MATHEMATICAL MODELLING OF THE PROCESS OF ELECTROCHEMICAL PRODUCTION OF NaClO FROM DILUTED CHLORIDE SOLUTIONS

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ABSTRACT

The sodium hypochlorite synthesis using diluted chloride solutions represents an actual problem considering the number of applications of this compound - as an antiseptic, for the waste waters treatment, etc. The goal of this work is the elaboration of a mathematical model describing the relationship between the quantity of the obtained hypochlorite and the electrical energy consumption from one part and the current value and the concentration of the initial chloride solution, from the other. The experiments were carried out in cell (200 ml) with cathodes – from iron and anodes – from ruthenium and titanium oxides. The initial concentration of the chloride solutions varied in the range 0.05 – 0.45 g/l. The chosen experimental model was the full factorial one with two levels of the factors. According to this model, the mass of the obtained sodium hypochlorite is maximal for the maximal sodium chloride concentration and the maximal current value. The correlation coefficient is 99 %, which confirms the validity of the model. Concerning the energy consumption E, the minimal values correspond respectively to the highest sodium chloride concentration and current values. The correlation coefficient in this case is however equal to 75 % and some supplementary studies for the model in this respect precision are needed.

Keywords: electrosynthesis, sodium hypochlorite, mathematical model, correlation coefficient.

INTRODUCTION

The process of electrochemical production of NaClO from diluted chloride solutions is important regarding the purification of natural and industrial waters, the extraction of highly toxic compounds from waste waters (e.g. cyanides), the fabrication of pharmaceuticals, etc. That is why, the investigations related to the effect of the different experimental conditions: current density, composition of the solutions, rate of the flow across the electrolysis cell on the process of production, represents an interest [1-9].

As it is known a characteristic for the electrolysis of low concentrated solutions is the low current efficiency. In order to improve this parameter of the process, electrodes and after all anodes, containing noble metals as platinum, ruthenium etc. are used [10-14]. The disadvantage of those electrodes consists in their high price. Consequently, more of the investigations are dedicated to the possibility of their substitution. Anodes from graphite, MnO_2, PbO_2, magnetite, etc. have been proposed. However, because of their insufficient effectiveness, the possibilities of using anodes covered with an active spinel layer are studied. As known, the minerals from the class of the complex oxides with a general formula AB_2O_4, where A is a bivalent ion Zn, Mn, Co, Ni, etc and B is a trivalent ion Al, Fe, Cr, Mn, Ti belong to them. Useful to the solution of the problem with the substitution of the noble metals could be the inert electrodes investigated regarding some galvanic systems – chrome, alloys, etc. [21-24].

The investigation of the mentioned process is also important because of the fact that the productiveness of the electrolysis is 10 fold lower than that of the purely chemical synthesis. In this aspect, studies related to modeling and optimization of this electrochemical process are actual. As known, due to the possibilities of the computer data treatment, the methods of mathematical
modeling and optimization play an important role for the development of technological regimes and construction of electrochemical reactors [25-28].

The purpose of this work is the development of models correlating some factors of the process of electrochemical synthesis of NaClO from diluted solution of NaCl and especially the mass of the product and electrical energy consumption (output parameters) from one part and the current value and concentration of the initial chloride solution (input parameters), from the other part. These investigations represent a continuation of our previous studies [29], resulting in the development of models for the process of electrolysis of concentrated chloride solutions.

EXPERIMENTAL

The experiments were carried out in an electrolysis cell (PVC) with a volume of 200 ml. The cathodes (steel 1X18H9T) and the anodes (ruthenium and titanium oxides) were disposed in a package, vertically (4 cathodes and 3 anodes) with a distance between them 0.8 cm. NaCl – p. a. was used for solution preparation. The experiments were performed maintaining a constant current value (galvanostatically), using a regulated power supply (TES-9). The working solution flow across the electrolysis cell was insured due to the gravitation. The rate was keeping constant through a system of stopcocks. The hypochlorite concentration was determined using a iodometrical method modified for small quantities of active chlorine. The experimental device is schematically presented in Fig. 1.

RESULTS AND DISCUSSION

Investigations on the influence of the current density

The relationship between the current value and the mass of the active chlorine, the current efficiency and the specific energy consumption is presented in Fig. 2. All of the experiments were carried out in the following conditions: solution volume of 1 dm³ and initial NaCl concentration – 0.05 g/l. The current values correspond to current density from the order of 1x10⁻³ – 1x10² A dm⁻².

As shown in the figure, the increase of the current value leads to an increase of the mass (the concentration) of the active chlorine, as well as of the current efficiency; this relationship has another character concerning the specific energy consumption – a decrease in energy consumption is observed. The values of the current efficiency are relatively low and those of the specific energy consumption are high and the characteristic for the electrolysis of low concentrated solutions.

Investigations on the influence of the NaCl concentration

The obtained experimental data are presented in Fig. 3, a, b, c.

As shown in the figures, the increase of the initial NaCl concentration leads to an increase of the quantity of the active chlorine. For example, for a concentration of the NaCl equal to 0.05 g dm⁻³, the mass of the active chlorine is 7.04 mg and for a NaCl concentration of 0.6 g dm⁻³, it is 52.4 mg. By analogy of the influence of the current density, here an increase of the current efficiency and a decrease in the energy consumption are also observed. For the cited concentrations, the current efficiency is 13.2 % and 26 % respectively and the energy consumption – 40.5 wh/g and 15.9 wh/g.

Planning of the experiments

Based on the performed and describe above experiments, a conclusion could be made that the relationship between the input parameters (NaCl concentration and current value I) and the output parameters (mass of the active chlorine and energy consumption) has an exponential character, i.e. it is not linear.

The elaborated plan of experiments is presented in Table 1. A full factorial experiment with two levels of the factors was chosen.
Mathematical models

The obtained mathematical models according to the plan of the experiments can be expressed with the following equations: 

\[ m = 1,6 - 4,02 C_{NaCl} - 0,0475 I + 0,0732 C_{NaCl}^2 I + 1,86C_{NaCl} + 0,000407 I^2 \]

\[ E = 630 - 598 C_{NaCl} - 13,5 I + 1,22C_{NaCl} I + 1011 C_{NaCl}^2 + 0,0797 I^2 \]

where: \( m \) – the mass of the sodium hypochlorite, \( g \); \( C \) – the concentration, \( g/l \); \( I \) – the current, mA; \( E \) – the specific energy consumption, Wh/g;

It is evident, considering the equation of the first model, that maximal quantities of active chlorine can be obtained for the corresponding maximal concentrations of the initial NaCl and for current values in the studied ranges of these parameters. The analysis of the model shows that the influence of the chloride concentration is stronger that this of the current through the electrolysis cell. This fact can be explained taking into consideration that with the increase of both the chloride concentration and the current, the first parameter acts in higher degree on the current efficiency of the process of active chlorine synthesis.

In accordance to the equation of the second model, for maximal values of the input parameters, a minimum is observed regarding the specific energy consumption. In this case the influence of the NaCl concentration is more strongly too. The concentration increase provokes a decrease in the energy consumption of the process, because of the decrease of the solution resistance. The current efficiency for the product increases, too.

The current influence is a result of the action of opposite factors. From one side, the current efficiency increases, but from the other side – the voltage of the electrolysis cell increases and the energy consumption, too. It is evident (and the described experiments confirm this fact), that the decrease of the energy consumption due to the increased current efficiency “gets ahead” of its increase because of the higher sell voltage.

The verification made for the adequacy of the models shows that the correlation coefficients are 99% (for the first model) and 75% (for the second model) respectively.

These values of the correlation coefficients confirm that the first model is significant.

Additional experiment are needed for the second model, in order to reach a higher degree of correlation.
Table 1. Plan of the experiment.

<table>
<thead>
<tr>
<th>CNaCl, g/l</th>
<th>I, mA</th>
<th>m, mg</th>
<th>W, W.h/g</th>
<th>CE, %</th>
</tr>
</thead>
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<td>96.1</td>
<td>7.2</td>
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<td>0.05</td>
<td>80</td>
<td>0.550</td>
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<tr>
<td>0.25</td>
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<td>71</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<tr>
<td>0.45</td>
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<td>2.698</td>
<td>13.59</td>
<td>33.59</td>
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</table>

CONCLUSIONS

The investigations on the process of electrochemical production of NaClO using diluted solutions the important influence of the NaCl concentration and the current value on the product concentration and the electrical energy consumption. The obtained mathematical models confirm that maximal NaClO masses and minimal energy consumption are present for maximal values of the input parameters (concentration and current) in the studied ranges. The models equation are of second degree, i.e. they are not linear.

Acknowledgment

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