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EXERGIC BALANCE AND EFFICIENCY OF REVERSE OSMOSIS MODULES

О.О. Кардасевич, В.В. Чиченін, І.Д. Шуляк, Н.В. Демченко. **Ексергетичний баланс і ефективність зворотноосмотичних модулів.** Запропоновано варіант використання ексергетичного методу аналізу зворотньоосмотичних (мембранних) установок (ЗОУ) для підготовки додаткової води, отримуючих поширення при реконструкції хімцехов українських АЕС. Виконана оцінка эксергетической ефективності мембранних модулів очищення води і виявлено характер впливу основних параметрів ЗОУ на термодинамічну ефективність їх роботи. Зроблено висновок про можливі напрямки вдосконалення таких установок.

Ключові слова: зворотньоосмотичні установки, ексергетичний аналіз, термодинамічна ефективність

O.O. Kardasevich, V.V. Chichenin, I.D. Shulyak, N.V. Demchenko. **Exergic balance and efficiency of reverse osmosis modules.** In this paper the option of using exergy analysis method is proposed for preparing make-up water by reverse osmosis systems (ROS), which are spreading in the reconstruction of the chemical departments of Ukrainian nuclear power plants. The estimation of exergy efficiency of water purification by membrane units is made and the nature of influence of the ROS main parameters on thermodynamic efficiency is identified. The conclusion on the possible ways of facilities improvement is drawn.

Keywords: reverse osmosis systems, exergy analysis, thermodynamic efficiency

Introduction. Improving the preparation of high-quality water for the needs of nuclear power plants led to active introduction of reverse osmosis (membrane) technologies, which allow full automation of the process of preparation of make-up water in the contours of nuclear power plants. At the same time, the thermodynamic efficiency of such facilities has been studied only partially. The purpose of this work is to evaluate the efficiency of reverse osmosis plants using the exergy method of analysis.

As known, exergic balances of technical objects allow to correctly evaluate the effectiveness of processes occurring in them, to identify ways to improve these processes, to make them clear, convincing. In addition, exergy balance sheets provide a more accurate picture of the real possibilities of such improvement taking into account the specific state of the medium.

In most other methods some comparison operations are used for these purposes (for example, comparing changes in the entropy of the system), in relation to which the indicators of the studied object are evaluated. The results of such analysis, of course, depend on the successful choice of comparison operations. Exergic analysis eliminates the need to select these operations for existing installations, and for new (projected) ones allows immediate identifying the possibility of their implementation in production by comparing the minimum required costs with available resources.

Relatively new method of thermodynamic analysis – exergetic, as shown in the publications [1, 2], remains an actual direction of research in power engineering and heat engineering, and also gaining a place in the chemical industry and in a number of other industries.

The advantage of the exergy method is to take into account not only the quantity, but also the quality of energy flows and multicomponent material flows characterizing the energy balance of any energy technology system. This fact puts this method on the first place in its objectivity in comparison with the traditional methods of thermodynamic analysis.

The complexity of the exergic analysis of devices with multicomponent flows, in which the processes of separation, for example, of aqueous solutions occur, consists in the fact that the main tech-

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nical effect of the process is demonstrated in two ways. In one case, the main task is to obtain a flow of pure water, in another case – a concentrate flow [3, 4].

For the first case, the exergic effect is demonstrated in an increase in the exergy of the pure water flow (water treatment at TPP and NPP, desalination) [2, 3].

In processes where the main task is thickening of the solution, the beneficial effect consists in increasing the exergy of the concentrate (chemistry, food technology, concentration of liquid, including radioactive, solutions). It may be useful to consider both of these processes (water cooling system of NPP).

Thus, exergic balances and analysis of such processes require taking into account not only the traditional for heat energy concept of exergy as a workable component of heat energy and work reserves [1], but also as a chemical component [3]. This complicates both calculations and balancing, the choice of criteria for the effectiveness of the separation processes in general and at individual stages, as well as parts of the installations (steps) into which the complex process is usually broken down.

Materials and methods. An exergetic analysis of the efficiency of the separation (water purification) process was carried out using the example of calculations of a membrane module of a specific productivity with variation of individual parameters. For simplicity, the calculations are limited to a single-component solution.

During the analysis on the basis of material balances it is necessary to solve the problem of determining costs and concentrations of individual constituents in the initial solution, retentate and permeate.

Especially important here was the determination of mole concentrations, which allow us to calculate and balance the exergy flows.

With the help of exergy balances the prospects for improving the processes taking place in technical devices, under terrestrial conditions, are clearly presented, that is taking into account the specific state of the medium.

Let us recall that the concept of exergy was proposed by Z. Rant in 1953 and its use created a whole section of thermodynamics. Exergy, as well as energy, possesses the property of additivity. This simplifies the calculation of exergy of complex systems and processes. In contrast to energy, exergy is lost due to the course of irreversible processes. It is said that in such processes exergy turns into anergy.

This characteristic of exergy brings it together with the terms “value” and “monetary circulation” and creates prerequisites for the transition to a thermo-economic analysis of processes and devices.

The exergetic method was most widely developed and widely used in the analysis of cycles and basic processes of TPPs and NPPs. Therefore, we will borrow the approaches developed there and limit ourselves here only to a reminder that for any reserves, flows and transformations of energy resources in specific medium conditions (T_0, p_0) one can calculate their exergy, i.e. that component of energy resources, which is transformed entirely into work and any other kind of energy. In this regard the following types of exergy are considered: specific, complete exergy and exergy of heat flow.

The specific exergy (kJ/kg) of mass flow of the medium (neglecting the kinetic and piezometric components) is calculated from the formula:

$$e = (h - h_0) - T_0(s - s_0)\,, \tag{1}$$

where h and h_0 – enthalpy in the given state and the state of the medium, respectively, kJ/kg,
s and s_0 – entropy in the given state and state of the medium, respectively, kJ/(kg K),
T_0 – temperature in the state of the medium, K.

The complete exergy (kW) of the flow is calculated by the formula:

$$E = me\,, \tag{2}$$

where m – mass flow of medium, kg/s.

The heat flow exergy (kW) is calculated by the formula:

$$E_q = \Phi\left(1 - \frac{T_0}{T}\right), \qquad (3)$$

where T – temperature in the given state, К;

Φ – heat flow, kW.

In the case of chemical transformations, it becomes necessary to supplement the concept of the medium and expand its parameters.

In the case of purification devices, including reverse osmosis units, this may be an indication of the state in which the main impurities, that are removed by the device, are located in the medium (for example, hereafter one of the most common components of natural waters is considered – NaCl).

It is most convenient to use its molar concentration in the source (natural) water. Then in order to calculate the increment of specific exergy (J/kmol) of the two separate flows obtained, one can use the specific work in the reversible transition process of the component into the state of the medium, taken modulo:

$$e_x = -RT_0 \sum\nolimits_1^n x_i \ln\left(\frac{x_i}{x_{0i}}\right), \qquad (4)$$

where R=8314 J/(kmol·К) –absolute gas constant;

x_i, x_{0i} – molar impurity concentrations in the given flow and in the state of the medium, respectively.

Let us call this exergy chemical exergy. It will be referred to the flow of solution during the separation process. Therefore, the exergy of the flow in the process of separation is calculated as follows:

$$E_x = N_i e_x \text{, W,} \qquad (5)$$

where N_i – flow of the medium, kmol/s (or kg/s).

If the flow of the medium is expressed in kg/s, then the specific exergy should be expressed in J/kg.

Analysis of the expression (4) indicates that the exergy of the flow will be positive when the impurity concentration in the solution is less than in the natural water.

Reversible work in this case can be obtained due to an impurity in the water of the medium.

Another statement is also true: reversible work can be obtained from a solution with a higher impurity concentration than in the medium (water).

In this regard the modulus of the value obtained from equation (4) is used in calculations of specific exergy.

When considering a reverse osmosis installation, in order to simplify the calculations, it is established that the “thermal” component of exergy is associated only with the use of an increased pressure flow as the source water, and there is no thermal interaction (Φ=0). Thus, it is the increased pressure that is the main reason for the presence of a reserve of exergy both in the source and in the process (concentrate or, as is customary in osmosis – retentate) water. The components associated with the flow velocity and the arrangement of the device along the level – as already noted above – are being neglected, for simplicity.

In this paper important are the following parameters of the medium: T_0=300 K; p_0=1 bar=$1\cdot10^5$ Pa. For water this corresponds to h_0=112.66 kJ/kg, s_0=0.3931 kJ/(kg K).

Additional parameters of the medium for calculations of chemical exergy are molar concentrations of source water and impurities. In the work they are marked, like other parameters of the medium, by the index “0”. Thus, the molar impurity concentration satisfies the condition $x_{2_0}=x_{2f}$, and the molar concentration of water is given by the condition $x_{1_0}=x_{1f}$.

Thus, for calculations of chemical exergy, the medium was considered as an infinitely large capacity of practically unchanged natural water.

The experiment was carried out as follows. An aqueous solution of sodium chloride (NaCl) with a salt concentration C_f=(10…0.5 kg/m^3) and a flow rate of 500 kg/h was fed into the membrane module.

Other characteristics of the module were the following: the hydraulic resistance of the module Δp was $(2.0…10.0)\cdot10^5$ Pa; the input pressure p_f was higher than the osmotic pressure and was equal $25\cdot10^5$ Pa; specific membrane productivity v_p=0.1 $m^3/(m^2\times h)$; the selectivity to the substance (NaCl) was 95...70 %, i.e. R=(0.95…0.70); working surface of the module F=0.5 m^2; operating temperature T_0=300 K.

In view of low concentration in order to simplify the calculations it is assumed that the density of the initial aqueous solution ρ_f differs little from the density of pure water and equals 1000 kg/m^3.

In the calculations, the following notations are used: flows and water concentrations – with subscript 1, flows and concentrations of dissolved solids – with subscript 2. As additional indices for flows and concentrations the following are chosen: for the initial solution – subscript f; for permeate (filtrate) – subscript p; for retentate (concentrate) – subscript w.

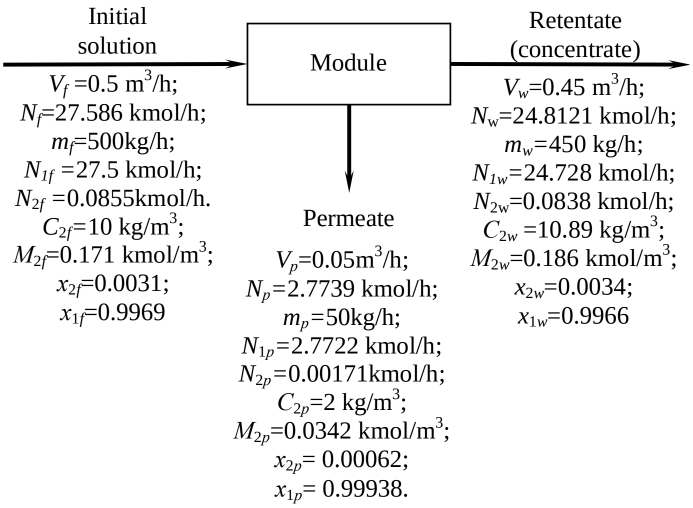

Fig. 1. Material balance of osmotic module

For the indicated conditions the molar concentrations are the following: for water, M_{1f}=990/18 = 55 $kmol/m^3$; for sodium chloride – M_{2f}=10/58.5=0.171 $kmol/m^3$.

Calculations of concentrations and material flows of the reverse osmosis module were performed separately for the initial solution, permeate and retentate.

Material flows according to the previously introduced initial parameters for convenience of analysis are shown schematically in Fig. 1.

Flows of energy and exergy were also calculated for each of the flows. Calculations of exergic flows were carried out according to equation (4) using data on material flows and molar concentrations shown in Fig. 1. Like the rest of the calculations, they were performed separately for the initial flow, the retentate flow and the permeate flow. For each flow the thermal and chemical components of the exergy, as well as their sum, were determined.

A visual representation and perception of the performed calculations is given by the scheme of energy and exergy flows, shown in Fig. 2.

This scheme provides only a qualitative comparison of energy and exergy flows in the reverse osmosis module. It is not possible to represent these flows on a scale, since they are not comparable. For example, the energy flow Φ*f* at the input is 15.95 kW, and the exergy flow Ef at the input is only 335 W. The flow of chemical exergy is even less.

The quantitative parameters of the exergy transformation in the reverse osmosis module are shown in Fig. 3.

The exergy losses L were calculated from the balance of exergy flows as the difference in values for the input (E_{in}) and outlet (E_{out}) flows:

$$L = E_{in} - E_{out}, \qquad (6)$$

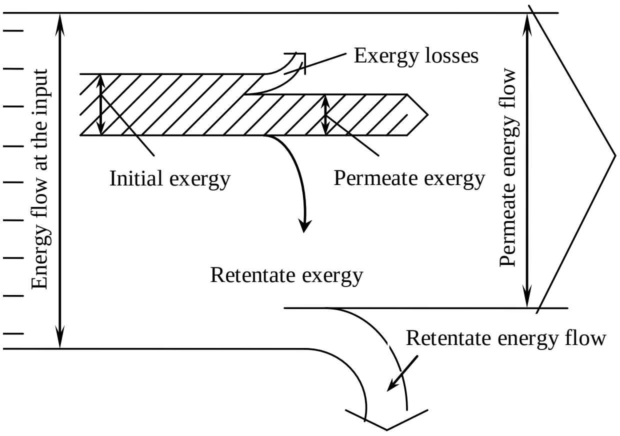

Fig. 2. Scheme of energy and exergy flows in reverse osmosis module

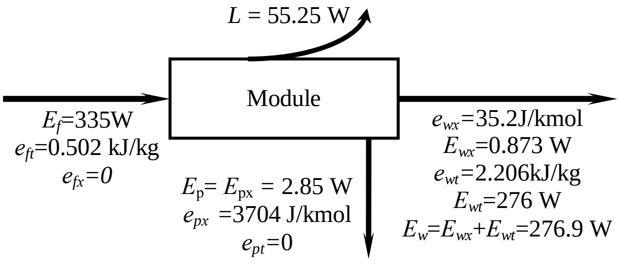

Fig. 3. Scheme of exergy flows in reverse osmosis module

For example, for the initial data shown in fig. 3, the exergy losses will amount to:

$$L = E_{in} - E_{out} = 335 - (276.9 + 2.85) = 55.25 \text{ W}.$$

Two approaches are possible for evaluation of thermodynamic efficiency of transformations in a module based on dimensionless indicators.

If we assume that the usefully spent exergy is the exergy flow of permeate (filtrate), and the available exergy is the exergy of the source condensate water flow, then this kind of efficiency, which is called the degree of excellence, can be represented as:

$$\eta_{exl} = \frac{E_p}{E_f}, \tag{7}$$

where η_{exl} – degree of excellence, %.

Or for the given variant of calculations

$$\eta_{exl} = \frac{E_p}{E_f} = 2.85/335 = 0.0085 \text{ or } 0.85\ \%$$

This data allows us to conclude that a significant part of the exergy is not used and either is lost or is in transit with a permeate flow.

This transit flow of exergy can be used in the future, especially its thermal component. For example, it can be recycled using a hydraulic turbine, which is typical for operating reverse osmosis installations.

From the above presented diagrams and calculations it can be seen that such a solution significantly reduces the consumption of initial energy resources.

Non-recoverable losses of exergy in the reverse osmosis module are also very significant and exceed the effect of water purification. Therefore, their subsequent analysis and clarification of the reasons for the irreversibility of the processes, as well as the sections of exergy losses on the module, are important. Let us assume that the main exergy losses in the studied example are related to the hydraulic resistances of the module. Therefore, their reduction will have the greatest effect on increasing thermodynamic efficiency.

It is also possible to estimate the thermodynamic efficiency of the exergy transformations in the module on the basis of another approach. In order to do this, we use the notions of available and used exergy parts. Thus the used exergy is considered only the increment of the exergy of the main flow, in our case – the increment of the exergy of the purified water. In fact it coincides with the exergy of the retentate. Only the part that does not take into account the “transit” exergy flow is considered to be an available exergy. In our case it is a concentrate exergy flow, which in principle can be used in other transformation processes of energy resources.

In the framework of this approach the received dimensionless index can be called the exergy efficiency factor of the reverse osmosis module and expressed as the ratio of used and available exergy:

$$\eta_{ex} = \frac{\Delta E_{us}}{\Delta E_{av}}. \tag{8}$$

Let us calculate the exergy efficiency factor using the values indicated in the scheme in Fig. 3:

$$\eta_{ex} = \frac{\Delta E_{us}}{\Delta E_{av}} = \frac{E_{px} - E_{fx}}{E_f - E_w} = \frac{2.85 - 0}{335 - 276.9} = 0.049 \text{ or } 4.9\ \%.$$

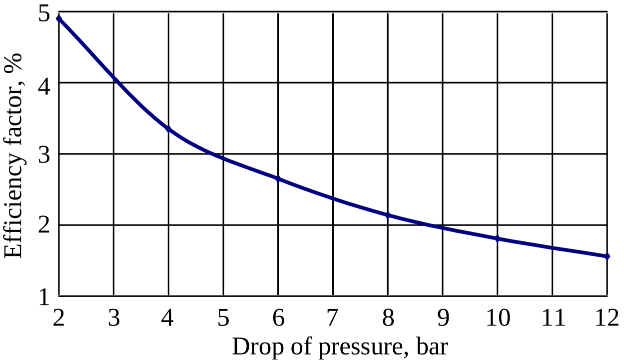

Fig. 4. Dependence of exergy efficiency factor on drop of pressure

This indicator more correctly reflects energy transformations in the reverse osmosis module than the degree of excellence.

The thermodynamic efficiency of processes in the reverse osmosis module is affected by a significant number of parameters: firstly, the hydraulic resistance of the membranes – Δp, secondly, the membrane selectivity – R, and also the concentration of the initial solution – C_f. It is impossible to express the nature of this influence explicitly, however, variant calculations allowing to evaluate this influence are possible. In order to determine the influence of the parameters of the reverse osmosis module on the exergy efficiency, calculations were carried out using the Δp values in the 2...10 bar range, varying concentrations from 10 to 0.5 kg/m^3 and changing selectivity of the membranes from 75 to 95 %.

The results of calculations are presented in a form of graphical dependences in Fig. 4, 5, 6. Material flows with variation of the analyzed parameters in the given range vary little. In this case, they qualitatively reflect the results presented in Fig. 1. On the other hand the exergy flows are undergoing substantial changes, which is reflected in a significant change in the exergy efficiency factor (Fig. 4–6).

The nature of the dependence of the exergy efficiency on the source water concentration is not so definite and can differ significantly from the given calculation performed at fixed values of Δp and membrane selectivity.

This is due to a much more complicated dependence of the exergy efficiency on the initial concentration, since this dependence also reflects the fact that the starting point, namely the impurity concentration in the source water, changes.

The most predictable is the dependence of the exergy efficiency on membrane selectivity (Fig. 6).

Here the tendencies of more favorable changes coincide, both for the technological perfection of membranes and the thermodynamic efficiency of the processes taking place in them.

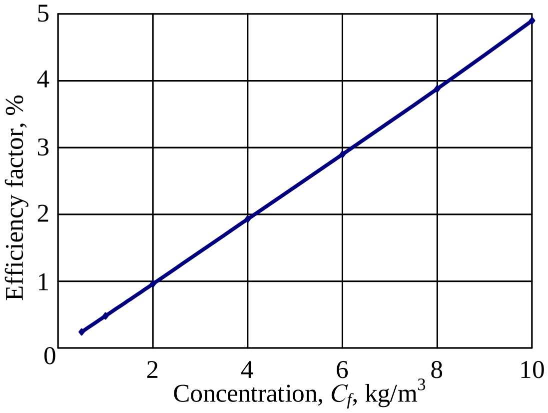

Fig. 5. Dependence of exergy efficiency factor on source water concentration

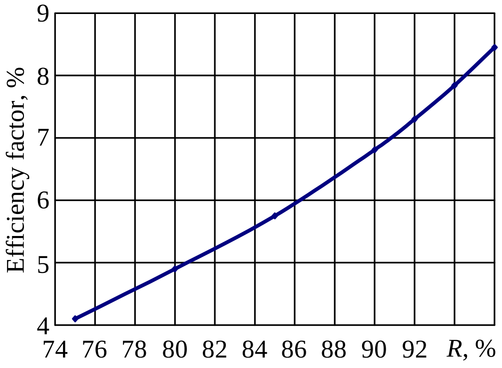

Fig. 6. Dependence of exergy efficiency factor on membrane selectivity R

Conclusions. The thermodynamic efficiency of water purification using membrane technologies (reverse osmosis) is generally characterized by very low values. It should be noted that for the thermal methods of water purification on evaporating installations the same picture is also true.

The most significant effect on exergy efficiency of reverse osmosis plants is the membranes selectivity, the increase of which can be considered as the main task of improving membrane technologies of water purification.

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