Analysis of Economic Efficiency of Production of Low-Concentrated Sodium Hypochlorite by Direct Electrolysis of Natural Waters

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Abstract. The study presents the economic efficiency of direct electrolysis of natural waters in comparison with the waters artificially prepared by electrolysis of the 3% sodium salt solution. The study used sea water (Black sea water); mineral water (underground water of the Melikhovskaya station, "Ognennaya" hole); brackish water (underground water from the Grushevskaya station of the Aksai district); 3% solution of sodium salt. As a result, the dependences characterizing the direct electrolysis of natural waters with different mineralization, economic, and energy parties are shown. The rational area of the electrolysis for each of the investigated solution is determined. The cost of a kilogram of active chlorine obtained by the direct water electrolysis: Black sea from 17.2 to 18.3 RUB/kg; the Melikhovskaya station “Ognennaya” hole - 14.3 to 15.0 Rubles/kg; 3% solution of NaCl – 30 Rubles./kg; Grushevskogo St. – 63.0-73.0 Rubles/kg.

In the total of operating costs for the production of sodium hypochlorite (SH), along with the cost of electricity, the greatest impact is caused by the cost of salt used as a source of chloride ions [1-4]. Therefore, one of the most promising and less expensive methods of chemical biocide water treatment is SH obtaining by electrolysis of chloride-containing solutions which can be taken in marine, groundwater and surface water.

The method of direct electrolysis has such disadvantages as low productivity on active chlorine (up to 1-2 kg/day), a significant tightening of conditions for the operation of anodes at low concentrations of chlorides and temperatures (less 10°C), low output chlorine current efficiency (15 20 %) [5-9].

The examination of the direct electrolysis of natural groundwater and surface water are provided in the papers [5-16]. Thus, in the research of Basin D. L. [8] it is established that the treatment of natural waters with the chloride content 20-350 mg/l chlorine output on the electrodes of ORTA is 4-30 %, the cost of electricity 20-200 kW·h per 1 kg of active chlorine. The method of direct electrolysis is recommended for the chlorination of water containing >20 mg/l of chlorides [8].

In the studies [17,18] laboratory and industrial investigations of direct electrolysis of the River Don water with chloride concentration of 100-130 mg/dm3 [17] and groundwater of the Grushevskata station [18] with the concentration of chlorides 200-230 mg/dm3 are presented.

In the study [17] the optimal operation of the electrolytic cell with the following parameters is determined: the current density to 100 A/m2; the speed of water flow in the cell 0.2–0.3 m/s; the
working electrode in the anode mode $\tau + 300$, in the mode of cathode $\tau - 1$ h the electrode – oxide-
iridium-ruthenium-titanium anode (OIRTA) with the mass ratio of ruthenium and iridium of 20:80.

The results of the field tests [18] showed the possibility of natural water disinfection by direct
electrolysis with the following parameters: current density 25 А/m²; the feed rate of water into the cell
of 0.3-0.5 m/s (flow rate 16 m³/h); the working electrode in the mode of the anode 300, the cathode 1
h ($\tau + 300$ C, $\tau - 1$ h) eliminating the deposits on the electrode surface and increasing the lifetime
of an electrode up to 4,000 hours; the electrode OIRTA consisting of Ru–20% and Ir to 80%.

It can be expected that natural mineralized water with elevated concentrations of chloride ions will
provide significant cost saving in case of its obtaining from SH solutions as well as simplify the
technological scheme of production. However, due to significant differences in the composition
of natural waters, especially in the concentration of chloride ions, mineralized water electrolysis may
occur in the economically inefficient zone with a large power consumption and a low yield of active
chlorine which makes it relevant in determining the economically efficient production of low-
concentrated sodium hypochlorite by direct electrolysis of natural water.

As the test solutions were used (see table. 1): seawater (Black sea water) [19, 20]; mineral water
(underground water article of the Melikhovskaya station, "Ognennaya" hole diluted to a 3%
concentration for NaCl); brackish water (underground water of the Grushevskaya station of the Aksai
district); 3% solution of sodium salt.

Table 1. Composition of the studied mineral waters.

| Index                     | Mineralized underground water (Melikhovskaya station) | Mineralized underground water (Melikhovskaya station) diluted to 3% NaCl | The table white salt solution (3% NaCl) | The black sea water | Brackish underground water (Grushevskaya station) |
|---------------------------|--------------------------------------------------------|------------------------------------------------------------------------|----------------------------------------|---------------------|-------------------------------------------------|
|                           | mg/l mEq/l                                             | mg/l mEq/l                                                             | mg/l mEq/l                             | mg/l mEq/l          | mg/l mEq/l                                       |
| Ca²⁺                    | 2,000.0 100.0                                         | 1,160 58.0                                                             | 130.0 6.5                              | 200.0 10.0          | 176.0 8.8                                        |
| Mg²⁺                    | 972.0 80.0                                           | 449.6 37.0                                                             | 54.68 4.5                              | 733.9 60.4          | 75.33 6.2                                        |
| Ca²⁺ + Mg²⁺             | 2,972.0 180.0                                         | 1,609.6 95.0                                                           | 184.68 11.0                            | 933.9 70.4          | 251.33 15.0                                      |
| Na⁺ + K⁺                | 16,640.5 723.5                                       | 10,221.2 444.4                                                         | 11,782.9 512.3                         | 6,131.8 266.6       | 385.25 16.7                                      |
| HCO₃⁻                    | 610.0 10.0                                           | 244.0 4.0                                                              | 189.1 3.1                              | 183.0 3.0           | 378.2 6.2                                        |
| CO₃²⁻                    | - - -                                                 | - - -                                                                 | - - -                                  | 15.0 0.5            | - - -                                           |
| SO₄²⁻                    | 960.0 20.0                                           | 576.0 12.0                                                             | 187.2 3.9                              | 1248.0 26.0         | 385.25 8.0                                       |
| Cl⁻                      | 30,948.0 873.0                                       | 18,568.7 523.8                                                         | 18,303.0 516.3                         | 10,919.0 308.0      | 230.0 6.4                                        |
| Fe³⁺                    | 9.4 0.5                                               | 7.5 0.4                                                                | 0.4 -                                   | - - -               | - - -                                           |
| P, mg/l                 | 52,139.9 31,227.0                                    | 30,646.9 19,430.0                                                      | 1,630.0                                |                     |                                                 |
| pH, pc.                 | 7.4 7.34                                              | 7.9 8.4                                                                | - - -                                  |                     |                                                 |

The electrolysis of the studied solutions was carried out in a bladderless electrochemical cell ($V_{cell}$
= 66 ml) at constant electric current in the flow-through mode (Fig. 1) with the current density of 1000
A/m². Due to the low salinity the electrolysis of underground water of the Grushevskaya station was
investigated at a current density of 100 A/m². In the process of electrolysis the authors measured the
voltage at the electrochemical cell and determined the concentration of active chlorine. The study was
carried out at a temperature of 22-24°C. The study used oxide-iridium-ruthenium-titanium anodes
(OIRTA) with the interelectrode distance of 2 mm [21-24]. The working area of the anode and cathode
were equal and amounted to 14 cm², the size of electrodes 70x10 mm, the thickness 1 mm. The
inverter in the power supply, brand GW INSTEK 3610, with the system of automatic maintenance of constant current was used as a constant voltage source.

As can be seen from the Table 1 in the test water (mineralized underground water of the Melikhovskaya station), there is iron, its presence in the cell is undesirable since oxidation consumes the hypochlorite ion. Therefore, before supplying water to the electrolysis cell, the iron was removed by air oxidation with oxygen airizing the required volume of the investigated solution and then filtering out the precipitate Fe(OH)₃ on paper filter.

During the experiment, the water flow through the cell was changed (0.1-6.0 l/h) and the concentration of active chlorine in the resulting SH was determined. The results of the experiment are presented in Figure 2 in a graph based on the concentration of active chlorine from the residence time of the electrolyte in the cell.

![Figure 1](image1.jpg)

Figure 1. The experimental setup flow type: 1 – electrolytic cell; 2 - electrodes; 3 – power unit; 4 – capacity drive; 5 – peristaltic pump; 6 – thermometer; 7 – thermostat; 8 – nozzle inlet and outlet of the cooling water; 9 – sampling bag; 10 – pH-meter; 11 – magnetic stirrer; 12 – drive SH.

The dependences of the changes in the concentration of active chlorine (Figure 2) are characterized by curves reaching some limiting value depending on the nature of the electrolyte, its salinity and chloride concentration. In the electrolysis of the studied solutions the following maximum concentration of chlorine was obtained: the water of the Black sea is 5.5 g/l, water of “Ognennaya” hole - 6.5 g/l; 3% solution of NaCl and 6.6 g/l and groundwater of the Grushevskaya station 0.09 g/l (Figure 2).

![Figure 2](image2.jpg)

Figure 2. The dependence of the concentration of active chlorine on the residence time of the electrolyte in the cell: 1 – Black sea water; 2 – “Ognennaya” hole 3 – 3% NaCl solution; 4 – underground water of the Grushevskaya station.
To determine the economic efficiency of SH production by direct electrolysis of natural water, the cost of electricity for electrolysis was estimated and the unit cost of a kilogram of active chlorine was determined.

The amount of electricity consumed to produce a kilogram of active chlorine can be calculated according to the formula:

\[ W = \frac{I \cdot U}{C \cdot q} \]

where \( W \) is the power consumption for obtaining 1 kg of chlorine, kWh/kg; \( I \) – current intensity; \( U \) – voltage of the electrochemical cell; \( C \) – the concentration of active chlorine, g/l; \( q \) – flow of the electrolyte, dm³/h.

Figure 3 shows the dependences characterizing the power consumption for obtaining 1 kg of active chlorine from the electrolysis duration of the studied solutions.

Figure 3. The dependence of electricity consumption is used for production of 1 kg of active chlorine from the duration of electrolysis is studied solutions: 1 – Black sea water; 2 – “Ognennaya” hole; 3 – 3% NaCl solution; 4 – underground water of the Grushevskaya station.

The increasing duration of electrolysis (the reduction of waste) causes the increase of energy consumption to produce one kilogram of active chlorine. Thus, during the electrolysis of water of the Black sea it was in the range of 4.2-9.1 kWh/kg; water “Ognennaya” hole – 3.6-7.0 kWh/kg; 3% solution of NaCl and 3.1-5.6 kWh/kg; water of the Grushevskaya station – 15.0-49.5 kWh/kg (Figure 3).

The graphs shown in Figure 4 were obtained by calculating the cost per kilogram of hypochlorite which is the 3% solution of sodium salt, \( C_{3\%NaCl} \), which amounts to, RUB./kg:

\[ C_{3\%NaCl} = W \cdot C_{el} + 5 \cdot C_h \]

where \( C_{el} \) cost of a kilowatt – hour of electricity 4.06 RUB./kW-h; \( C_h \) is the cost of a kilogram of salt, 3.5 Rubles.

Similarly, for natural water, \( C_{pv} \), in RUB/kg:

\[ C_{pv} = W \cdot C_{el} \]
The cost per SH unit produced by electrolysis of the 3% solution of common salt was at the level of 30-40 RUB/kg due to the cost of salt which is 40% to 60% of the cost of a kilogram of active chlorine. The high cost of a kilogram of active chlorine (up to 200 RUB./kg) was obtained by electrolysis of saline groundwater from the Grushevskaya station (Fig. 4) that is obviously associated with its low salinity (1.63 g/l) and relatively low concentration of chlorides (up to 230 mg/l).

In Figure 4, the curves 1 and 3 intersect, and therefore, electrolysis of the water of the Black sea is economically more profitable than the electrolysis of sodium chloride solution to a concentration of 5.0 g/l active chlorine (Figure 4).

To determine the most effective region of the electrolysis, consider the dependence of the yield of chlorine from the current duration of the electrolysis (Figure 5). The electrolysis of the studied solutions was conducted with a maximum output chlorine current 75-90% (16.6% of water of Grushevskogo St.) when the duration of electrolysis was 2.5 - 5 minutes. This period of time is characterized by the lowest specific electricity consumption for the electrolysis and the minimum cost of a kilogram of active chlorine which accounted for (Figure 4) the waters of the Black sea equal to 17.2-18.3 Rubles/kg; “Ognennaya” hole water - 14.3 to 15.0 Rubles/kg; 3% NaCl solution – 30.1 Rubles/kg; water of Grushevskogo St. – 63.0-73.0 Rubles/kg.
The results of the experiments (Figure 2-5) are summarized in the Table 2. The values presented below characterize the entire range of operation of the cell the optimal work area is given in parentheses.

Table 2. Indicators of the efficiency of electrolysis of the studied solutions.

| Figure | The black sea water | Mineralized underground water (Melikhovskaya station) diluted to 3% NaCl | 3% NaCl solution | Brackish underground water (Grushevskaya station) |
|--------|---------------------|---------------------------------------------------------------------|------------------|-----------------------------------------------|
| The concentration of active chlorine, g/l | 0.25-5.5 | 0.3-6.4 | 0.3-6.6 | 0.005-0.09 |
| Voltage, V | 4.91 | 3.9 | 3.72 | 3.4 |
| W, kW•h/kg | 4.2-9.1 | 3.6-7.0 | 3.1-5.6 | 15.0-49.5 |
| The unit cost of chlorine, $/kg | 17.2-37.1 | 12.7-29.8 | 30.1-40.2 | 63.0-201.0 |
| Output chlorine current, % | 40.9-87.7 | 40.8-81.2 | 50.0-90.0 | 36.7-16.6 |

Conclusion
1. The possibility of obtaining sodium hypochlorite by direct electrolysis of natural water with a chloride concentration of 230 mg/l to 18.6 g/l was determined. To determine the actual cost of electricity and the cost of a kilogram of active chlorine direct electrolysis of natural water is necessary to maintain a certain current density, corresponding the concentration of chloride ions in the solution and its mineralization. For the establishment of such a relationship (the current density - concentration of chlorides) it is necessary to conduct further research.
2. The cost of a kilogram of active chlorine obtained by the direct electrolysis of water: Black sea of 17.2 to 18.3 RUB/kg; the Melikhovskaya station “Ognennaya” hole - 14.3 to 15.0 Rubles/kg; 3% solution of NaCl – 30 Rubles./kg; the Grushevskogo St. – 63.0-73.0 Rubles/kg.

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