

# Modeling of the process of electrolysis production of caustic, chlorine and hydrogen

E A Shulaeva<sup>1</sup>, N S Shulaev<sup>1</sup>, J F Kovalenko<sup>1</sup>

<sup>1</sup>Branch of the Ufa State Petroleum Technological University, 2, October PR, Sterlitamak, Bashkortostan 453118, Russia

E-mail: [eshulaeva@mail.ru](mailto:eshulaeva@mail.ru)

**Abstract.** The present work describes the modeling parameters of an electrolyzer in production of caustic, hydrogen and chlorine by electrolysis. The dependence of temperature on the current-voltage characteristics of the electrolyzer and the ratio that determines the current as a function of the design parameters were found. It is shown that an increase in the current in the electrolyzer with increased temperature is due to decreasing viscosity of the electrolyte and reducing the radii of solvated ions and sodium chloride. The yield of sodium hydroxide, chlorine and hydrogen was determined based on the technological and construction parameters of the cell. These relations are used in the developed simulation and modeling software.

## 1. Introduction

Improvement and modernization of chemical-technological processes for obtaining sodium hydroxide, chlorine and hydrogen require a corresponding development of computer-modeling systems that provide determination of physical and chemical parameters that can not be directly measured in the course of chemical reactions, determination and maintenance of optimal regimes pro-conduct processes promoting an accident-free operation. To use these intelligent systems of modeling and control of technological systems requires professionals with certain skills to operate computer systems and to have knowledge of the features of chemical technology of the process. The development of information technology makes it possible to create computer training systems that allow obtaining professional skills for process management, complementing [1-4].

This article demonstrates the possibility of simulation and modeling of the complex of one of the most common chemical productions - the process of obtaining sodium hydroxide, chlorine and hydrogen by electrolysis - which allows simulating the operation of the technological equipment when changing process parameters (current-carrying capacity, the concentration of NaCl in brine, temperature).

## 2. Results and Discussion

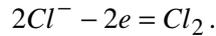
The first stage of the process of obtaining caustic soda with the formation of chlorine gas and sodium amalgam is carried out in the electrolyzer. Then the amalgam is fed to decomposer, wherein caustic soda and hydrogen are obtained; circulation of mercury is performed by a pump [5, 6].

The electrolyzer has a floating mercury cathode. An anode is generally made from ruthenium and

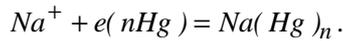


titanium oxides with a titanium base.

The main process on the anode is the discharge of chloride:



The basic process of the mercury cathode electrolytic cell suitable for the purpose of industrial electrolysis is a bit of sodium ions.



As follows from the stoichiometry of chemical reactions and the conservation law of electric charge, when the charge of 1000 Ah (3600C) is passing through the cell, then 1.323 kg of chlorine (Cl), 0.0376 kg of hydrogen (H<sub>2</sub>), and 1.492 kg of sodium hydroxide solution (NaCl) is released.

Thus, the consumption rates of the charge are as follows:

- for chlorine  $K_{Cl} = 3.675 \cdot 10^{-4}$  kg/C;
- for hydrogen  $K_H = 1.044 \cdot 10^{-5}$  kg/C;
- for hydroxide solution  $K_{NaOH} = 4.144 \cdot 10^{-4}$  kg/C.

To develop a computer-simulation software to model electrolyzer operations, a mathematical model linking technology parameters, such as current, voltage, temperature, etc. and design parameters of the cell are required [7-10].

To determine the effect of the design parameters of the cell performance and the cost of electricity, it is necessary to establish the dependence of the electric current on the technological parameters. The electric current between the anode and cathode of the electrolytic cell is given by

$$I = en_{Na}v_{Na}S + en_{Cl}v_{Cl}S, \quad (1)$$

where  $n_{Na}$ ,  $n_{Cl}$  – the concentration of sodium and chloride ions in the electrolyte;  $v_{Na}$ ,  $v_{Cl}$  – speed directional motion of the ions;  $S$  – anode electrolysis area.

$Na^+$  ions are moving to the mercury cathode and  $Cl^-$  ions are moving to the anode in the electric field between the anode and cathode. To determine  $v_{Na}$  speeds,  $v_{Cl}$ , let us write the equation of motion based on the forces of the electric field and the viscous resistance:

$$m_{Na} \frac{dv_{Na}}{dt} = eE - F_{Na}, \quad (2)$$

$$m_{Cl} \frac{dv_{Cl}}{dt} = eE - F_{Cl}, \quad (3)$$

where  $m_{Na}$  – solvated mass ion Na;  $m_{Cl}$  – solvated mass ion Cl;  $E = \frac{U}{d}$  – the electric field intensity in the gap between the anode and the cathode;  $U$  – the potential difference (voltage);  $d$  – distance between the anode and the cathode.

$F_{Na} = 6\pi\mu r_{Na}v_{Na}$ ,  $F_{Cl} = 6\pi\mu r_{Cl}v_{Cl}$  – viscous drag forces when driving solvated ions  $Na^+$ ,  $Cl^-$ ;  $\mu$  – the dynamic viscosity of the electrolyte;  $r_{Na}$ ,  $r_{Cl}$  – characteristic radii of solvated ions;  $m_{Na}$ ,  $m_{Cl}$  – mass of solvated ions

Radii of solvated ions may be evaluated by:

$$r_{Na} \approx r_{Cl} = R_C = \left( \frac{ep_e}{6\pi\epsilon_0 kT} \right)^{\frac{1}{2}} \left[ 1 + \frac{3\pi\epsilon_0 kT p_e}{2e^3} \right]^{\frac{1}{2}} + \frac{p_e}{2e}, \quad (4)$$

where  $e = 1.6 \cdot 10^{-19}$  C - elementary charge;  $p_e$  - dipole moment of water molecules (H<sub>2</sub>O);  $\epsilon_0 = 8.86 \cdot 10^{-12}$  F / m - electric constant;  $k = 1.38 \cdot 10^{-23}$  J / K - Boltzmann constant;  $T$  – absolute temperature of the electrolyte.

Weights of solvated ions may be determined from the following relations:

$$m_{Na} = \frac{\mu_{Na}}{N_A} \left[ 1 + \frac{\mu_{H_2O}}{\mu_{Na}} \left( \frac{2R_C}{d_{H_2O}} \right)^3 \right], \quad (5)$$

$$m_{Cl} = \frac{\mu_{Cl}}{N_A} \left[ 1 + \frac{\mu_{H_2O}}{\mu_{Cl}} \left( \frac{2R_C}{d_{H_2O}} \right)^3 \right], \quad (6)$$

where  $\mu_{Na}$ ,  $\mu_{Cl}$ ,  $\mu_{H_2O}$  - molar weight of Na, Cl, H<sub>2</sub>O, respectively;  $d_{H_2O}$  - characteristic diameter of molecule H<sub>2</sub>O;  $N_A = 6.02 \cdot 10^{23}$  1/mol - Avogadro's constant.

From the solutions of equations (2) and (3), we can determine the speed of movement of sodium and chloride ions in the interelectrode space:

$$v_{Na} = \frac{eU}{6\pi\mu r_{Na}d} \left( 1 - \exp\left(-\frac{t}{\tau_{Na}}\right) \right), \quad (7)$$

$$v_{Cl} = \frac{eU}{6\pi\mu r_{Cl}d} \left( 1 - \exp\left(-\frac{t}{\tau_{Cl}}\right) \right), \quad (8)$$

where  $\tau_{Na}, \tau_{Cl}$  - the time of "acceleration" of sodium and chloride ions in the electric field.

$$\tau_{Na} = \frac{m_{Na}}{6\pi\mu r_{Na}}, \quad (9)$$

$$\tau_{Cl} = \frac{m_{Cl}}{6\pi\mu r_{Cl}}. \quad (10)$$

Considering that  $\tau_{Na} \ll 1, \tau_{Cl} \ll 1$ , so that  $\exp\left(-\frac{t}{\tau_{Na}}\right) \ll 1$  and  $\exp\left(-\frac{t}{\tau_{Cl}}\right) \ll 1$ , the velocity of the ions can be calculated by formulas

$$v_{Na} = \frac{eU}{6\pi\mu r_{Na}d}; v_{Cl} = \frac{eU}{6\pi\mu r_{Cl}d}. \quad (11)$$

Knowing the velocity of directional motion of the ions, let us determine the dependence of the current in the electrolyzer from structural and technological parameters of the process:

$$I = \frac{e^2 S}{6\pi\mu d} \left( \frac{n_{Na}}{r_{Na}} + \frac{n_{Cl}}{r_{Cl}} \right) U. \quad (12)$$

Considering that the concentration of chlorine ions in the electrolyte solution of sodium is practically the same and is determined by the concentration of NaCl in the brine, this relation can be written as

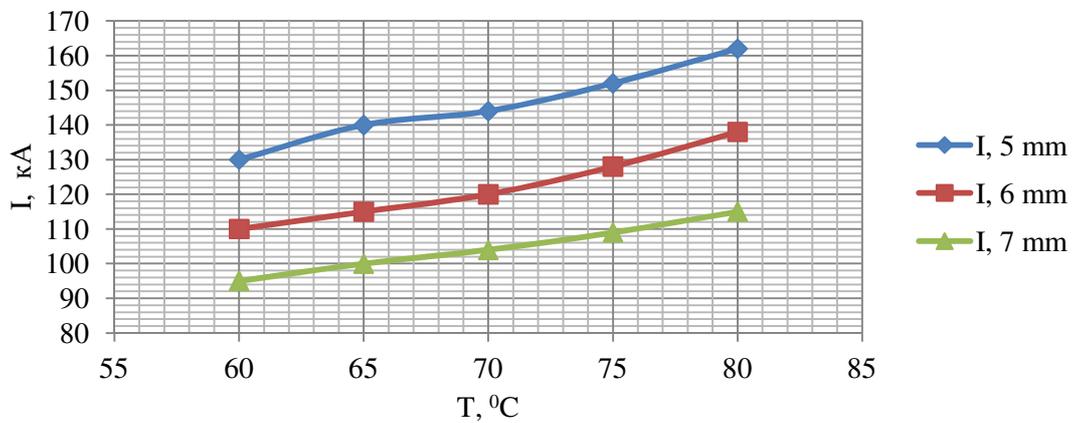
$$I = \frac{n_i e^2 S}{6\pi\mu d} \cdot \frac{U}{\left( \frac{ep_e}{6\pi\epsilon_0 kT} \right)^2 \left[ 1 + \frac{3\pi\epsilon_0 p_e kT}{2e^3} \right]^2 + \frac{p_e}{2e}}. \quad (13)$$

From the last relation, it follows that the dependence of the current in the electrolyzer is defined as the design parameters, in particular, the areas of anode and cathode  $S$ , the distance between electrodes  $d$ , and process parameters:  $n$  - concentration of brine  $n_i$  and temperature  $T$ ,  $\mu$  - dynamic viscosity.

Equation (13) also makes it possible to determine the temperature dependence of the current, voltage characteristic of the electrolyzer, taking into account changes of viscosity of the electrolyte when the temperature changes (Figure 1.). Knowing the dependence of the current on the design and process parameters, it is possible to determine electrolyzer performance and specific energy costs  $G$  (J / kg) (fig.2,3).

$$G_{Cl} = \frac{U}{k_{Cl}}; G_H = \frac{U}{k_H}; G_{NaOH} = \frac{U}{k_{NaOH}}, \quad (14)$$

where  $U$  - voltage on the electrolyzer determined at a predetermined current according to formula (13).

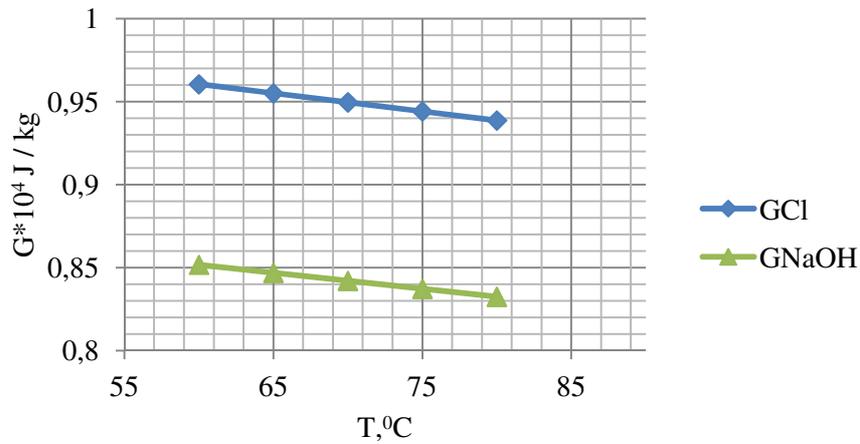


**Figure 1.** Dependence of the current on temperature in the electrolyzer at a fixed inter-electrode distance and the voltage of 3.65 V.

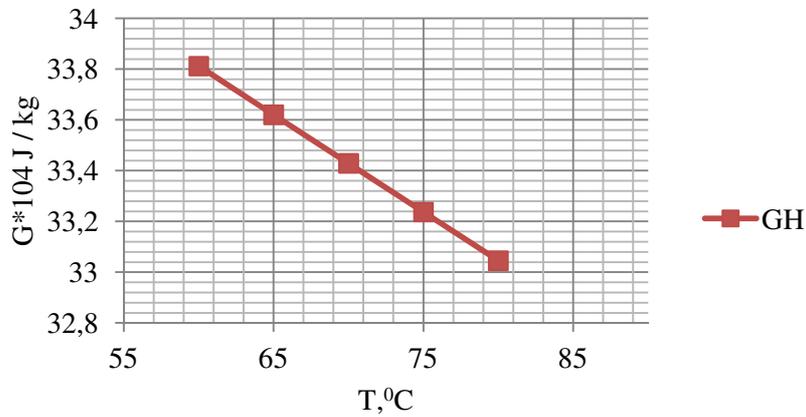
From formula (13), it follows that for a specified current in the cell, the voltage on the electrodes is determined by formula

$$U = \frac{6\pi\mu d}{n_t e^2 S} \cdot \left[ \left( \frac{ep_e}{6\pi\epsilon_0 kT} \right)^{\frac{1}{2}} \left[ 1 + \frac{3\pi\epsilon_0 p_e kT}{2e^2} \right]^{\frac{1}{2}} + \frac{p_e}{2e} \right] I. \quad (15)$$

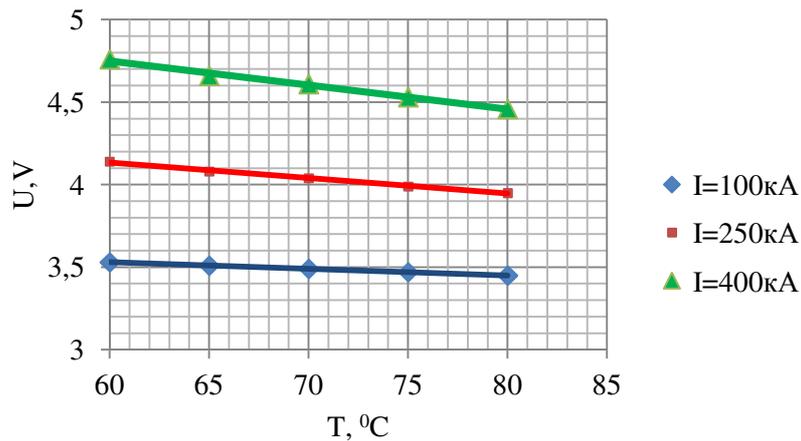
From which it follows that with the increase of temperature of the electrolyte the voltage decreases. Figure 4 shows the temperature dependence of the voltage on fixed current values when the inter-electrode distance is 5 mm.



**Figure 2.** Specific energy consumption G for chlorine and caustic.



**Figure 3.** Specific energy consumption G for hydrogen.



**Figure 4.** The temperature dependence on the voltage at fixed current values when the inter-electrode distance is 5 mm.

The resulting dependence realized in the simulation modeling complex is an "electrolysis stage of production of caustic, chlorine and hydrogen."

### 3. Conclusion

Using the developed simulation and modelling software will help to ensure optimum modes of technological processes, to predict the changing parameters in the event of emergency situations that increase the level of fail-safe operation.

In the training and supervising operating modes using simulation and modeling, software can quickly assess the level of training, as well as to carry out its own training on the basis of the included modules of virtual simulation of the process if necessary.

Studies have found that an increase in the temperature of the electrolyte decreases the dynamic viscosity, and the diameters of solvated ions are reduced, resulting in increased conductivity and increased electrolytic current at a given value of the voltage between the anode and the cathode.

### 4. Acknowledgments

Research is being conducted with the support of the Foundation for Assistance to Small Innovative Enterprises in Science and Technology (Foundation to promote innovation (UMNIK)).

### References

- [1] Shulaeva E A, Kovalenko Y F, Shulaev N S 2014 Using simulation and modeling software of chemical technology in education *CSIT* **2014** 175-179
- [2] Shulaeva E A, Kovalenko Y F, Shulaev N S 2014 Simulation and modeling software in chemical technology: polymerization of vinyl chloride. *Advanced Materials Research*. **2040** 581-584
- [3] Brusov 2010 Technological equipment: safety and efficiency of industrial production **13** 50-51
- [4] Syzrantsev V, hammer M, Cherezov K 2006 Computer simulators for training students in oil and gas areas *Drilling and oil* **10** 34-37
- [5] Samodurov V M, Kovshova N. O, Klushin V N 2015 To assess the optimal conditions for obtaining caustic and precipitation of carbonate, molybdate and chromate of calcium from waste production of propylene oxide *Advances in chemistry and chemical technology* **29-8 (167)** 105-107
- [6] Meneghini D, Bertin R. Device for the separation of mercury from caustic plants production of chlorine and caustic 12.04.2007 *The patent for invention RUS* **2426821**
- [7] An E D, Afanasyev F I, Podtsepnyak S E, Gavrilin I A, Fedorov A M, Kazakov B A, Datsuk G V, Khabibullin R V 12.08.2008 The electrolyzer with a horizontal mercury cathode *The patent for invention RUS* **2403322**
- [8] Abdrashitov J M, Gorin V N, Dmitriev Yu K, Izosenkov R I, Lerner A S, Gainetdinov F F, Fedorov A M, Phil M Yu, V I Beril, Yaprntsev V N, Yaroshevskii V V. 13.09.2001 Method of regulating the voltage on the anodes of a mercury electrolytic process of obtaining chlorine and caustic. *The patent for invention RUS* **2209257**
- [9] Afanasyeva R A 2006 New directions in the production of chlorine, caustic and construction of electrolytic cells *Chemical technology* **3** 18-26
- [10] Yakimenko L M 1989 Production of chlorine, caustic and inorganic floorproducts **600**