Mathematical modeling of a multistage electrolysis plant for producing heavy and light water

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Abstract. The work is devoted to the simulation of a multi-stage separation cascade of electrolyzers, designed to produce heavy water as the main product while producing light water as a by-product. The calculation is based on the model of an ideal countercurrent separation cascade without mixing at the entrance to each stage, in which one of the cut coefficients can be chosen arbitrarily in the range of its allowable values, and the value of which is an optimization parameter. It is assumed that taking into account the optimization of the design of the electrolyzer and taking into account energy recovery, the cost of light water will be about $0.09/kg, and the cost of heavy water about $945/kg.

1. Introduction

As is well known, any water, depending on the content of a heavy hydrogen isotope in it – deuterium can be light or heavy. Heavy water is widely used in the nuclear industry, physics, chemistry, biology. Heavy is water with a deuterium content above 99%. In recent years, the problem of deuterium content in drinking water, especially in water obtained by desalination of sea or ocean waters, has been widely discussed. The deuterium content in freshwater bodies ranges from 120 to 155 ppm. In the oceans, the deuterium content is slightly higher and averages 155 ppm. At the same time, drinking water, depending on the content of the deuterium, can be useful and prolong life or, conversely, reduce it and promote the development of diseases. From the results of studies on the effect of deuterium content in the water on the processes of life of animals and plants, it follows that a decrease in its content has a positive effect on metabolic processes and immune activity of organisms [1], increases the yield and germination of plants [2]. The most important property of light water is a beneficial effect on the human health [3-5].

Reducing (increasing) the concentration of deuterium in desalinated water is a task for the separation of hydrogen isotopes, and its solution requires the use of appropriate separation technologies. At the industrial level, for the separation of hydrogen isotopes, such methods as water electrolysis, the distillation of various hydrogen-containing compounds (ammonia, water, molecular hydrogen), chemical isotopic exchange are used [6–9]. Water electrolysis is one of the most well-known and well-researched methods of hydrogen isotope separation. However, it has several advantages compared with other methods. These advantages include a high separation factor,
simplicity of the technological process, its continuity, the possibility of the most complete automation, the absence of moving parts in the electrolytic cell. The economy of the electrolysis process mainly depends on the cost of electricity. In the production costs of electrolysis, the cost of electrical energy is about 85%. This method is also attractive because it is the most universal concerning the use of primary energy sources. In connection with the development of atomic energy, a new flourishing of electrolysis of water is possible based on the cheap electric power of atomic power stations, in particular, low-capacity transport power stations [10].

In this paper, the method of electrolysis is considered to produce heavy and light water, mathematical modeling of a multi-stage separation cascade from electrolyzers is performed, and the cost of producing products is estimated. The calculation was based on the model of an ideal countercurrent separation cascade, in which there is no mixing of flows at the entrance to the stage. In this case, one of the cut coefficients in a cascade can be chosen arbitrarily in the range of its allowable values and the value of which is an optimization parameter.

2. Simulation of the separation cascade

In this model, the general theory of constructing cascades with arbitrary enrichment on the stage is considered. Figure 1 shows the scheme of the stage (separation element).

![Figure 1. Separation element.](image)

The main equations of the separation element are the equation for the enrichment function $f(c, \theta)$ (1) and the equation of balance (2):

$$f(c, \theta) = c^+ - c$$

$$c = \theta c^+ + (1 - \theta)c^-$$

where $c$ is the concentration of the valuable component in the feed flow $L$, $c^+$ is the concentration of the valuable component in the product flow $P$, $c^-$ is the concentration of valuable component in the depleted flow (the flow of the blade) $R$, and $\theta = \frac{P}{L}$ is the cut coefficient, defined as the ratio of the flow enriched in valuable component (deuterium) to the feed flow.

The problem of calculating the separation element is the correct definition of the enrichment function. In the first approximation for the electrolyzer, it can be assumed that the concentration of deuterium in the water passing through its slit remains constant. Thus, the convective component of mass transfer is neglected. Then the value of the separation factor $\alpha$ can be considered constant:

$$\alpha = \frac{c^+}{1-c^+} / \frac{c^-}{1-c^-}$$

where $\alpha$ is separation factor; for the electrolysis method $\alpha$ can lie in the range from 1.5 to 10 [8].

Substituting the expression for $c^+$, found from expressions (2) and (3) in (1), we obtain the desired expression for the enrichment function:

$$f(c, \theta) = \frac{(\alpha \theta + 1 - \theta - c + c \alpha) - \sqrt{(\alpha \theta + 1 - \theta - c + c \alpha)^2 + 4\theta(1 - \alpha)c^2}}{2\theta(\alpha - 1)} - c$$

Equations (2) and (4) are the complete system of equations for calculating the process of separation of a binary mixture in the separation element (electrolyzer).

At one separation element, it is impossible to obtain a product of special purity (in this case, heavy water with a deuterium content above 99%). Therefore separation cascades are used in which the separation elements are connected in series. Figure 2 shows the general scheme of the countercurrent...
separation cascade from electrolyzers for the separation of hydrogen isotopes and the release of heavy and light water.

![Figure 2. Scheme of countercurrent separation cascade.](image)

The figure introduces the following designations: N is the number of stages in the cascade, $F$ is the feed flow supplied to the first stage, $P$ is the product flow of the valuable component of the last stage, enriched with deuterium (heavy water), $W$ is the flow of the blade of the first stage, depleted deuterium (light water), $c_p$, $c_w$ is the concentration of deuterium in these flows, $c_i$ is the molar fraction concentration of deuterium at the entrance to the $i$-th stage, $c_i^+$ is molar fraction concentration of deuterium in the enriched flow at the exit of the $i$-th stage (the stream enriched in deuterium is not subjected to electrolysis), $c_i^-$ is molar fraction concentration of deuterium in depleted flow at the exit of the $i$-th stage (the stream depleted in deuterium is subjected to electrolysis), $L_i$ is the flow at the entrance to the $i$-th stage, $P_i$ is the deuterium-enriched flow from $i$-th stage, and $R_i$ is the deuterium-depleted flow from the $i$-th stage, which undergoes electrolysis.

The main problem in calculating cascades is the choice of optimal parameters. In this regard, it is convenient to use the concept of an ideal cascade. The ideal cascade for the separation of binary mixtures is called a cascade without mixing flows at the entrance to the stage. Mathematically, this condition is as follows:

$$c_i^- = c_i^- = c_i^+$$

Taking into account the non-mixing condition, the basic equations of the ideal separation cascade can be written in the form:

$$c_{i+1} - c_i = f(c_i, \theta_i)$$

$$c_i = \theta_i c_i^+ + (1 - \theta_i) c_i^-$$

$$\theta_i = \frac{c_i - c_{i-1}}{c_i - c_{i-1}}$$

$$L_i = \frac{P(c_p - c_i)}{\theta_i f(c_i, \theta_i)}$$

The boundary conditions for the first and last stages are as follows:

$$\theta_N L_N = P$$

$$(1 - \theta_i)L_i = W$$

$$c_p - c_N = f(c_N, \theta_N)$$

$$c_1 - c_w = \theta_1 f(c_1, \theta_1)$$

Balance equations are defined as:

$$F = P + W$$

$$F c_f = P c_p + W c_w$$

The cascade without mixing is characterized by the fact that one of the cut coefficients in the cascade can be chosen arbitrarily in the field of its permissible values. This is explained by the fact that equations (6) and (8) are reduced to difference equations of the second order, which require two initial conditions for their solution. One of the conditions is the value of the deuterium concentration in the feed flow $c_f = c_1$, and the value of the cut coefficient $\theta_i$ can be used as another condition. The value of the selected coefficient is an optimization parameter [11]. This is the fundamental difference
between the above approach and the approach of Cohen [12], which he developed in the middle of the 20th century.

Equations (5)-(15) describe an ideal countercurrent separation cascade. The initial data for the calculation of the cascade model were: \( N=17, \alpha = 5, \theta_1 = 0.31, P=1.0 \text{ kg/h}, c_f=c_i=0.000150 \).

Based on these values and equations (6) and (8), all \( c_i \) concentrations and cut coefficients \( \theta_i \) for an arbitrary number of stage \( i \) are determined. The deuterium concentrations in the enriched and depleted \( i \)-stage flow \( c_i^+ \) and \( c_i^- \) are determined using equation (7) and the non-mixing condition (5). The entrance flows \( L_i \) is calculated according to the formula (9). The flows \( P_i \) and \( R_i \) are determined based on the values \( \theta_i \) and the balance equations. Thus, all the characteristics of the stages of the cascade are determined.

3. Simulation results

Figures 3-5 show the simulation results of a cascade of \( N = 17 \) separation stages. The figures represent the dependences of the entrance flow \( L_i \), the deuterium concentration at the entrance to the stage \( c_i \) and the cut coefficient \( \theta_i \) on the stage \( i \) number. For comparison, the graphs show the dependences for different values of the cut coefficient \( \theta_1 \).

During the simulation, it was found that with electrolytic separation of hydrogen isotopes in a cascade of \( N=17 \) stages with a separation factor \( \alpha = 5 \) on each at \( \theta_1 = 0.31 \), it is possible to get about \( W = (1-\theta_1)L_1 = 12000 \text{ kg/h} \) of light water with a deuterium content of \( c_w = 67 \text{ ppm} \) in the first stage in flow of the blade of the cascade. At the same time it is possible to get \( P=1.0 \text{ kg/h} \) of heavy water HDO with a deuterium content of \( c_p = 99.2 \% \) in the product flow at the last stage of the cascade. Note that for a cascade with arbitrary enrichment, it is impossible to obtain an exact concentration value in
the product flow, so the calculation ends when the concentration at the output stage begins to exceed the specified value.

Based on the graphs, we can conclude that the selected value $\theta_1 = 0.31$ is optimal for this cascade. Interestingly, at this optimal value $\theta_1$, these characteristics are smooth functions (as opposed to $\theta_1 = 0.1$ and $\theta_1 = 0.9$ - the characteristics significantly deviate from the optimum). At the same time, the total flow $\sum_i l_i$ in the cascade at $\theta_1 = 0.31$ is minimal and amounts to 31 383 kg/h, which means the minimum energy consumption. Another feature of the cascade is the equality of deuterium concentrations at the entrance to the $c_i$ stage for odd-numbered stages.

In accordance with the technological process of electrolysis, the flow of hydrogen (protium) $Q_i$, formed at the $i$-th stage during electrolysis and interaction with oxygen released on another electrode, forms a deuterium-depleted flow $R_i$ ($W$ for the first stage, i.e. light water) and additional energy, which can be recovered (figure 6). At the same time, the flow $P_i$ is enriched with deuterium (heavy water).

![Figure 6. Scheme of the $i$-th electrolyzer.](image)

The specific consumption of electricity going to produce hydrogen $H_2$ (protium) in the electrolysis process is 5 kW·h/m³ [7]. The total energy consumption $\sum_i E_i$ in the cascade for hydrogen evolution and production of 12 000 kg/h of light and 1.0 kg/h of heavy water (where $E_i$ is the energy consumed at the $i$-th stage) is estimated to be 135 MW·h. For comparison, the calculated specific energy consumption for the production of heavy water in the rectification method is about 240 MW·h/kg.

One of the problems arising in the processing, formed as a result of the electrolysis of hydrogen, is the drying of gas, which can contain up to 2-3 % water vapor [13]. This is necessary to reduce its corrosion activity and obtain a high-purity product. The purity of hydrogen and oxygen is a very important indicator of the technological regime of the electrolysis plant. In practice, the adsorption method with vacuum-thermal regeneration of the sorbent (silica gel) is used to dry hydrogen from moisture and obtain a high-purity product. Also used the installation of hydrogen dehydration by cooling, which includes chillers, evaporators, and expansion valves.

In electrolysis plants, the drying of hydrogen is carried out by cooling it in the evaporator of a refrigerating machine to -5 °C. At this temperature, the main amount of water vapor is removed from the hydrogen in the evaporator.

In this paper, for drying formed during the electrolysis of hydrogen, it is proposed to use the method of drying according to the patent of the Russian Federation № 185232 [14], based on the Peltier effect. The compressed gas (hydrogen) dryer based on Peltier elements according to this patent consists of a thermoelectric dryer comprising an assembly of thermoelectric Peltier elements, having a hot and cold contact surface, as well as a DC power supply unit. The advantage of the method is to improve the energy efficiency of the hydrogen drying process due to the execution in a single package of the thermoelectric assembly of Peltier elements, the condensation chamber and the heat exchange chamber, which allows to significantly simplify and cheapen the gas drying process.

4. Calculation of the cost of light and heavy water and ways to reduce it
The amount of electricity consumed to produce only light water in one stage is about 6.25 kW·h/kg [7]. Taking into account the average cost of one kilowatt-hour of electricity ($0.08$/kW·h), the cost of obtaining light water will be $0.5/kg. Taking into account depreciation and operating costs (here $k =$
1.25 is the coefficient taking into account depreciation and operating costs), the final cost of light water will be about $0.6/kg.

The cost of obtaining heavy water is determined by the total energy costs \( \sum E_i \), as well as depreciation and operating costs. Assuming that the coefficient taking into account depreciation and operating costs will be equal to 1.25, it is possible to estimate the cost of obtaining heavy water equal to $13,500/kg.

Taking into account the fact that the profit received from the sale of 12,000 kg of light water at a price of $0.6/kg is 7,200 $, the final cost of 1 kg of heavy water will be determined as the difference between the costs of obtaining heavy water and this profit and will be $6,300/kg.

According to the literature data [15], by optimizing the design of the electrolyzer, electricity costs can be reduced more than twice, following which we obtain the cost of light water \( 0.6/2 = 0.3 \) kg and heavy water $3,150/kg.

Besides, energy recovery (figure 6) allows reducing specific costs several times [15]. Following this, even if the recovery will increase the cost of equipment (take \( k = 1.5 \)) the cost of light and heavy water will decrease significantly. Then finally, if the unit cost will be reduced at least 4 times the cost of light water \( C_{LW} \) will be about $0.09/kg, and the cost of heavy water \( C_{HW} \) will be about $945/kg.

5. Conclusions
Heavy water is more profitable to obtain by electrolysis (135 MW·h/kg) than by rectification (240 MW·h/kg), but it will become competitive in price if energy recovery is used to reduce energy consumption by 5 times or more (the market value of heavy water is $770-1230/kg). It is profitable to obtain light water by electrolysis since the maximal costs will be about $0.6/kg, which is less than three times at rectification.

6. References
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