Method for Calculation of the Current Concentration of Alkali in the Electrolyte During the Water Electrolysis Process

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The article proposes a method for calculation of the current concentration of alkali in the electrolyte, taking into account the consumption and replenishment of feed water in the electrolyzer, which allows to estimate the specific electrical conductivity of the electrolyte during electrolysis process. This is important to increase the efficiency of the water electrolysis process. The calculated change of the current concentration of alkali in the electrolyte in high-pressure electrolyzers taking into account the volume of produced hydrogen is given. With the usage of the proposed method, it is established that the current concentrations of alkali in the electrolyte during the operation of the developed high-pressure electrolyzers are in the range of optimal concentrations, where the specific electrical conductivity of the electrolyte is close to maximum and changes according to alkali concentration change.

Introduction

To achieve the global goal of reducing exhaust emissions into the atmosphere, hydrogen is taken as the main alternative to carbon. Decomposition of water into hydrogen and oxygen by electrolysis is a key solution for decarbonization of the environment. Electrolysis of water with the usage of renewable energy sources (sun, wind) makes it possible to minimize energy consumption and emissions for green hydrogen obtaining. This allows us to consider the electrolysis of water as a promising method of hydrogen production for transport and zero emission power plants [1–11].

Alkaline electrolyzers are widely used for the production of green hydrogen with the use of renewable energy sources [1, 3, 7–9]. During the operation of electrolysis plants, the concentration of alkali in the electrolyte changes due to the fact that the electrolysis consumes water, which is part of the electrolyte, and the alkali contained in the solution serves only to transfer ions. After consuming part of water from the electrolyte, it is periodically replenished. Replenishment of feed water is carried out upon reaching the boundary minimum volume of electrolyte.

The calculated determination of the change in the current concentration of alkali during the operation of electrolysis plants is an important component of the electrolyte specific electrical conductivity assessment to determine the efficiency of water electrolysis.

The purpose of this paper is to develop a method for calculation of the current concentration of alkali in the electrolyte, taking into account the consumption and replenishment of feed water in the electrolyzer.

Selected model and calculation methodology

During the consumption and periodic replenishment of feed water in the alkaline electrolyzer, the electrolysis process occurs at a variable concentration of alkali in the electrolyte. This leads to a change in the specific electrical conductivity of the electrolyte (**Fig. 1, 2**), which affects energy consumption during the production of hydrogen and oxygen.
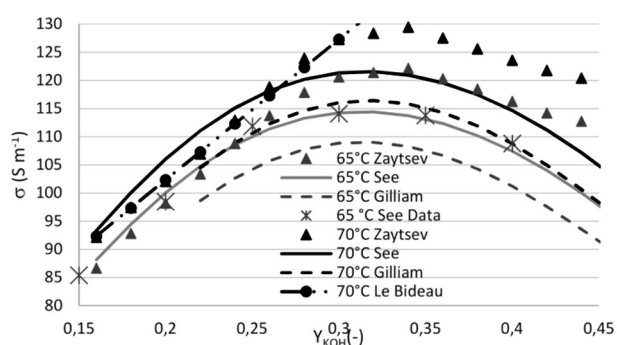

Figure 1. Dependence of specific electrical conductivity of KOH aqueous solutions on alkali concentration [12].
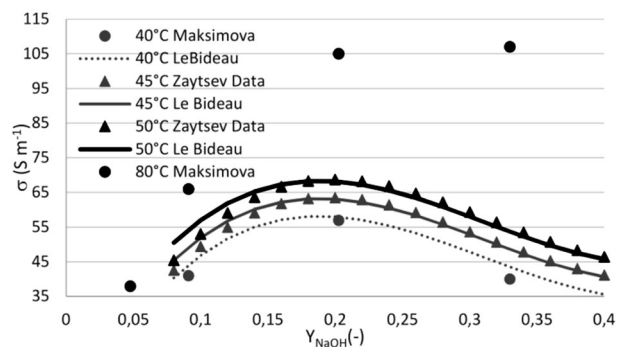

Figure 2. Dependence of specific electrical conductivity of NaOH aqueous solutions on alkali concentration [12].

The technique of calculation of parameters of feed water replenishment in the alkaline electrolyzer, taking into account the set optimum concentrations of alkali and real expense of electrolyte, is proposed in the article [13]. The formula for calculation of current concentration of alkali in electrolyte under the condition of known productivity of the electrolyzer by hydrogen and production time of consumable part of water during electrolysis is offered.

To obtain a generalized formula for calculated change in the current concentration of alkali in the electrolyte during the design and operation of alkaline electrolysis plants, we use the artificial method proposed in [13], according to which the amount of water in the electrolyte, which fills the electrolysis plant, is divided into two components:

– technological part, which is a technologically necessary minimum volume of water that ensures the functioning of the electrolyzer, i.e. the process of electrolysis;

– consumable part, which is water that decomposes in the process of electrolysis to

obtain hydrogen and oxygen during the operation of the electrolyzer without replenishment.

Then the mass of water in the electrolyte

$$m_w = m_{wt} + m_{wcons}, \qquad (1)$$

where m_w is the mass of water in the electrolyte; m_{wt} is the mass of the technological part of water in the electrolyte; m_{wcons} is the mass of the consumable part of water in the electrolyte.

The mass of the electrolyte that fills the electrolysis plant is defined as

$$m_{el} = m_w + m_{alk}, \qquad (2)$$

where m_{el} is the mass of the electrolyte in the electrolysis plant; m_{alk} is the mass of alkali in the electrolyte of the electrolysis plant.

The concentration of alkali in the electrolyte is defined as

$$C_{alk} = \frac{m_{alk}}{m_{el}}, \qquad (3)$$

where C_{alk} is the concentration of alkali in the electrolyte.

From (1), (2) and (3) we get

$$m_{el} = \frac{m_w}{1 - C_{alk}} = \frac{m_{wt} + m_{wcons}}{1 - C_{alk}}. \qquad (4)$$

In the process of electrolysis, the water that is part of the electrolyte is consumed, and the concentration of alkali in the electrolyte increases from the initial value of C_{init} (at the initial moment after replenishment) to the maximum value of C_{max} (after the production of all consumable water). The mass of alkali remains almost unchanged, and the mass of water in the electrolyte decreases to the mass of the technological part of water – m_{wt}. Given this and taking into account (4) the mass of the

technologically necessary part of the electrolyte is defined as

$$m_{el.t} = \frac{m_{wt}}{1 - C_{max}}. \qquad (5)$$

where $m_{el.t}$ is the mass of the technological part of the electrolyte; C_{max} is the concentration of alkali in the electrolyte after the production of all consumable water.

Then, given (5), the mass of alkali in the electrolyte

$$m_{alk} = m_{el.t}C_{max} = m_{wt}\frac{C_{max}}{1 - C_{max}}. \qquad (6)$$

From (1), (2), (4) and (6), and taking into account the initial concentration of alkali in the electrolyte, we obtain

$$m_{el}\frac{m_{wt} + m_{wcons}}{1 - C_{init}},$$

$$\qquad\qquad (7)$$

$$m_{el} = m_{wt}(1 + \frac{C_{max}}{1 - C_{max}}) + m_{wcons}),$$

where C_{init} is the concentration of alkali in the electrolyte at the initial moment of operation of the electrolyzer or after replenishment of feed water.

Electrolysis requires 0.820–0.850 kg of water, which is a part of the electrolyte, to obtain 1 m^3 of hydrogen and 0.5 m^3 of oxygen [14]. That is, through the amount of hydrogen obtained, one can determine the amount of water consumed during electrolysis

$$m_{wcons} = V_H \cdot \gamma_{cons}, \qquad (8)$$

where V_H is the volume of obtained hydrogen; γ_{cons} is feed water consumption to obtain 1 m^3 of hydrogen [14].

Using the system of equations (7) and formula (8), replacing C_{max} with C_i ($C_{init} \le C_i \le C_{max}$), we determine the current

concentration of alkali in the electrolyte during the production of consumable water by electrolysis

$$C_i = \frac{1}{\frac{m_{wt}}{(m_{wt} + V_{Hi} \cdot \gamma_{ccons}) \cdot (\frac{1}{1 - C_{init}} - 1)} + 1}, \quad (9)$$

where C_i is the current concentration of alkali in the electrolyte during the water electrolysis; V_{Hi} is the volume of hydrogen produced after replenishment of feed water, or the volume of hydrogen calculated by the formula

$$V_{Hi} = \tau_i \cdot P_{H2}, \quad (10)$$

where τ_i is the current duration of the electrolyzer operation without replenishment of feed water; P_{H2} is performance of the electrolyzer for hydrogen.

Taking into account (10) and replacing C_{init} by C_{min}, we get the formula for calculation of the current concentration of alkali in the electrolyte during water electrolysis, which is proposed in [13].

Thus, the obtained dependence (9) allows to use two options for calculation of the current concentration of alkali in the electrolyte – taking into account the produced hydrogen or based on the performance of the electrolyzer by hydrogen.

In the first option for the calculation of C_i by formula (9):

1.1) the amount of technological part of water in the electrolyte m_{wt} is set according to the design of the electrolyzer;

1.2) the initial concentration of alkali in the electrolyte C_{init} (set during the initial preparation of the electrolyte for the initial filling of the electrolyzer or measured after replenishment of feed water) is determined;

1.3) the consumption of feed water to obtain 1 m^3 of hydrogen γ_{cons} for a specific electrolysis plant is set;

1.4) the amount of total hydrogen V_{Hi} produced from the beginning or after replenishment of feed water to the current moment of operation of the electrolyzer (specified during development or measured for the existing electrolyzer) is determined.

In the second option for the calculation of C_i by formula (9) the first three points coincide with the first three points of the previous option:

2.1) the amount of technological part of water in the electrolyte m_{wt} is set according to the design of the electrolyzer;

2.2) the initial concentration of alkali in the electrolyte C_{init} (set during the initial preparation of the electrolyte for the initial filling of the electrolyzer or measured after replenishment of feed water) is determined;

2.3) the consumption of feed water to obtain 1 m^3 of hydrogen γ_{cons} for a specific electrolysis plant is set;

2.4) the performance of the electrolyzer P_{H2} for hydrogen is set or determined (during all operation or in different operation modes of the electrolyzer);

2.5) the current duration of operation of the electrolyzer without replenishment of feed water τ_i (set or measured) is determined.

Based on these data, you can use the formula (9) to calculate the current

concentrations of alkali in the electrolyte for both research and operational tasks.

Results and their discussion

The obtained calculated dependence allows to calculate the current concentration and range of changes in the concentration of alkali in the electrolyte both during the development and operation of existing alkaline electrolyzers.

In the first case of calculation of the current concentration of alkali in the electrolyte one does not need to take into account the operation modes of the electrolyzer or its stop. This option is acceptable for both electrolysis plants under development and for existing ones.

The second option for calculation of the current concentration of alkali in the electrolyte can be used in the development of new electrolyzers. This is based on the fact that the operation modes of the electrolyzer, namely changes in the performance of the electrolyzer for hydrogen during operation of the existing electrolyzer are difficult to determine. In particular, it is especially difficult to determine the operation of the electrolyzer in combination with renewable energy sources, which are characterized by instability of electricity generation.

The application of the obtained dependence for alkaline electrolyzers with periodic replenishment of feed water under development and for existing electrolyzers provides an opportunity to analyze the nature of

changes in the specific electrical conductivity of the electrolyte, i.e. to evaluate the efficiency of the electrolysis process. This will improve alkaline electrolysis plants and provide additional information for the development and configuration of feed water supply systems to maintain the optimal concentration of alkali in the electrolyte.

For the production of hydrogen and oxygen in the membraneless high-pressure electrolysis plants developed by IPMach NAS of Ukraine [15, 16], KOH aqueous solutions are used as electrolytes. During operation, electrolyzers require periodic replenishment of feed water consumed from the electrolyte. To ensure the maximum specific electrical conductivity of the electrolyte and taking into account the design features of the developed electrolyzers, the range of changes in the concentrations of KOH in the electrolyte was selected 25-30 % [13].

Table 1 shows the operational parameters of the high-pressure electrolyzers EHP 1.0-150 and EHP 0.5-150 developed in IPMach NAS of Ukraine and the demonstration model of the high-pressure electrolyzer DM-0.002-3.

Table 1. Operational parameters of high-pressure electrolyzers developed in IPMash NAS of Ukraine.

Electrolyzer	P_{H2}, m³/h	m_{wt}, kg	γ_{cons}, kg/m³	C_{init},
EHP 1.0-150	1.0	142.0		
EHP 0.5-150	0.5	71.0	0.82	0.25
DM-0.002-3	0.002	1.7		

Table 2 shows the calculated change in the current concentration of KOH in the electrolyzers EHP 1.0-150, EHP 0.5-150 and DM-0.002-3, taking into account the volume of hydrogen produced after replenishment of feed water.

Table 2. The change of the current concentration of KOH in electrolyzers EHP 1.0-150, EHP 0.5-150 and DM-0.002-3.

Electrolyzer	V_{Hi}, m^3	C_i, %
EHP 1.0-150	1.3	25.14
	2.1	25.27
	5.4	25.58
	11.9	26.27
	18.2	26.92
EHP 0.5-150	0.6	25.13
	2.4	25.52
	7.3	26.55
	9,8	27.06
	12.3	27.57
DM-0.002-3	0.0007	25.006
	0.0016	25.014
	0.0029	25.261

Table 2 data show that the current concentrations of KOH during the operation of the electrolyzers EHP 1.0-150, EHP 0.5-150 and DM-0.002-3 are in the range of optimal concentrations, where the specific electrical conductivity of the electrolyte is close to the maximum and does not change much when the alkali concentration changes (**Fig. 1**).

Thus, the calculated determination of the current concentration of alkali during the operation of electrolysis plants allows to assess, in particular with help of [12], the specific electrical conductivity of the electrolyte, which is important for improving the efficiency of water electrolysis.

Conclusions

Under the conditions of consumption and periodic replenishment of feed water, the process of electrolysis in the alkaline electrolyzer occurs at a variable concentration of alkali in the electrolyte, which leads to changes in the specific electrical conductivity of the electrolyte and affects energy consumption during the production of hydrogen and oxygen.

The proposed dependence allows to determine changes in the current concentration of alkali and, taking them into account, to analyze changes in the specific electrical conductivity of the electrolyte during electrolysis. This provides additional opportunities to increase the efficiency of the process of water electrolysis with alkaline electrolyzers and improve the feed water replenishment systems to ensure maximum specific electrical conductivity of the electrolyte.

The calculation of the current concentration of alkali in the electrolyte showed that the range of changes in the concentration of alkali during the operation of the developed high-pressure electrolyzers is in the range of optimal concentrations, where the specific electrical conductivity of the electrolyte is close to maximum. This demonstrates the effectiveness of the proposed method.

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