Special Features of the Water Decarbonation in Thermal Jet-Type Open Deaerators

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Abstract—This paper presents the results of calculation-based and experimental investigations into static and kinematic conditions of removing free and chemically bonded carbon dioxide from water in jet-type open deaerators.

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Thermal open deaerators are used for treating make-up water at thermal power plants as deaerators of feedwater for low- and intermediate pressure boilers, evaporator plants, and heat networks. The efficiency of operation of deaerators with respect to removal of corrosive gases from water significantly affects the reliability of heat power equipment of thermal power plants, boiler plants, and pipelines of heat networks.

The values of residual concentration of gases in the deaerated water are determined by design parameters and operating conditions, the number of combinations of which is so great that, in practice, an optimum technological regime of the operation of a deaerator is determined in the course of large-scale tests, which involves considerable material and labor costs. In this connection, the construction of mathematical models for determining indicators of the operating conditions of deaerators with the needed accuracy is of current interest. Their use will make it possible not only to reduce expenses on tests of existing facilities, but also to increase the validity of design solutions for new ones.

Certain mathematical models for calculating the processes of heat exchange and desorption of dissolved oxygen in jet and barbotage deaeration elements are to be found in works on the theory and practice of thermal deaeration [1, 2]. Classified data that would make it possible to predict the operation of a deaerator on removal of carbon dioxide CO_2 from water are lacking. But, by the way, the efficiency of water decarbonation substantially affects the corrosion rate of metals, especially in the presence of dissolved oxygen in water, as well as the scale formation intensity in pipelines and the equipment (on deaeration of poorly softened or hard water).
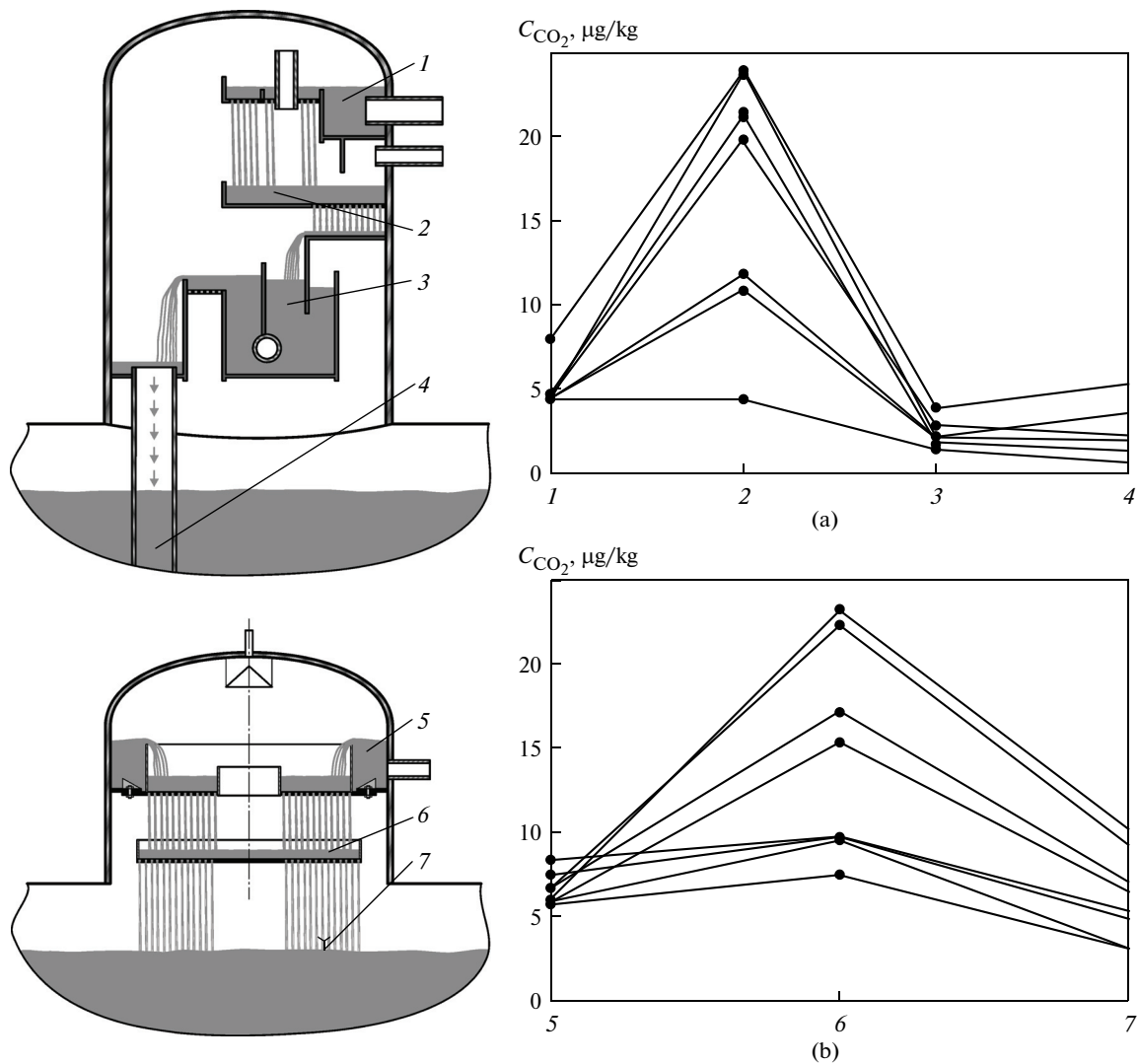
The efficiency of water decarbonation is characterized by a pH value pH_{25} (at 25°C) of deaerated water that, together with the residual concentration of dissolved oxygen, is a standardized index. The practice of adjusting open deaerators shows that it is simpler to achieve an effective absorption of dissolved oxygen than to obtain technologically acceptable values of pH_{25} of deaerated water. In most cases we can consider that, with providing the guideline standard values of pH_{25} of deaerated water, the content of dissolved oxygen in it meets the standard as well. This means that at modeling the processes of thermal water deaeration the closest attention should be given to the problem of decarbonation.

The main problem is to identify the qualitative and quantitative influence of design parameters and operating conditions of a deaerator on the efficiency of CO_2 removal from water. For solving this problem experimental investigations were carried out of DA-300m and DSA-300 deaerators that operate on the Na-cationized water. The system of thermotechnical and chemical control involves water sampling from internal jet and barbotage components of deaerators; the measurement assurance of investigations was carried out for the most part by means of the reference measuring equipment. The experimental data obtained in 69 experiments made it possible to set up criterial equations for calculating the processes of water heating-up and desorption of dissolved oxygen from water in jet compartments of deaerators at the jet-drop hydrodynamic mode of their operation [3], as well as to identify similar mathematical models of unperforated bubble plates.

Further, the processes of mass exchange of carbon dioxide are discussed in more detail. Figure 1 illustrates the change in the mass concentration of free carbon dioxide C_{CO_2} in the components of deaeration columns under experimental conditions (within adjustment ranges of the change in operating conditions). It can be seen that upper jet compartments operate largely as absorbers, and the content of free carbon dioxide in water downstream of the deaeration column differs unessentially from its content in source water. Published results of testing open deaeration col-

Fig. 1. The change in the mass concentration of free carbon dioxide in components of deaeration columns of the DA-300m (a) and DSA-300 (b) deaerators under conditions of experiments. $1-7$—points of water sampling.

umns are available [1, 2], and they are similar to the results obtained in the present work. In this respect, in order for such a situation to be explained, the hypothesis on mechanical capture of carbon dioxide from the vapor phase by the strongly turbulized water flow was suggested, since, in the authors' opinion, the equilibrium mass concentration of carbon dioxide dissolved in water, like that of oxygen, is considerably lower than the actual mass concentration in any part of the column.

Such an explanation seems to be incomplete: if the reason for this were merely the presence of the disperse absorption of CO_2 by water in the jet compartments, then a similar effect would be observed for oxygen as well, but it is not found. This fact can only be attributed to the distinctive feature of static (equilibrium) conditions of the reversible processes of absorption and desorption of gases that are characterized by a

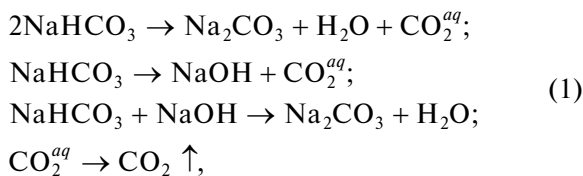relationship between equilibrium and actual gas content in water.

Experimental investigations that have been carried out on DSA-300 and DA-300m deaerators made it possible to calculate equilibrium mass concentrations of oxygen and carbon dioxide in water in various points of the deaerators. In this case, the actual mass concentrations of gases in the vapor phase with respect to deaeration components were determined from equations of material balances of water, vapor, and gases, and, as a phase equilibrium law, the Henry law was used. The results of calculations for carbon dioxide are given in Fig. 2.

The data obtained make it possible to conclude that the equilibrium mass concentration of free carbon dioxide in water differs relatively little (as compared to oxygen) from its actual mass concentration (analogous concentration of dissolved oxygen differ from
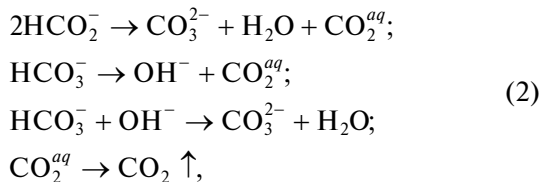
one another by a factor of 100 and more). It can also be expected that carbon dioxide contained in vapor, being gas that is less soluble in water as compared to oxygen, must concentrate near the interphase boundary, which still further deviates the system from equilibrium into the absorption area. Thus, it should be concluded that the system "oxygen–water," under conditions of operation of the upper jet compartments of deaerators, is always far from the equilibrium state and is located in the desorption area, while the system "carbon dioxide–water," on the contrary, is close to the equilibrium state (transition from the desorption area to the absorption area is possible). With a relatively small difference between equilibrium and actual concentrations (driving force of the deaeration process), an intense gas exchange should not be expected from dissolved free carbon dioxide, let alone its chemically bonded forms. Hence, during the operation of an open deaerator virtually all loads needed for removing free, and, especially chemically bonded carbon dioxide fall on the deaerator tank.

On deaeration of Na-cationized water the following mechanism of the non-reversible process of thermal decomposition of hydrocarbonates can be imagined:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2^{aq};$$
$$NaHCO_3 \rightarrow NaOH + CO_2^{aq};$$
$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O; \quad (1)$$
$$CO_2^{aq} \rightarrow CO_2 \uparrow,$$

or, in the ionic form,

$$2HCO_2^- \rightarrow CO_3^{2-} + H_2O + CO_2^{aq};$$
$$HCO_3^- \rightarrow OH^- + CO_2^{aq};$$
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O; \quad (2)$$
$$CO_2^{aq} \rightarrow CO_2 \uparrow,$$

where CO_2^{aq} is carbon dioxide dissolved in water.

The mechanism (1), (2) shows that free carbon dioxide, which occurs in the process of thermal decomposition of hydrocarbonates, first is present in water in the dissolved form, ànd then, after the supersaturation of solution, is dispersed in the form of gas bubbles.

In accordance with this mechanism, the kinetic equation of the non-reversible chemical process of thermal decomposition of hydrocarbonates can be written as:

$$\frac{dC^2}{d\tau} = -KC^2, \quad (3)$$

where C^2 is the mass concentration of hydrocarbonates in water, μg-equiv/kg; K is reaction rate constant, kg/(μg-equiv s); τ is time, s.

It is customary to make an estimate of the efficiency of removal of chemically bonded forms of car-

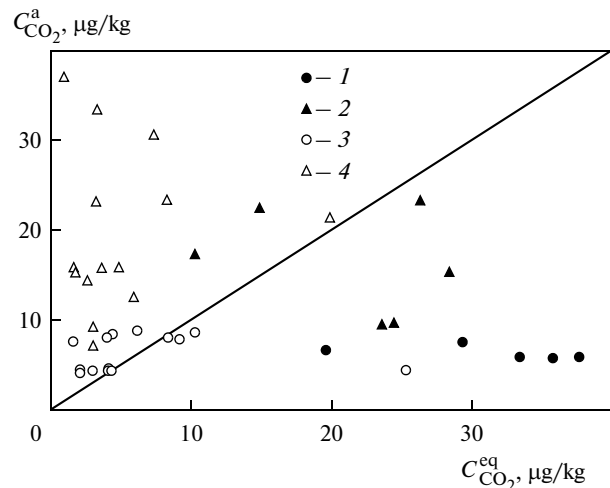**Fig. 2.** Comparison between actual ($C_{CO_2}^a$ and equilibrium $C_{CO_2}^{eq}$ concentrations of free carbon dioxides in upper jet compartments of DSA-300 (1, 2) and DA-300m (3, 4) deaerators.
Parts of a compartment: *1, 3*—upper; *2, 4*—lower.

bon dioxide from water in the deaerator from a value of the degree of hydrocarbonate decomposition σ that can be calculated from values of total alkalinity A_{tot} and alkalinity with respect to phenolphtalein A_{pp} of dearerated water:

$$\sigma = \frac{2A_{pp}}{A_{tot}}. \quad (4)$$

The value of σ for deaerators in question depends on the water residence time in the deaeration tank T, the presence of the submerged bubble device in this tank, and its type (Fig. 3). The longer T, the higher σ. When the submerged bubble device is installed, the value of σ is higher than in its absence. In this case the relationship between parameters mentioned is linear. At $T = 1$ h, it can be expected that for deaerators with the submerged bubble device σ = 0.6, while without it, σ = 0.4 [4].

A knowledge of the constant K of the rate of resulting chemical process of decomposition of hydrocarbonates, as well as of the degree of decomposition σ of hydrocarbonates, is necessary in order to predict the efficiency of removal of free and chemically bonded carbon dioxide in the deaerator.

Thus, the published data [4] for deaerators with bubbling in the water space are confirmed, while the data for deaerators without bubbling differ from the previously published ones, and in this case, considerable spread of experimentally obtained values of σ is observed.

Experimental and calculation-based data presented in Figs. 1–3 prove that jet compartments of open-type deaerators, which are steam exhaust deaer-
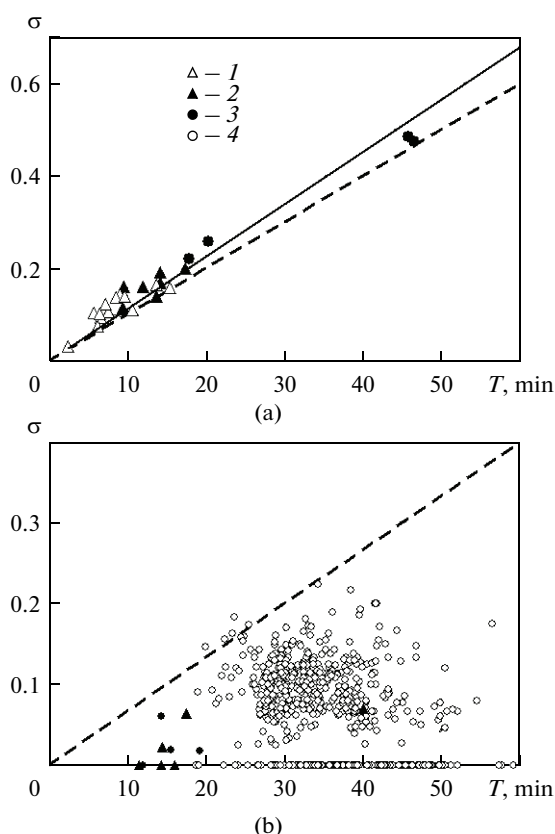
Fig. 3. Experimental values of a degree of dissociation of hydrocarbonates in open-type deaerators having different design, depending on water residence time in the deaerator in the presence (a) and the absence (b) of steam bubbling un the water space of the deaerator tank.

Experimental data: *1*—DA-300m; *2*—DSA-300, two jet compartments in the deaeration column; *3*—DSA-300, one jet compartment in the deaeration column; *4*—DA-50; *5*—approximation of experimental data (the least-squares method); and *6*—data [4].

Fig. 4. Experimental values of K for open-type deaerators having different design, depending on A_{tot} of source water in the presence (area "A") and the absence of steam bubbling in the water space of the deaerator tank.

Notations *1—4* see Fig. 3.

ators, can operate under conditions of the physical absorption of free carbon dioxide by water, and this, together with the presence of disperse absorption of gases by water flow, is responsible for the non-stability of its content in water downstream of jet compartments, whereas in the absence of a downstream bubble, this stage has reasonable available water residence time in it, and downstrean of the deaerator as well. Hence, the implementation of the barrier steam bubbling in the water space of the deaerator tank makes it possible to considerably increase the efficiency of removal of free and, especially, chemically bonded carbon dioxide.

If the water decarbonation rate is supposed to be governed by the process (1), (2), then the values of the rate of the process of thermal decomposition of hydrocarbonates can be calculated in Eq. (3) from the experimental data obtained. Figure 4 shows the results of its calculation depending on the total alkalinity A_{tot}^s
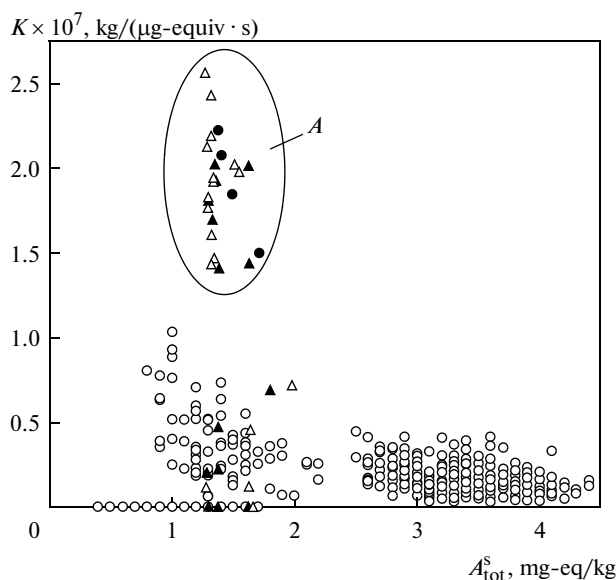
of source water In calculations both inflow of free and chemically bonded carbon dioxide into the deaerator and the removal of CO_2 with flash steam and deaerated water were taken into account.

The spread of obtained values of K may depend not only on the accuracy of the quantitative chemical analysis and the measurement of thermotechnical parameters affecting flow rates of water and steam, but also on the incompleteness of the hypothesis on the mechanism of the process of thermal decomposition of hydrocarbonates in the deaerator [Eqs. (1), (2)] postulated previously. A more precise determination of this mechanism is the subject of an additional investigation that is convenient to be carried out using the methods of chemical thermodynamics, with organizing an appropriate laboratory-scale experiment. In doing so, one should take into account, besides the likely reactions between CO_2 and water admixtures, hydration of molecular carbon dioxide, and dissociation of carbonic acid being formed as well.

Nonetheless, the obtained kinetic characteristics of the processes of thermal dissociation of hydrocarbonates in the deaerators in the presence or the absence of steam bubbling in the water space of the deaerator tank makes it possible to predict indicators of the effective removal of free and chemically bonded carbon dioxide from water.

Considering results of the analysis of equilibrium conditions of absorption-desorption, the presence of free carbon dioxide in the deaeration columns, and the essential dependence of kinetic characteristics of the processes related to removal of chemically bonded

carbon dioxide contained in the deaerator tank on the presence of steam bubbling, the study of performance characteristics of submerged bubble devices installed in deaerator tanks becomes particularly important. The data on the deaerators with steam bubbling in the deaerator tank presented here relate to apparatuses with the bubbling device in the form of a single perforated header, located at the bottom of a tank about 8 m long, with 185 holes 12 mm in diameter arranged in two rows.

The experimental data make it possible to conclude that a minimum necessary value of steam rate needed for bubbling when such device is used, by the conditions of deoxygenation and decarbonation of water, is 15 and 20 kg/t, respectively; at lower values the deaeration efficiency decreases sharply, while at higher values no marked increase in the effectiveness was observed. It is also important that when the steam rate needed for bubbling is equal to 20 kg/t and more, the efficiency of water deaeration in the tank virtually does not depend on other thermohydraulical parameters of the deaerator operation, except the water residence time in it.

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