https://doi.org/10.15407/scine20.02.079

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OPTIMIZATION OF THE ANTI-SCALE CORRECTIVE TREATMENT OF WATER BY ORGANIC PHOSPHONATE

Introduction. *Anti-scale corrective treatment (ACT) is an important part of power plant operations, especially in cooling systems. The treatment of cooling water with 1-hydroxyenelyleden-1,1,-diphosphonic acid (HEDP) has been widely used in circulating cooling systems of power plants (CCS), and its use needs to be optimized to achieve maximum treatment efficiency.*

Problem Statement. *The effectiveness of ACT reagents depends on their dose, contact time, temperature, and pH. The dosage of HEDP is determined at the stage of designing a power plant and is often implemented in fixed concentrations, irrespective of subsequent changes in technology and cooling water quality indicators during the operation.*

Purpose. *The purpose of this study is to optimize the use and to minimize the discharge of HEDP in water bodies during ACT of CCS.*

Materials and Methods. *The CCS Rivne Nuclear Power Plant (Rivne NPP) is the object of the study. Standard chemical control methods and statistical methods have been used in the research.*

Results. *Data from long-term monitoring and maintenance of the water chemistry regime and discharges of Rivne NPP cooling water have been analyzed. The total hardness of the cooling water has been used as a criterion for the variability of the HEDP dosage. During the period of variable dose, there have been reported a decrease by 30% in the total amount of HEDP used for cooling water treatment, a decrease in the concentration of HEDP in the auxiliary water (from 0.410 to 0.204 ppm), and a minimization of HEDP discharge into the Styr River with the return water after Rivne NPP discharge (from 0.36 to 0.105 ppm).*

Conclusions. *The model of variable dose of HEDP has been implemented for Rivne NPP in order to minimize its use and corresponding discharge to water. During the period of variable dose of HEDP, as compared with constant concentration dose, the amount of HEDP used while maintaining the efficiency and the concentration of the CCS makeup and return cooling water decrease, and the HEDP discharges with return water have been minimized.*

Keywords: circulating cooling system, 1-hydroxyenelyleden-1,1,-diphosphonic acid, dosage optimization, and discharge of wastewater.

Citation: Kuznietsov, P. M., Biedunkova, O. O., Yaroshchuk, O. V., and Pryshchepa, A. M. (2024). Optimization of the Anti-Scale Corrective Treatment of Water by Organic Phosphonate. *Sci. innov.*, 20(2), 79—90. https://doi.org/10.15407/scine20.02.079

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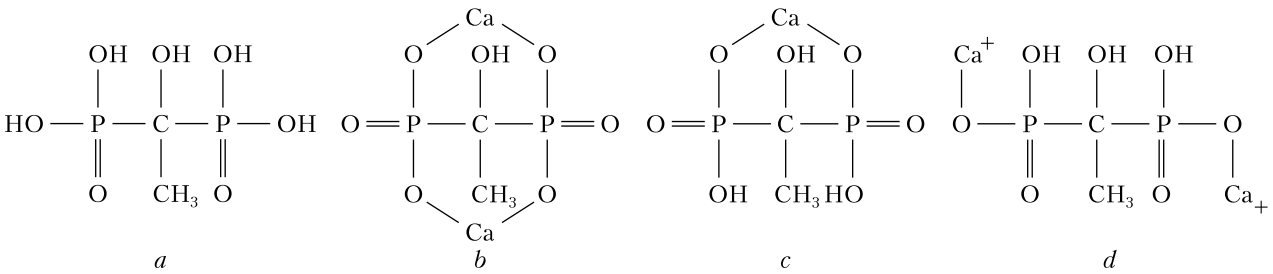


Fig. 1. Schematic structure of HEDP and the formation of precipitates and complexes with calcium ions: *a* — schematic structure of HEDP; *b* — Ca-HEDP precipitate (2 : 1); *c* — Ca—HEDP precipitate (1 : 1); and *d* — Ca-HEDP complex (1 : 1)

In circulating cooling systems (CCS) of power plants, the main source of contamination of condensers is the formation of hard mineral deposits of calcium carbonate scale. The formation of scale in cooling systems is caused by the fact that increasing mineralization of cooling water as compared with the mineralization of additional water, as a result of its evaporation, leads to the disintegration of calcium bicarbonate dissolved in water, which turns into a calcium carbonate precipitate [1]. All this during the operation of the SCS leads to a decrease in the transfer efficiency of the heat exchange equipment and clogging of the pipes [2].

To prevent the formation of scale, the following methods are used: CCS blowing that reduces the degree of evaporation, the hardness of the cooling water (in particular liming) and stabilizing anti-scale treatment (in particular phosphonates) [3]. Since the 1960s, organic phosphonates have been used for corrective treatment of CCS cooling water, as effective and inexpensive inhibitors to prevent the formation of calcium carbonate ($CaCO_3$) scale [4].

Presently, organic phosphonates are the dominant scale inhibitors with acceptable efficacy and low cost. There are two classes of organic phosphonates used as scale inhibitors: the substances having one or more groups of acid residues — PO_3H_2 and the substances having a C—P—C connection with the formation of —PO_2H—. Widely distributed organic phosphonates are HEDP, 2-phosphonobutane1,2,4-tricarboxylic acid, polyamino polyether methylene phosphonic acid, and amino-tris-(methylenephosphonic acid). HEDP (Fig. 1, *a*) is a white crystalline powder that dissolves well in water, its melting point is 198—199 °C. HEDP dissociation constants are as follows: $pK_1 = 1.7$; $pK_2 = 2.47$; $pK_3 = 7.28$; $pK_4 = 10.29$; and $pK_5 = 11.13$. In aqueous solutions, when calcium ions interact with HEDP, it is possible to form precipitates with a Ca-HEDP ratio of 2:1 (Fig. 1, *b*), 1 : 1 (Fig. 1, *c*), and a complex compound (Fig. 1, *d*) [5]. At a temperature that is typical for circulating cooling systems of turbine condensers, HEDP does not undergo hydrolytic decomposition and retains its stabilizing properties; in the concentration range from 0 to 20 ppm. Also, it does not affect the change in the hydrogen pH indicator [6].

The mechanisms of HEDP inhibition and the formation of $CaCO_3$ precipitate have been investigated by studying the surface charge and crystalline form of the scales [1, 7]. Studies of the structure of $CaCO_3$ precipitate formation in the presence of HEDP have proven that the shape of the precipitate changes due to the absorption of HEDP on already formed $CaCO_3$ crystals, and the formation of the solid phase of the $CaCO_3$ precipitate is inhibited by HEDP, as a result of which the entire process of $CaCO_3$ formation is greatly slowed down [8].

Organic phosphonates can lead to a high level of phosphorus in CCS return water that is discharged into a water body, and the concentration of total phosphorus can increase and reach 1—15 ppm [9]. Due to the natural mechanisms of phosphonate elimination, the long-term release of bioavailable orthophosphate from phosphonates in natural waters is ensured, thus, eutrophication processes are

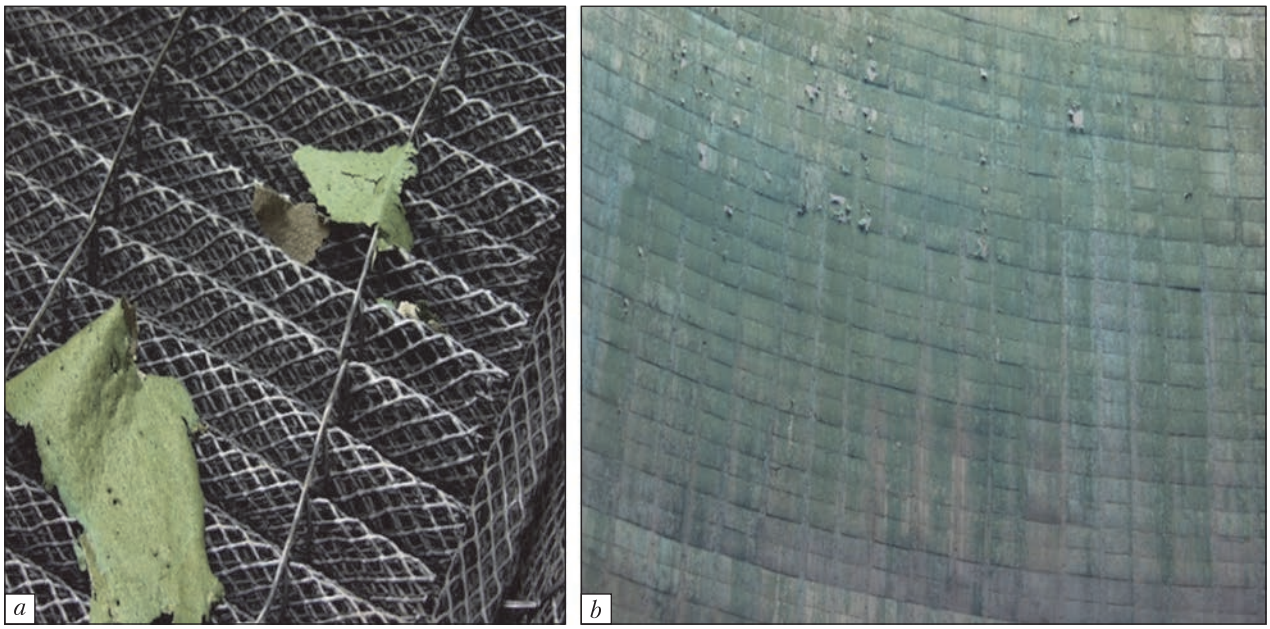


Fig. 2. Biological contamination of cooling towers of the Rivne NPP by algae in 2019: *a* — water distribution network; *b* — exhaust tower

not excluded [10]. Total phosphorus content above 1 ppm can lead to the eutrophication of the aquatic environment, both the CCS aquatic environment (Fig. 2) and the natural water body where CCS return water is discharged [11, 12].

The appearance of biological fouling, as well as the requirements for the need to provide CCS with a significant amount of water and compliance with environmental standards for return water, force power plant operators to develop and implement optimal methods of using chemical reagents [13]. To maintain the optimal water-chemical regime of CCS, it is necessary to minimize the content of phosphorus dosed into the cooling water to avoid its negative impact on water bodies. Improving the activity of a nuclear power plant with the introduction of control and diagnostic methods is an urgent task [14].

According to the EU directive [15], the following requirements are established for the maximum concentrations of total phosphorus (including organic phosphonates) when discharging treated effluents into water bodies sensitive to eutrophication: cities with a population of more than 100,000 conditional residents — 1 ppm; cities with a population of 10,000 to 100,000 conditional residents — 2 ppm; and cities with a population of less than 10,000 conditional residents shall reduce the concentration of total phosphorus by at least 80%. Contents of HDEP in surface waters for Ukraine are regulated by the requirements for maximum permissible concentrations (MPC) in reservoirs for fish farming (0.9 ppm) [16]. In the literature, there is a limited amount of data on the concentration of HEDP in the surface waters of the river: 0.3—1.6 ppb HEDP in six German rivers [17] and 0.088 ppb HEDP in Chinese river [18]. HEDP accumulates in the surface waters of reservoirs in both dissolved and adsorbed forms [19].

The use of chemical reagents for water preparation and maintenance of the water-chemical regime of technological environments of power plants affects the economic efficiency of the operation of the power plant as a whole [20]. To increase the efficiency of work, measures should be taken to eliminate the possibility of unjustified excess do-

sing of reagents with the introduction of effective mechanisms for optimizing their use. The minimization of the use of chemical reagents for power plants with the discharge of return water into water bodies is also due to the need to minimize the discharge of polluting substances and their impact on the environment.

The purpose of our study is to optimize the use of HEDP for the anti-scaling water treatment of CCS power plant water by implementing a dosing variability model to minimize phosphonate emissions without reducing the effectiveness of HEDP anti-scaling water treatment.

Our studies have been conducted for the technological waters of the CCS Rivne NPP and the surface water of the Styr River. The Rivne NPP nuclear power plant has four power units of the VVER type, located in Eastern Europe, in Ukraine. The Rivne NPP cooling system is an open-type CCS with water cooling in tower cooling towers. The cooling water consumption of power units No. 1, 2 (VVER-440) is 91 thousand m^3/h for each power unit, power units No. 3, 4 (VVER-1000) — 188.9 thousand m^3/h each. For powering the CCS Rivne NPP water from the Styr River is used with a flow rate of 4.000 to 8.000 m^3/h. The discharge of return water is carried out in the Styr River without preliminary treatment, the permissible dump volume of discharge of cooling water into the river is 2483.75 m^3/hour, and the actual dump volume is 1419.72 m^3/h.

In the course of our research, the HDEP concentration has been measured by the photocolorimetric method [21], and chloride ions and total hardness have been measured by the titrometric method [22, 23]. Sampling and control of samples have been carried out according to the requirements [24] by the certified measuring laboratory of Rivne NPP (certificate of recognition of measuring possibilities No. R-8/11-57-5 dated 22.12.17), with the use of measuring tools that have been verified in the field of the State Metrological Supervision of Ukraine. The chemical control data of CCS Rivne NPP and water of the Styr River has been analyzed based on the results given in the reports on the assessment of factors of non-radiation impact on the environment of Rivne NPP. The permission of Rivne NPP for the publication of control data in open sources was obtained (Rivne NPP Act No. 036-08 —A—Zag.B dated 02.03.2023).

CCS makeup water treatment at Rivne NPP includes pre-treatment of the water of the Styr River by liming in bicarbonate mode, as a result of which the content of calcium ions and total mineralization in the additional cooling water decreases (Table 1). HEDP dosages for the treat-

Table 1. **The Range of Changes* of Hydro Chemical Water Quality Indicators of the Styr River, Additional Cooling and Cooling Water of CCS Rivne NPP (2012—2022)**

Components	Water of Styr river	Makeup water CCS Rivne NPP	Cooling water CCS Rivne NPP
Total mineralization, ppm	369.7 (339.3—621.6)	290.3 (305.6—526.4)	756.4 (509.25—1150.6)
Sulphate ions, ppm	38.63 (23.79—61.28)	49.55 (25.61—85.63)	128.4 (70.36—185.63)
Chloride ions, ppm	15.04 (11.34—19.15)		58.14 (30.11—79.22)
Calcium ions, ppm	95.41 (87.35—105.96)	68.40 (35.64—78.52)	170.35 (125.46—220.34)
Magnesium ions, ppm	15.04 (11.34—19.15)		58.14 (30.11—79.22)

* *Note:* —369.7 average value, (339.3—621.6) minimum-maximum value.

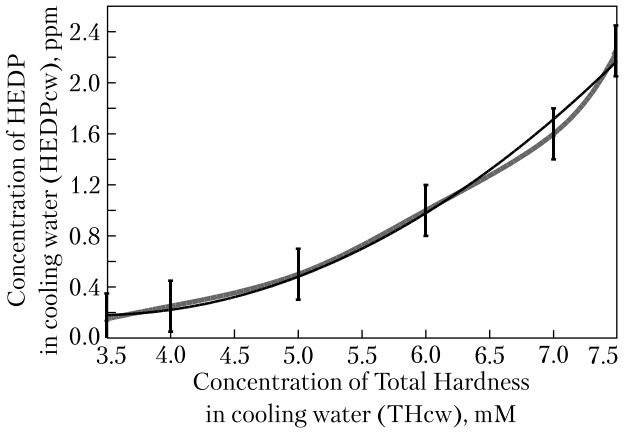


Fig. 3. Dependence of HDEP concentration (HDEPcw, ppm) in cooling water and total hardness (THcw, mM) of CCS cooling water to inhibit calcium carbonate formation

ment of additional CCS water, according to the Rivne NPP design decisions, provided for a constant dosage with maintenance of a constant concentration in the makeup cooling water of 0.5 ppm. Sustainable dosing of HEDP does not take into account technological modes of operation and quality indicators of the water-chemical mode of CCS cooling water.

The intensity of scale formation in the cooling water at CCS Rivne NPP is controlled by the ratio of the difference in the evaporation coefficients ϕ, as calculated by chloride ions, and ψ, as calculated by total hardness. To ensure an acceptable amount of scale formation at CCS Rivne NPP, the difference in evaporation coefficients ϕ and ψ should, according to equation (1), not exceed 0.2 [11]:

$$\phi\left(\frac{\text{Clcw}}{\text{Clmcw}}\right)-\psi\left(\frac{\text{THcw}}{\text{THmcw}}\right)\le 0.2\phi\left(\frac{\text{Clcw}}{\text{Clmcw}}\right), \quad (1)$$

where Clcw, Clmcw (THcw, THmcw) are the content of chloride ions (total hardness), ppm (mM) in the cooling and the makeup cooling waters, respectively.

The variable dosage of reagents is a model of the regulation of the dosage of reagents in water treatment processes, which provides effective management of water quality and saves of operating costs. The basis of the variable dosing model

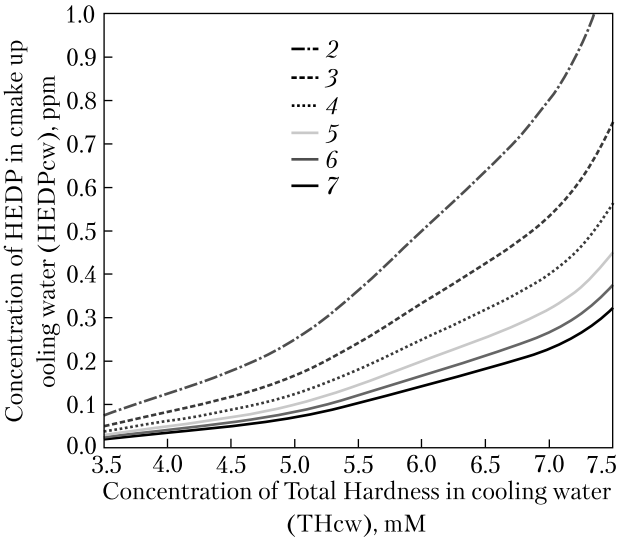


Fig. 4. Dependence of HDEP concentration in makeup cooling water (HDEPmwc, ppm) and total hardness (THcw, mM) of CCS cooling water on evaporation coefficients from 2 to 7

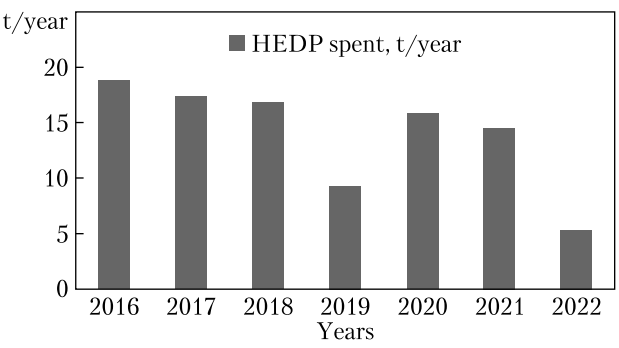


Fig. 5. Average annual amount of HEDP used for the water treatment for the CCS Rivne NPP

is the control of water quality indicators and the regulation of the dosing of reagents depending on the change in these parameters, which ensures the optimal use of reagents and reduces their costs.

The model variable dosage HDEP for cooling water treatment at CCS Rivne NPP is based on the dependence of the concentration of HDEP (HDEPcw, ppm) and the total hardness (THcw, mM) in the cooling water (Fig. 3), the maintenance of which allows inhibiting the formation of calcium carbonate $CaCO_3$.

The necessary concentration HDEP (HDEPmwc, ppm) for dosing into CCS makeup cooling water is set by the values of total hardness (THcw, mM) and evaporation coefficient φ in CCS according to Fig. 4.

With an increase in the evaporation coefficient ϕ in CCS, the necessary dosage of HDEP to inhibit the formation of $CaCO_3$ calcium carbonate decreases (Fig. 4), therefore, for the rational use of the HDEP reagent, maintaining higher evaporation coefficients by reducing water use for blowing and feeding the CCS is reasonable. Variable dosing of HEDP determines technological modes of operation of CCS, given the concentration processes, in terms of the actual evaporation coefficient φ, and the quality indicators of the water chemical mode of CCS cooling water in terms of the determined total hardness that forms the main component of the scale, i.e. calcium ions. According to the criterion of dosage variability HDEP for CCS cooling water treatment Rivne NPP established that with the overall stiffness of cooling water less than 3.5 mM dosage HDEP is not carried out (Fig. 4).

Table 2. **Average Annual HEDP Content in CCS Makeup Cooling Water and Styr River after Discharge from Rivne NPP**

Year	Statistical parameter	Concentration of HEDP, ppm	
		Makeup cooling water	Water of the Styr River after discharge
Constant HEDP dosage			
2016	M ± SE	0.41 ± 0.07	0.36 ± 0.04
	min–max	0.38–0.50	0.22–0.38
	Cv	17.5	11.1
2017	M ± SE	0.42 ± 0.08	0.37 ± 0.07
	min–max	0.37–0.50	0.26–0.46
	Cv	19.6	18.9
2018	M ± SE	0.40 ± 0.07	0.35 ± 0.08
	min–max	0.18–0.50	0.15–0.46
	Cv	18.2	21.9
Dosage of HEDP according to the criterion of variability			
2019	M ± SE	0.19 ± 0.07	0.07 ± 0.01
	min–max	0.12–0.35	0.05–0.09
	Cv	36.8	14.2
2020	M ± SE	0.22 ± 0.09	0.12 ± 0.02
	min–max	0.20–0.46	0.08–0.18
	Cv	40.9	16.6
2021	M ± SE	0.23 ± 0.11	0.13 ± 0.02
	min–max	0.11–0.35	0.08–0.16
	Cv	47.82	15.3
2022	M ± SE	0.175 ± 0.07	0.10 ± 0.02
	min–max	0.07–0.25	0.07–0.14
	Cv	40.0	20.0

Note: * M is arithmetic mean of the results; ±SE is standard error of deviation; min, max are minimum and maximum values in the sample; Cv is the coefficient of variation.

The average amount of HDEP used at constant dosing (2016–2018) is 17.5 t. With variable dosing, the average amount of HDEP is 13.05 t. Figure 5 shows a significant variation in HDEP dosing ranging from 5.05 t/year to 16.6 t/year. The coefficients of variation (Cv) for the HDEP concentration values in the CCS additional cooling water during the periods of variable dosing are significantly higher than the reduced values for steady-state dosing (Table 2).

The concentration of HDEP in the CCS makeup cooling water, according to the dosage variability model, can periodically be both smaller and larger than the fixed constant values (Table 2) and is determined by the value of the total hardness of the cooling water (Figs. 3, 4). Because of this, sometimes both increases and decreases in HDEP costs for CCS regenerative anti-scaling cooling water treatment can be observed. However, during the period of application of HEDP variable dosing at the Rivne NPP (2019–2022), a decrease in the average annual HEDP costs for CCS stabilization treatment (Fig. 5) is observed by an average of 4.5 t/year, which corresponds to a decrease of 30% from the average of the amount of spent HEDP, determined at constant dosage (2016–2018). Reducing the amount of HEDP dosed into the CCS leads to a decrease in the operating costs, which increases the efficiency of

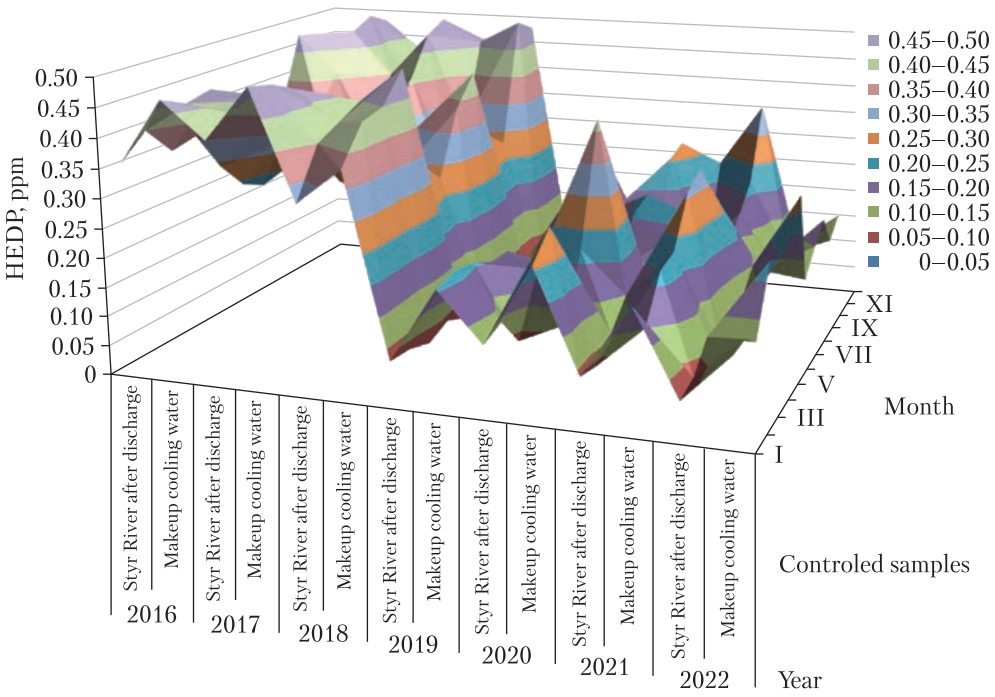


Fig. 6. Concentration of HDEP in the CCS makeup and cooling water at Rivne NPP and the water of the Styr River after discharge of the return water at the CCS Rivne NPP

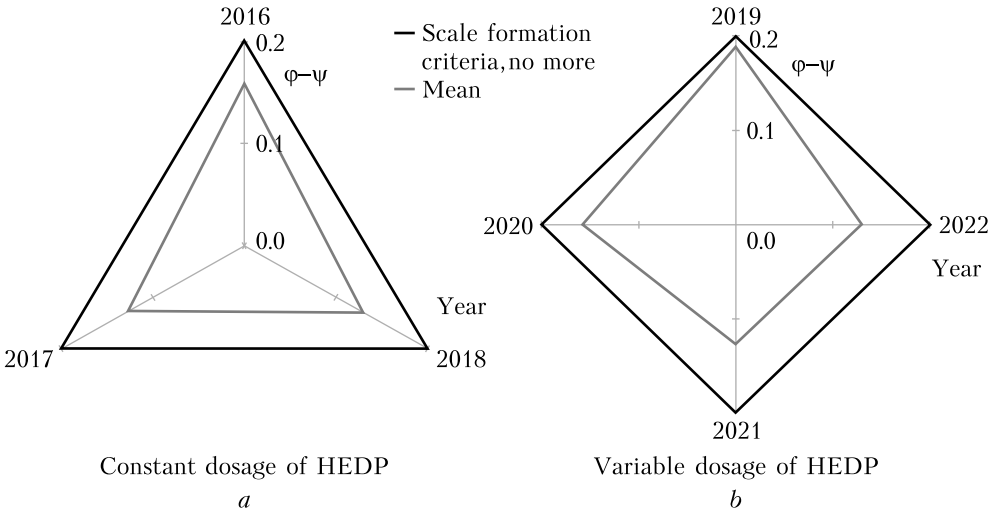


Fig. 7. Average annual levels of scale control intensity criterion (ϕ–ψ) in CCS Rivne NPP: *a* — for a period of constant dosage HEDP (2016—2018); *b* — for the period of variable dosage HEDP (2019—2022)

NPP operation. It also eliminates the possibility of inappropriate over dosing of reagents, minimizing the environmental impact of return water.

A reduction in HEDP dosing costs for cleaning water from the CCS scale during the period of variable HEDP dosing led to a decrease

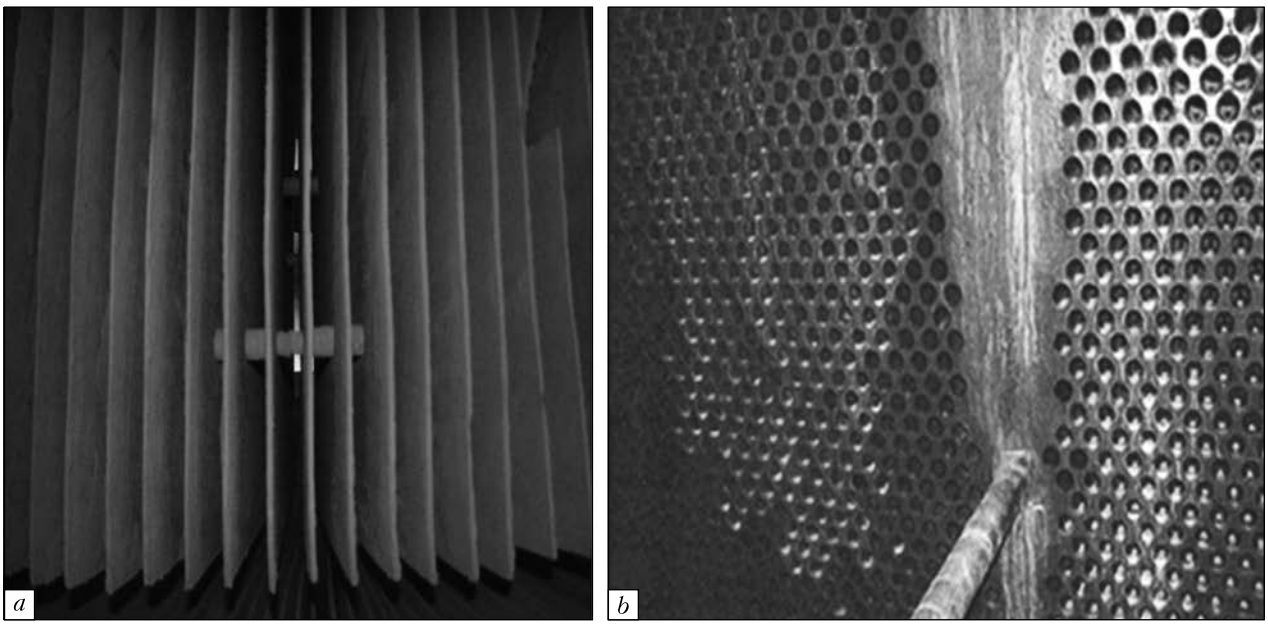


Fig. 8. Visual condition of the equipment of CCS Rivne NPP: *a* — irrigators of cooling towers; *b* — internal surfaces of turbine capacitor (2022)

in the concentration of HEDP in the makeup cooling water at CCS Rivne NPP (Fig. 6). During the period of stable dosing of HEDP (2016—2018) the average concentration HEDP in CCS makeup cooling water Rivne NPP (M ± SE) is 0.410 ± 0.07 ppm in the concentration range min-max 0.37—0.50 ppm, and for a period of variable dosage (2019—2022), it further decreases to M ± SE 0.204 ± 0.085 ppm in the concentration range min–max 0.12—0.46 ppm. During the period of variable dosage, there have been noted the periods (2019—2022) of no dosing, according to the criterion of variability (THcw ⩽ 3.5 mM) dosage of HEDP to CCS cooling water.

The average levels of the difference ϕ and ψ in CCS cooling water at Rivne NPP, which characterize the scale formation intensity (equation 1), for the period 2016—2022, do not exceed the standard value of 0.2 and characterize the cooling water as not prone to scale formation (Fig. 7). The levels of the difference ϕ and ψ for periods of constant and variable HEDP dosing are comparable, and HEDP dose reduction and partial periods of no HEDP dosing (at THcw ⩽ 3.5 mM) into CCS Rivne NPP cooling water did not lead to intensification of scale formation processes.

The results of low scaling intensity in CCS Rivne NPP, obtained by control results values of scale formation criterion levels of the difference ϕ and ψ are confirmed by the actual satisfactory condition of the irrigators of cooling towers (Fig. 8, *a*) and internal surfaces of the condensers (Fig. 8, *b*), and compliance with the normative levels of the temperature pressure consumers of CCS Rivne NPP.

The concentration of HEDP in the surface water of the Styr River, after the discharge of CCS Rivne NPP return water, according to the environmental regulations in force in Ukraine, should not exceed the maximum permissible concentration of HDEP (0.9 ppm) [15]. The dynamics of changes in the concentration of HDEP in the water of the Styr River after the Rivne NPP water intake during the period of research indicate that the established standard is not exceeded (Fig. 9). During the period of stable dosing of HEDP (2016—

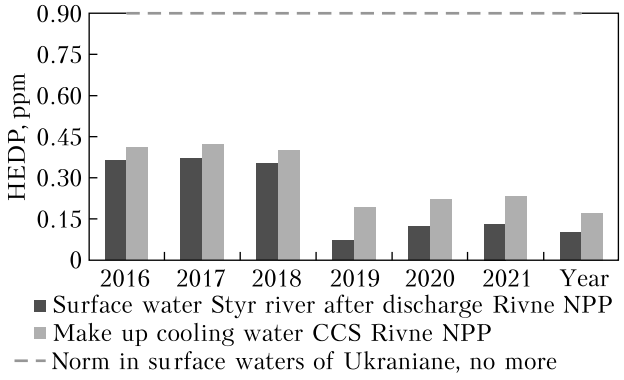


Fig. 9. Average annual HDEP concentrations in the CCS makeup cooling water at Rivne NPP and water of the Styr River after discharge of return water at CCS Rivne NPP

2018), the average concentration of HEDP in the surface water of the Styr River after discharge of the return water from the CCS Rivne NPP is M ± SE 0.36 ± 0.06 ppm in the concentration range min-max 0.15—0.46 ppm. For the period of variable dosing (2019—2022), it further decreases to M ± SE 0.105 ± 0.05 ppm in the concentration range min-max 0.05—0.18 ppm (Table 2, Fig. 9). The coefficients of variation (Cv) for the HDEP concentration in the CCS makeup cooling water during the variable dosing and steady-state dosing periods are within a comparable range (Table 2). Optimizing the use of chemicals in power plants with effluent discharge to water bodies can minimize the discharge of pollutants and prevent negative environmental impacts, as shown by the example of HDEP.

CONCLUSIONS

The regime of the anti-scale corrective treatment of CCS cooling water with organic phosphonates, in particular HEDP, allows an effective reduction in the processes of scale formation in the cooling systems of power plants. Optimizing the use of reagents for anti-scale corrective treatment of CCS cooling water allows minimizing the amount of reagent used for treatment, as well as the discharge of pollutants into water bodies during the operation of cooling systems. The criterion for the optimization of reagents for the anti-scale corrective treatment of CCS cooling water is compliance with the conditions for ensuring the water-chemical mode based on the scale formation intensity criteria.

The use of HEDP for the anti-scale water treatment of CCS Rivne NPP cooling water has been optimized by the variability that is determined by the polynomial equation of the dependence of the HEDP dose in the makeup cooling water on the content of the total hardness. The implemented HEDP reagent variable dosing model for CCS Rivne NPP cooling water treatment is determined by the actual values of the total hardness of the cooling water and the CCS evaporation coefficient ϕ, and the HEDP dosing variability criterion is established, in which no dosing is performed. For CCS Rivne NPP, during the period of variable HEDP dosing, as compared with fixed concentration HEDP dosing, there have been reported a reduction in the amount of HEDP used for CCS treatment while maintaining the effectiveness of the anti-scale treatment, a reduction in HEDP concentrations in the additional cooling water, and a minimization of HEDP discharges into the water body with inverse by CCS Rivne NPP waters. The implemented HEDP reagent variable dosing model for CCS Rivne NPP cooling water treatment is determined by the actual values of the total hardness of the CCS cooling water and the evaporation coefficient φ, and the HEDP dosing variability criterion is established, in which no dosing is performed.

The variability of HEDP dosing can have periodic dose variations, as compared with dosing at a constant concentration. In the CCS Rivne NPP, during the period of variable dosing, there have been reported a decrease in HEDP consumption for CCS treatment, an average of 4.5 t/year (30% of the total), a decrease in the concentration of HEDP in the additional cooling water, and a minimization of the flow of HEDP to the river water body. The use of variable dosage of HEDP did not affect the intensification of scale formati-

on processes at CCS Rivne NPP. Therefore, the use of a variable dosage of HEDP for the anti-scale water corrective treatment of cooling water is expedient from a technological, economic and ecological point of view. The research results can be applied to other CCS at power plants when implementing anti-scale treatment with organic phosphonates.

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Received 16.05.2023
Revised 17.09.2023
Accepted 18.09.2023

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ОПТИМІЗАЦІЯ АНТИНАКИПНОЇ КОРЕКЦІЙНОЇ ОБРОБКИ ОРГАНІЧНИМ ФОСФОНАТОМ

Вступ. Антинакипна корекційна обробка (АКО) є важливою складовою процесу експлуатації електростанцій, особливо у оборотних систем охолодження (ОСО). Обробка охолоджуючої води оксиетиледендифосфоновою кистотою (ОЕДФ) широко розповсюджена для АКО ОСО електростанцій, однак, для досягнення максимальної ефективності обробки, необхідно оптимізувати її використання.

Проблематика. Ефективність використання реагентів для АКО визначається їхньою дозою, часом контакту, температурою та pH. Дозування ОЕДФ визначається на етапі проєктування електростанції та часто реалізується в дозуванні сталих концентрацій, не враховує подальші зміни технології і показників якості охолоджуючої води при експлуатації.

Мета. Оптимізація використання та мінімізація скиду ОЕДФ у водні об'єкти при здійсненні АКО ОСО.

Матеріали й методи. Об'єктом дослідження є ОСО Рівненської атомної електричної станції (РАЕС), застосовано методи стандартні методи хімічного контролю та статистичні методи.

Результати. Здійснено аналіз даних багаторічного контролю й забезпечення водно-хімічного режиму та скидів ОСО РАЕС. Як критерій варіабельності дозування ОЕДФ прийнято вміст в охолоджуючій воді загальної жорсткості. За період варіабельного дозування спостерігається зниження 30 % від загальної кількості витрат ОЕДФ для обробки ОСО, зниження концентрації ОЕДФ у додатковій воді (з 0,410 до 0,204 ppm) та мінімізація потрапляння ОЕДФ до р. Стир зі зворотними водами (з 0,36 до 0,105 ppm) після скиду зворотної води РАЕС.

Висновки. Для мінімізації використання та відповідного скиду у водні об'єкти, для АКО ОСО РАЕС впроваджено модель варіабельного дозування ОЕДФ. За період варіабельного дозування ОЕДФ, порівняно з дозуванням ОЕДФ у сталій концентрації, спостерігається зниження кількості використання ОЕДФ, із дотриманням її ефективності, зменшення концентрацій ОЕДФ у додатковій та зворотній охолоджуючій воді ОСО та мінімізація скидів ОЕДФ.

Ключові слова: оборотна система охолодження, оксиетиледендифосфонова кистота, оптимізація дозування, скид зворотних вод.