | 2,1                 | 0,37                           | 10,58 |
| 2  | 15                 | 9,20               | 2,6                 | 0,46                           | 10,24 |
| 3  | 20                 | 10,10              | 2,5                 | 0,44                           | 9,56  |
| 4  | 25                 | 9,20               | 2,3                 | 0,41                           | 9.65  |

 Table 4. Dependence of the amount of active chlorine on the process temperature

### Conclusion №1

1. The hydrogen index of the medium indirectly indicates the amount of alkali or acid in the product. Accordingly, the large pH at a low temperature means that the chlorine produced in the process is more absorbed in water and participates in the production of sodium hypochlorite.

2. The height of rN and the amount of active chlorine in the 2 experiments with a temperature of 15  $^{\circ}$ C were at a maximum value, although the time spent was at a minimum,

indicating that the range of 15-20  $^{\circ}$ C is the most favourable temperature.

Above the temperature of 25  $^{\circ}$ C, the mobility of the gases is high; their absorption into the water is low, and the rate of chlorine gas escaping to the air increases, which leads to a decrease in the productivity of the process.

Based on the results of the first stage, the temperature was kept at  $18 \pm 10$  °C during the study of the dependence of electrolysis on the amount of raw materials. Other quantities in the process are listed in table 5 below.

| N⁰ | The amount<br>of table salt<br>% | Current<br>density,<br>A/dm <sup>2</sup> | Time taken<br>for 0.5 l, min | Hydrogen indicator<br>of the environment,<br>pN | $V_{{\scriptscriptstyle N}a_2S_2O_3}$ ml | Amount of<br>active chlorine,<br>g/l |
|----|----------------------------------|--|------------------------------|---|--|--------------------------------------|
| 1  | 5                                | 2,0                                      | 7,05                         | 5,40  | 11,6                                     | 2,05                                 |
| 2  | 10                               | 2,0                                      | 7,00                         | 5,35  | 15,8                                     | 2,80                                 |
| 3  | 15                               | 1,67                                     | 7,14                         | 5,79  | 26,8                                     | 4,75                                 |
| 4  | 20                               | 1,33                                     | 7,41                         | 9,02  | 55,3                                     | 9,80                                 |
| 5  | 25                               | 1,33                                     | 7,44                         | 9,25  | 40,3                                     | 7,14                                 |
| 6  | 30                               | 1,33                                     | 8,26                         | 8.41  | 31,0                                     | 5,49                                 |

Table 5. Dependence of the amount of active chlorine on the number of raw materials

Fig. 6. Amount of table salt



### Conclusion №2

1. The productivity of hypochlorite in a continuous-mode electrolyzer with a vertical electrode depends on the amount of table salt in

the solution when the temperature is below 20  $^{\circ}$ C. During the study, the current density was reduced from 0.2A/dm<sup>2</sup> in a 10% solution to 0.167A/dm<sup>2</sup> in a 20% solution due to the possibility of large amounts of chlorine escaping into the air at high currents.

2. The light yellow colour of the product in experiments 1, 2 and 3 indicates the presence of free chlorine molecules in the reaction mixture and the presence of colourless sodium hypochlorite in the product of experiments 4 and 5.

3. If we analyze the hydrogen indicator values of the medium in both stages, according to the law of equivalents, chlorine and hydrogen in equivalent amounts undergo electrolysis in the process, but at low temperatures, chlorine gas binds with hydroxyl anions in the solution, gives one electron, and forms a solution of hypochlorous acid in water as a positive univalent cation. The hydrogen cations in this solution are attracted to the cathode and replaced by sodium cations. Thus, the hydrogen cation is reduced in the reaction mixture, leaving water molecules, sodium cations, hydroxyl and hypochlorite anions. Therefore, at low temperatures, the values of ambient rN are high.

4. At this point, it is worth mentioning that it is wrong to understand that, as written in reaction 8 above, a water molecule at the cathode receives two electrons and breaks down, and one molecule of hydrogen gas produces 2 hydroxyl anions. Because the water molecule does not disintegrate at such a low voltage, distilled water does not conduct current even at 220 V. In practice, the hydrogen cations present in the aqueous solution of sodium chloride are returned by accepting electrons at the cathode. E = -0.83 V is the reduction potential of the hydrogen cation.

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