EXPERIMENTAL STUDY OF TRANSFORMATION OF CARBONATE SYSTEM COMPONENTS COOLING WATER OF RIVNE NUCLEAR POWER PLANT DURING WATER TREATMENT BY LIMING

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The article presents research results on carbonate system components of cooling water, which has previously undergone water treatment by liming, depends on the cycle of concentration and absorption of carbon dioxide, which simulate the processes of evaporation and aeration in circulation cooling systems (CCS) of power plants. pH was an indicator chosen to identify components of carbonate system components of the given research. Were carried out experimental studies, control data were analyzed regarding pH and carbonate system component changes of technological and circulating water of the CCS during water treatment by liming according to the stabilization treatment method, namely the use of mineral – sulphuric acid. It was shown that during cooling water aeration in the cooling tower the absorption of carbon dioxide from the air occurs, which causes a shift in the equilibrium of the carbonate system with a decrease or increase of carbonate alkalinity, bicarbonate content, carbonate ions and pH with or without applying stabilization treatment by sulphuric acid.

INTRODUCTION

Along with corrosion and biofouling, there is a problem of scale formation in circulating cooling systems (CCS) of nuclear power plants. Depending on the source of water supply, which can be surface water from rivers or groundwater, the cooling system can experience these problems to varying degrees. In the case of using surface waters of rivers, scale formation on cooling tower components increases in proportion to the number of cooling cycles [1]. In addition, the rate of scale formation depends on the initial concentrations of carbon dioxide, bicarbonate and carbonate ions in the water [2].

Carbon dioxide, carbonate and carbonate ions are the main components of the carbonate buffer system for the most kinds of natural waters, these components ensure the ability to neutralize the acid, identify the water alkalinity. Free carbon dioxide is the most dynamic component of the carbonate system. The ratio of carbon dioxide, bicarbonate and carbonate ions is the main indicator that determines pH [3]. Each form exists in a certain pH interval, the presence of one or another form in the carbonate system components determines one or another value of water pH, that stipulates the coexisting forms of carbonate system components. If pH ≤ 4.4 water can contain only carbon dioxide, when pH range is from 4.4 to 8.37 two forms are in equilibrium, that is carbon dioxide and bicarbonate ions, and the concentration of bicarbonate ions increases with pH increase and reaches its maximum value at pH of 8.37. When pH range is from 8.37 to 12 hydrocarbonate and carbonate ions are in equilibrium, when pH > 12 then only carbonate ions exist.

Dissolved carbon dioxide interacts with water and forms bicarbonate and carbonate ions, an increase of pH in water as an important component of carbonate-calcium equilibrium leads to its shift towards the formation of calcium carbonate [4]. By means of mathematical modeling of the kinetics of carbon dioxide dissolution and changes in the components of the carbonate system, the relationship between the components of the carbonate system was established, which is expressed as a system of five related nonlinear ordinary differential equations with 14 independent parameters [5]. The investigation of river carbonate systems led to the conclusion that in the water with higher alkalinity atmospheric equilibrium occurs more slowly, since the part of the carbon dioxide entering the river flow is transformed into bicarbonate ions, the result of this direct buffering is the constancy of maintaining pH and alkalinity index, but the dissolved inorganic carbon indicator increases [6]. For carbonate system of oceans, components and concentration of the carbonate system were obtained using thermodynamic modelling [7]. The impact of hydrobiological processes is revealed by pH increase during the season of active vegetation of planktonic organisms due to the consumption of carbon dioxide. During photosynthesis of aquatic plants, assimilation of carbon dioxide occurs with bicarbonate ions. If this process is intensive, the deficiency of carbon dioxide begins recovering from bicarbonate ions, forming carbonate ions [8].

All the described processes explain the presence of scale-forming agents in natural waters, in the case of their use in circulating cooling systems of nuclear power plants, which is of significant technological and economic importance for water treatment [1]. One of the most common methods of water treatment is water clarification by liming [9]. Improving work with the introduction of promising control methods is an urgent task in the operation of nuclear power plants [10].

The purpose of this article was to conduct experimental research on the changes in the components of the carbonate cooling water system of the Rivne hydropower plant during water treatment by liming. The object of the study is the carbonate system of process and return waters of the Rivne NPP.

The water intake and discharge of cooling water of Rivne NPP CCS is carried out into the Styr River. The water of the Styr River, at the water intake site, like most rivers of Polissya zone of Ukraine, has a hydrocarbonate-calcium composition [11], and is formed by surface runoff, runoff from small rivers and drainage systems, which introduce an additional amount of carbonate and bicarbonate ions into the water composition [12]. Water intake from river is performed with amount from 4000 to 8000 m^3/year, the permissible volume of cooling water discharge into the river is 2483.75 m^3/year, the actual – 1419.72 m^3/year.

pH indicator was chosen to identify carbonate system components of this research. According to the requirements to the composition and properties of water bodies of drinking water points, recreation areas, as well as fishing reservoirs, the pH should not go beyond the range of values of 6.5...8.5 [13, 14]. The measuring method pH index in surface, underground, circulating water is regulated by [15].

TEORY AND RESEARCH METHODS

Rivne NPP has been operating a cooling water treatment system, in which they carry out the following: liming, flocculation with polyacrylamide and stabilization treatment with 1-hydroxyenelyleden-1,1,-diphosphonic (OEDF) and sulphuric acids. The average annual indicators of the Styr River water quality and the additional cooling water of the Rivne NPP are given in Table 1. Liming effectively decrease calcium ions (up to 50%) and reduces mineralization, content of iron and organic substances (see Table 1).

Table 1

Quality[1)] of the Styr River water and Rivne NPP additional cooling water (2012–2021)

Index	Water of the Styr River, ppm	Additional cooling water of Rivne NPP, ppm	
		without stabilization treatment H_2SO_4	with stabilization treatment H_2SO_4
Mineralization total	369.7 (339.32 – 621.6)	290.3 (305.62 – 526.42)	374.5 (368.25 – 647.62)
Sulphate ions	38.63 (23.79 – 61.28)	40.35 (25.61 – 60.26)	58.4 (50.36 – 85.63)
Chloride ions		15.04 (11.34 – 19.15)	
Calcium ions	95.41 (87.35 – 105.96)	36.4 (25.64 – 38.52)	

Note. [1)]369.7 – average value;
    (339.32 – 621.6) – minimum – maximum value.

Liming of water at the Rivne NPP is carried out in a bicarbonate lighting mode, construction lime is used as a reagent for liming, the quality of which corresponds to normalized value [16]. Liming is performed due to the

displacement of the carbonate equilibrium of the source water, and pH value rises to 8.8...9.8 [17]. The reason of lighting by liming is the removal of bicarbonate ion from water, and the following processes occur: carbon dioxide dissolves – equation (1), or calcium ions are bound and precipitated – equation (2).

$$2CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2, \tag{1}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + H_2O. \tag{2}$$
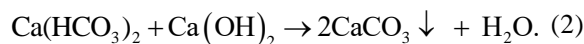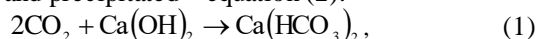
Stabilization treatment of additional cooling water of ORCS is carried out by the combined method of OEDF and sulphuric acid. When using OEDF acid, calcium ions are bound into complex chelating compounds, when sulphuric acid is treated with additional cooling water, the part of the carbonate hardness becomes a constant one in the reaction – equation (3). Treatment with sulphuric acid of additional cooling water is carried out during regulation of 7.5...7.8 pH, stabilization treatment with sulphuric acid increases the mineralization and the content of sulphate ions.

$$Ca(CO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O + 2CO_2. \tag{3}$$
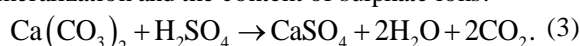
Control of the formation of scale in the cooling conductor of the CCS of the Rivne NPP based on the results of the difference of coefficients φ and ψ, the value of which should not exceed 0.2. The evaporation φ coefficient is calculated by chloride ions, ψ coefficient is calculated by total hardness according to equation (4), where Cl_{wc}, Cl_{mwc} (TH_{wc}, TH_{mwc}) is the content of chloride ions (total hardness), mg/dm^3 ($mmol/dm^3$) in cooling and additional waters, respectively.

$$\varphi\left(\frac{Cl_{cw}}{Cl_{mcw}}\right) - \psi\left(\frac{TH_{cw}}{TH_{mcw}}\right) \leq 0.2. \tag{4}$$

Preservation of the proportionality of the change in the values of φ and ψ according to equation (4) indicates the proportionality of the evaporation of calcium, magnesium and chloride ions with the absence of an intensive process of calcium precipitation in the form of calcium carbonate.

During the experimental studies, the actual conditions of operation of the CCS of the Rivne NPP were simulated, make up cooling water was used with quality indicators according to Table 1 that underwent lightening by liming, treatment of OEDF acid with at a dose of 0.3 mg/dm^3, without treatment with sulfuric acid (pH (9.6 ± 0.2)) and with treatment with sulfuric acid (pH (7.65 ± 0.15)). pH measurements were carried out with an ionometer "И-160" according to the method [15], measurements of chloride ions were carried out by the titrometric method with silver nitrate, and the total hardness by the titrometric method with Trilon B.

The temperature during sample did not exceed (50 ± 1) °C. The impact of air aeration on the cooling water in cooling towers was modeled in laboratory conditions was reproduced on the test bench (Figs. 1, 2) with passing air through "Тайфун-20-2" sampler was used with flow rate of 0.5 dm^3/min. Chemical data analysis was carried out in compliance with reports on evaluation of non-radiative impact of non-radiative factors of Rivne NPP in according to the standard [18].

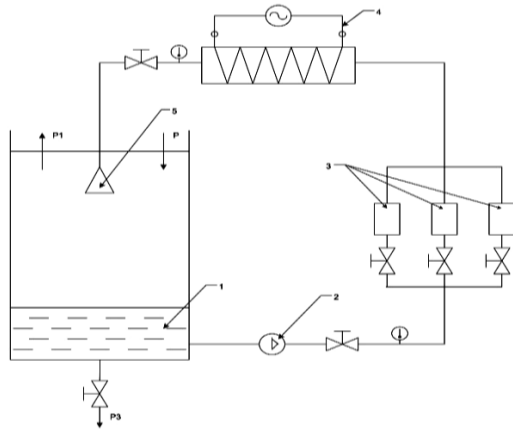*Fig. 1. Photo of the test bench for experimental studies*

Fig. 2. Schematic diagram of the test bench for experimental studies (1 – container with cooling water; 2 – circulation pump; 3, 4 – thermoelectric heaters; 5 – irrigator; P-1 – evaporation; P – feeding; P-3 flushing water)

RESEARCH RESULTS

The dynamics of changes in pH during concentration and aeration of cooling water samples without and with sulfuric acid stabilization treatment (Fig. 3) show that during concentration of cooling water that has not been treated with sulfuric acid, there is a decrease in pH with a change in the components of the carbonate system.
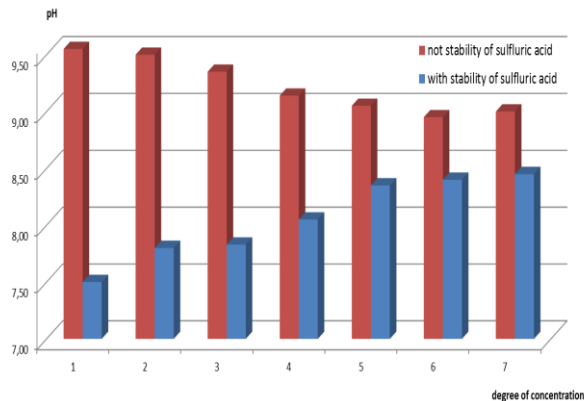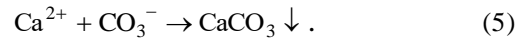

Fig. 3. Dynamics of pH sample changes depending on concentration of cooling water with/without sulphuric acid

Obviously, this is due to the processes of scale formation with the formation of calcium carbonate according to equation (5).

$$Ca^{2+} + CO_3^{-} \rightarrow CaCO_3 \downarrow . \qquad (5)$$

For a sample treated by sulphuric acid (see Fig. 3) an increase of pH is observed and is caused by the decomposition of bicarbonates, which is also accompanied by calcium carbonate formation according to the equation (6).

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + CO_2 + H_2O . \qquad (6)$$
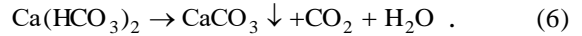
During air aeration through cooling water samples without sulphuric acid, absorption of carbon dioxide is observed, pH decreases to values of 8.3…8.5. During this process carbonates are neutralized and equilibrium of the carbonate system is shifted with the accumulation of bicarbonates (Fig. 4).
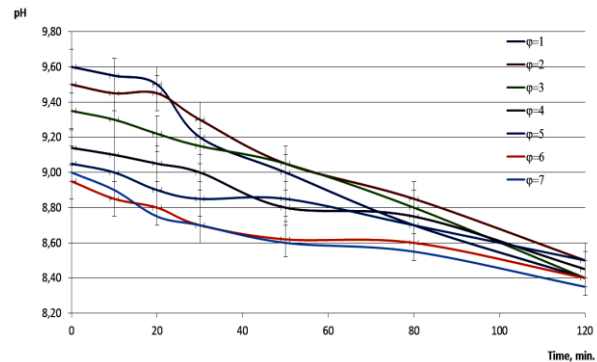

Fig. 4. pH change of cooling water samples during aeration without sulphuric acid treatment at different evaporation coefficients

For cooling water samples with sulphuric acid treatment during aeration pH increases to values of 8.3…8.6 (Fig. 5) due to the absorption of carbon dioxide with the accumulation of bicarbonates to equation (7).

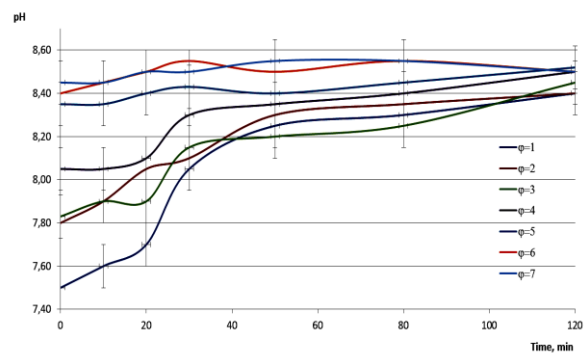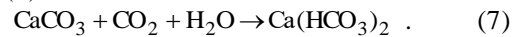$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 . \qquad (7)$$

Fig. 5. pH change of cooling water samples during aeration with sulphuric acid treatment at different evaporation coefficients

Normalized differences in coefficients φ - ψ, without the use of sulfuric acid, are provided at $\varphi = 3$ and less, and when treated with sulfuric acid at $\varphi = 4$ and less, which determines the expediency of using sulfuric acid to inhibit the formation of scale only when working with higher evaporation coefficients (Table 2).

The value evaporation coefficients in coefficients φ and ψ for samples of cooling water after evaporation and aeration without stabilization treatment H_2SO_4

Evaporation coefficients φ	Without stabilization treatment H_2SO_4*	
	Concentration of chloride ions $\pm \Delta$, mg/dm³	Scale formation indicator $(\varphi - \psi) \pm \Delta$
1	10.5 ± 1.1	–
2	20.3 ± 2.0	0.07 ± 0.01
3	30.1 ± 1.5	0.15 ± 0.02
4	39.5 ± 2.0	0.29 ± 0.03
5	51.3 ± 2.6	0.41 ± 0.04
6	62.1 ± 3.1	0.74 ± 0.07
7	69.4 ± 3.5	1.13 ± 0.11

Note. *Δ – absolute measurement error.

During the stabilization treatment with sulfuric acid, the intensity of scale formation is lower, which is indicated by the preservation of the proportionality of the changes in the coefficients φ and ψ (Table 3).

The value evaporation coefficients in coefficients φ and ψ for samples of cooling water after evaporation and aeration with stabilization treatment H_2SO_4

Evaporation coefficients, φ	With stabilization treatment H_2SO_4*	
	Concentration of chloride ions $\pm \Delta$, mg/dm³	Scale formation indicator $(\varphi - \psi) \pm \Delta$
1	10.5 ± 1.1	–
2	19.8 ± 2.0	0.05 ± 0.01
3	31.1 ± 1.6	0.08 ± 0.01
4	40.4 ± 2.0	0.14 ± 0.01
5	50.3 ± 2.5	0.28 ± 0.03
6	59.2 ± 3.0	0.39 ± 0.04
7	71.3 ± 3.6	0.62 ± 0.06

Note. *Δ – absolute measurement error.

In the case of feeding CCS Rivne NPP with additional cooling water neutralized with sulphuric acid (2013–2017), an increase of pH was observed in CCS water due to the processes of carbon dioxide absorption and water concentration with bicarbonate ions formation (Fig. 6).
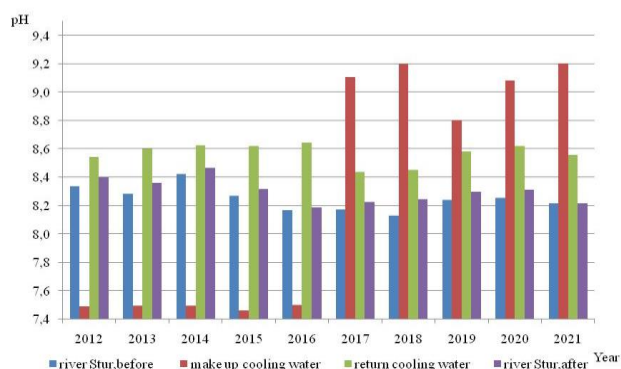

Fig. 6. Change of pH in the process water of the Rivne NPP and the water of the Styr River with / with out stabilization H_2SO_4 (2012–2021)

In the case of CCS feeding with additional cooling water not neutralized with sulphuric acid (2017–2021), pH decrease was observed in CCS water due to carbon dioxide absorption and water concentration that is followed by bicarbonate ions formation.

DISCUSSION

According to the experimental data obtained, the buffer properties of the carbonate system water depend on the fact that after removing the carbon dioxide and reducing the concentration of pH a part of the bicarbonate ions begins disintegrating with the formation of carbonate ions and the partial restoration of H+ deficiency. The kinetics of carbon dioxide absorption depends on the concentration degree of the sample (φ) and mineralization, the absolute value of pH change is less during aeration of carbon dioxide due to a more concentrated sample of cooling water.

Liming of water during cooling water treatment at Rivne NPP takes place in a bicarbonate lighting mode, lighting occurs due to the displacement of the carbonate equilibrium of the Styr River natural water, while the pH value rises to values of 8.8…9.8.

For the auxiliary cooling water of Rivne NPP after water treatment, which is not treated by sulphuric acid: during aeration in the cooling tower carbon dioxide is absorbed from the air, due to this process a further shift in equilibrium with a decrease in alkalinity and pH, and as a result the concentration of hydrogen ions is increased and absorbed carbon dioxide neutralizes carbonate ions, forming bicarbonate ions. For water after water treatment, during stabilization treatment with sulphuric acid, during aeration in the cooling tower, carbon dioxide is absorbed from the air, due to this the equilibrium is a shifted and pH is increased, absorbed carbon dioxide forms bicarbonate ions.

SUMMURY

The equilibrium of the carbonate system components in ecosystems and technoecosystems can be achieved naturally due to the absorption of carbon dioxide from the air, concentration, precipitation of calcium carbonate. The accumulation of bicarbonate ions and the neutralization of carbonate ions from an environmental point of view does not compensate the artificial introduction of sulphate ions into natural objects to use sulphuric acid for stabilization treatment.

pH change of the auxiliary cooling water, CCS cooling water of Rivne NPP is caused by accumulation of natural components of bicarbonate- and carbonate ions of the natural system due to the mixture of equilibrium during aeration and concentration. The equilibrium of the carbonate system in the cooling water of Rivne NPP is achieved by the stabilization of pH values of 8.2…8.6 units, regardless the initial pH values of auxiliary water during liming with or without use of sulphuric acid.

Taking into account the establishment of equilibrium in the carbonate system in CCS and natural water, the use of sulphuric acid for water treatment namely to ensure environmental standards for the pH value is impractical. The use of sulphuric acid can be

justified to optimize the water-chemistry mode in order to reduce scale in CCS.

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ЕКСПЕРИМЕНТАЛЬНІ ДОСЛІДЖЕННЯ ЗМІНИ КОМПОНЕНТІВ КАРБОНАТНОЇ СИСТЕМИ ОХОЛОДЖУЮЧОЇ ВОДИ РІВНЕНСЬКОЇ АЕС ПРИ ПРОВЕДЕННІ ВОДОПІДГОТОВКИ ШЛЯХОМ ВАПНУВАННЯ

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Представлені результати досліджень зміни компонентів карбонатної системи охолоджуючої води, яка попередньо пройшла водопідготовку вапнуванням, залежно від коефіцієнтів концентрації та аерації повітря, що імітує процеси концентрації та аерації в оборотних системах охолодження (ОСО) електростанцій. В якості показника, що визначає компоненти карбонатної системи даного дослідження, було обрано рН. Проаналізовано дані про зміни рН та відповідно компонентів карбонатної системи технологічних і зворотних вод ОСО під час водопідготовки вапнуванням залежно від способу стабілізаційної обробки, а саме використання мінеральної – сірчаної кислоти. Показано, що в охолоджуючій воді при аерації в градирні та концентруванні при випаровуванні в ОСО відбувається поглинання вуглекислого газу з повітря, що викликає зміщення рівноваги карбонатної системи зі зменшенням або підвищенням карбонатної лужності, вмісту бікарбонату, карбонатних іонів і рН при застосуванні або без застосування стабілізаційної обробки сірчаною кислотою.