Study of the influence of cooling water quality and inhibitors on the corrosion rate of brass in cooling water

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Abstract. At present, our country does not have an effective programme for the organization of water-chemical regimes of circulating refrigeration systems, solving three problems at the same time: the prevention of sedimentation, Reduction of corrosion rates of copper-based construction materials and avoidance of biological growth within the system and on heating surfaces. In addition, the influence of cooling water quality on the corrosion of copper-containing alloys in high-inertial water-cooling systems of turbine condensers has also been largely unknown. The use of film-forming amines (in particular, chelamine and octadesilamine) is a promising method to address this problem, but information on this issue is scarce. Therefore, it is essential to optimize the water-chemical modes of recycling cooling systems of turbine condensers in order to reduce the corrosion rate of brass. Thus, the aim of the work is to study the influence of the quality of cooling water and corrective reagents on the corrosion rate of brass in order to optimize the water-chemical modes of cooling systems of turbine condensers.

1. Introduction

The main industries using refrigeration systems are energy, metallurgy, chemistry and petrochemicals, food processing. Cooling systems account for most of the natural water used by modern industry (including energy). For example, for condensation of 1 kg of steam it is necessary from 60 to 100 kg of cooling water, and water consumption of a thermal power plant (TPP) of 800 MW is 100 thousand $\frac{m^3}{hour}$ [1-3]. It should be noted that a water supply scheme can be adopted both with the water turnover common to the whole industrial enterprise and in the form of closed cycles for individual production, workshops or installations [4, 5]. In the power industry, it is customary to adopt a general cooling system regardless of the number of working units.

Low-potential heating water [4, 5] should be considered in the design of recycling water cooling systems, but this is generally not achieved in the energy sector. The selection of the composition and size of water treatment, treatment and cooling facilities and equipment should be based on the maximum load conditions of these facilities. This rule leads to partial equipment downtime, resulting in additional requirements for the preservation and maintenance of water-chemical cooling systems (wcc).

2. Methods

The main serious problem in the operation of revolving cooling systems with cooling towers is the formation of deposits of mineral impurities, both in cooling towers and on the surface of tube condensers of turbines [6-8]. In addition, the sediments increase the hydraulic resistance of the tract, which increases the power consumption during operation of the system. To prevent the formation of mineral deposits in turbine capacitors:

    - blowing the system;
    - physical treatment of water in a magnet or acoustic field;
    - stabilizing water treatment with chemical reagents.

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The quantity of purge water from the cooling system to maintain its quality is limited by economic and environmental aspects, namely, the cost and volume of consumption of the source and discharge water, the cost of electricity for its transmission, the productivity of pumping stations, debit from water sources.

Magnetic water treatment is carried out in apparatuses in which the cooling water flow enters the magnetic field with a stress of up to $10^5 \frac{A}{m}$, generated by electromagnetic coil or permanent magnets [9, 10]. It has been determined that ferromagnetic impurities (Fe_3O_4, γFe_2O_3) are kept in a magnetic field flow and partially relieve carbonate water transfer, contributing to the formation of seed crystals and the conversion of dissolved unstable compounds into sludge.

The method of physical treatment of water in the magnetic field did not show stable results, so its application is limited by the reliability factor. The main method to avoid the formation of deposits is reagent treatment. In our country, the following types of reagent treatment are mainly practiced:

- acidification of circulation water;
- Recarbonization of water by outgoing gases;
- water phosphating.

Water acidification is carried out with a sulphuric acid solution to reduce the carbonate index below the saturation value. Acidification has been effective in controlling calcium deposits, but this has a number of disadvantages:

– reduction of pH value and, as a result, a sharp increase in corrosion rate of structural materials of cooling system;
- increase the corrosion-active impurity - sulphate - in circulating water;
- problems with the disposal of acid wastewater with high sulphate content;
- increased saline content.

The recarbonization of water by flue gas also reduces water leaching to calcium carbonate to the required level. Combustion products contain CO_2 and SO_2, nitrogen and oxygen. As a result of dissolution in water, the following reactions occur:

$$HCO_3^- + SO_2 \rightarrow HSO_3^- + CO_2 \quad \text{и} \quad 2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+.$$
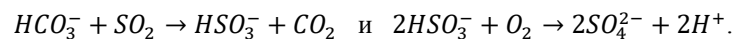
In recarbonization, the amount of sulphate in water is increased by an amount equivalent to a reduction in carbonate hardness. However, the recarbonization process is quite complex: it is necessary to continuously feed combustion products into circulation water, their ash cleaning in multicyclones and continuous dissolution. See Fig. 1 for recarbonization of water with flue gases.
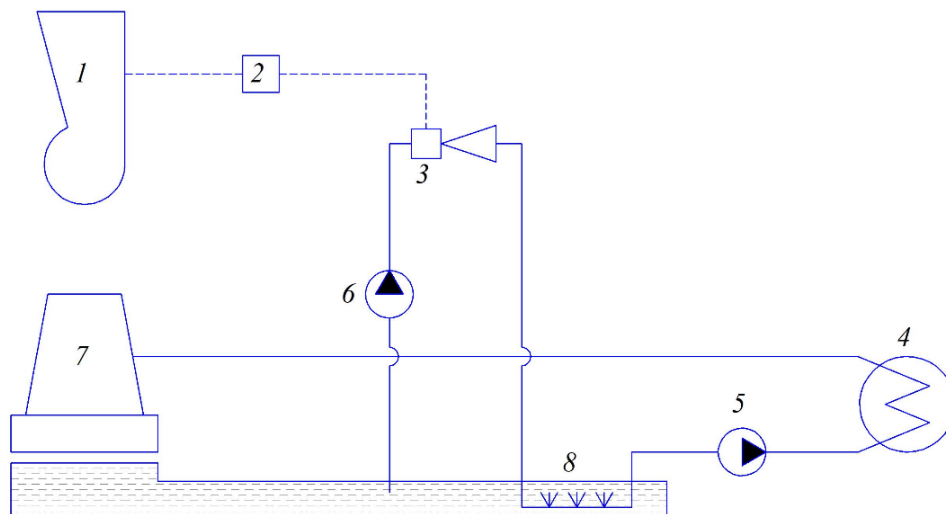

Fig. 1. Flue gas recarbonization scheme: 1 - smoke, 2 - ash catcher, 3 - water jet ejector, 4 - capacitor, 5 - circulating pump, 6 - water pump to ejector, 7 - cooling tower, 8 - bubble device.

This method has disadvantages similar to acidification of water. Circulation water phosphate to reduce solid phase formation $CaCO_3$, reduction of further growth of crystals and the degree of permissible excess solution. There are many different phosphate-based sediment inhibitors, in particular oxyethyland phosphonic acid $C_2H_8O_7P_2$, sodium hexamethophosphate (calgon) $(NaPO_3)_6$, mineral salt scale inhibitor (MSSI) and polyaminomethylenphosphonates (PAF-13A) [10].

When using sodium hexamethophosphate $(NaPO_3)_6$ with the concentration$1-2\ \frac{\text{мг}}{\text{дм}^3}$ in recalculation on PO_4^{3-} stable zero-pressure operation is observed up to carbonate hardness (C_h) values $C_h = 5,0 - 5,5\ \frac{mg-eq}{dm^3}$; when using oxylethyldiphosphonic acid $C_h = 7,5\ \frac{mg-eq}{dm^3}$. Dosing of these reagents should be carried out continuously.

Unfortunately, when dosing most of the listed reagents, water acidifies, resulting in an increased corrosion rate of brass tubes. In addition, phosphate inhibition has a clear threshold effect and does not reduce the corrosion rate of brass.

The recycled water of cooling systems is quite often used as the starting water of the main circuit recharging units and heat networks, which mainly use ion exchange filters. However, the influence of reagents such as oxyethyland phosphonic acid on the operation of ion exchange filters has not been investigated. Therefore, one of the tasks of this work was to study the influence of oxyethyland phonic acid on the operation of cationic filters.

In most thermal power plants, condenser tubes are made of copper alloys, particularly brass, but there is little evidence of the influence of cooling water quality on brass corrosion. From the analysis of data on water quality in various cooling systems of TPP [9, 11], it follows that the composition of water differs significantly and can strongly affect the corrosion processes in the cooling system.

Therefore, studies were carried out to study the corrosion rate of brass on the waters, the quality of which is typical for the reversible cooling systems in the TPP JSC system, as well as on the water, the quality of which is characteristic for the additive water of this power system. Table 1 shows the water composition used for the experiments. From these data it appears that the water used in the tests differs significantly primarily in terms of chloride and sulphate content, i.e., corrosion-active impurities.

Table 1. Water chemistry of the experiments

Indicator name	pH	Chlorides, $\frac{mg}{liter}$	Sulphates, $\frac{mg}{liter}$	Common iron, $\frac{mg}{liter}$	Solid residue, $\frac{mg}{liter}$	Copper Cu^{2+}, $\frac{mg}{liter}$	C, $\frac{mg-eq}{dm^3}$	A, $\frac{mg-eq}{dm^3}$
Water 1	8,41	29,7	26,4	0,26	321	0,030	-	-
Water 2	8,32	98,1	50,0	0,60	471	0,023	-	-
Water 3	8,45	71,8	44,4	1,00	-	0,070	5,68	4,0
Water 4	7,71	20,0	27,7	0,06	193	0,002	3,63	2,6
Water 5	8,89	54,2	46,9	-	323	-	5,60	3,9

The tests were carried out under laboratory conditions at water temperature of 22-25 °C. L-68 brass tubes were used as samples. Before the experiments, the surface of the samples was mechanically treated, washed with water, degreased with alcohol, again washed with water and dried. After preparation, the samples were weighed and placed in water. Three samples were used in each of the waters.

After the exposure time, the samples were removed from the solution and weighed. For; weighing- laboratory electronic scales of brand Adventure OHAUS were used. The weighing accuracy was 0.00005 g [12] The corrosion rate was determined by the mass difference of the samples, before and after the experiment, and by etching. The corrosion rate of these methods did not exceed 9%.

The corrosion rate of the samples was calculated by the formula:

$$\vartheta_{cor} = \frac{m_2 - m_1}{\tau \cdot F} = \frac{m_2 - m_1}{\tau \cdot \pi \cdot d \cdot l}, \tag{1}$$

where: ϑ_{cor} – corrosion rate, m_2 – sample mass after experience, m_1 – sample mass before experience, τ – duration of the experiment, F – sample surface, d – sample diameter, l – length of tube.

In accordance with the error measurement theory [13-21], both the instrument error and the random error of the measurements must be taken into account for the calculation of the total corrosion rate error. In order to calculate the instrument error, it is necessary to calculate the error of the indirect measurements. According to the error theory, the instrument (ins) error of the corrosion rate determination for each of the samples can be calculated using the following equation:

$$\Delta\vartheta_{cor}^{ins} = \sqrt{\left(\frac{\partial\vartheta_{cor}}{\partial m_2}\cdot\Delta m_2\right)^2 + \left(\frac{\partial\vartheta_{cor}}{\partial m_1}\cdot\Delta m_1\right)^2 + \left(\frac{\partial\vartheta_{cor}}{\partial m_T}\cdot\Delta T\right)^2 + \left(\frac{\partial\vartheta_{cor}}{\partial d}\cdot\Delta d\right)^2 + \left(\frac{\partial\vartheta_{cor}}{\partial l}\cdot\Delta l\right)^2}, \tag{2}$$

which, after differentiation, looks like:

$$\Delta\vartheta_{cor}^{ins} = \sqrt{\left(\frac{\Delta m_2}{\tau\cdot\pi\cdot d\cdot l}\right)^2 + \left(\frac{\Delta m_1}{\tau\cdot\pi\cdot d\cdot l}\right)^2 + \left(\frac{(m_2-m_1)\cdot\Delta\tau}{\tau^2\cdot\pi\cdot d\cdot l}\right)^2 + \left(\frac{(m_2-m_1)\cdot\Delta d}{\tau\cdot\pi\cdot d^2\cdot l}\right)^2 + \left(\frac{(m_2-m_1)\cdot\Delta l}{\tau\cdot\pi\cdot d\cdot l^2}\right)^2}, \tag{3}$$

To determine the random error of equation 4, the mean (m) corrosion rate was calculated, which in this case would be the same:

$$\Delta\vartheta_{cor}^m = \frac{\vartheta_1 + \vartheta_2 + \vartheta_3}{3}, \tag{4}$$

where ϑ_1, ϑ_2, ϑ_3 – corrosion rates of the first, second and third samples. The calculation of the mean square three measurements was performed according to the equation:

$$S = \frac{(\vartheta_1 - \vartheta_{cor}^m)^2 + (\vartheta_2 - \vartheta_{cor}^m)^2 + (\vartheta_3 - \vartheta_{cor}^m)^2}{2}. \tag{5}$$

After that, a random measurement (meas) error that is equal to:

$\Delta\vartheta_{cor}^m = t_{an} \cdot S$, где t_{an} – The Student coefficient, which for an accepted probability 95% is 3.2.

The full corrosion rate measurement error was calculated using the formula:

$$\Delta\vartheta_{\text{кор}}^{\text{полн}} = \sqrt{(\Delta\vartheta_{cor}^m)^2 + (\Delta\vartheta_{cor}^{ins})^2}, \tag{6}$$

and the relative measurement error was calculated using the formula:

$$\partial\vartheta_{cor}^{meas} = \frac{\Delta\vartheta_{cor}^{meas}}{\vartheta_{cor}}. \tag{7}$$

3. Results

The results of experiments on the influence of cooling water quality on the corrosion rate of brass are shown in Table 2 and Figure 2-5.

Table 2. Results of experiments on corrosion rate of brass L-68 on water of reversible cooling systems

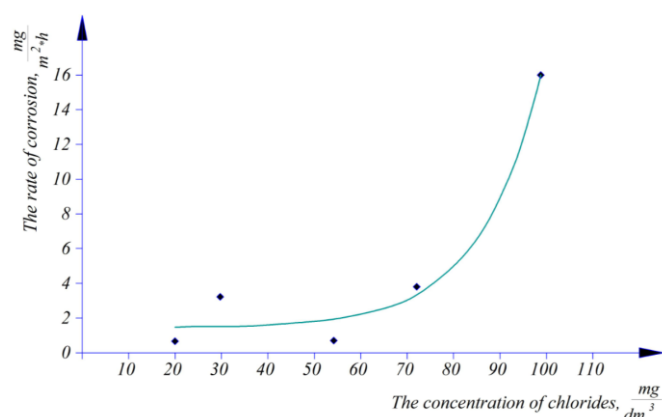| № test water	Test time, *hour*	Corrosion rate, $\frac{mg}{m^2 \cdot hour}$	Error Definition
water 1 ($C_{Cl}^- = 29,7 \frac{\text{мг}}{\text{дм}^3}$, $C_{SO_4}^{2-} = 26,4 \frac{\text{мг}}{\text{дм}^3}$, $pH = 8,4$)	790	3,40	8
		3,12	7
		3,21	7
Medium values		**3,24**	3
water 2 ($C_{Cl}^- = 98,1 \frac{\text{мг}}{\text{дм}^3}$, $C_{SO_4}^{2-} = 50,0 \frac{\text{мг}}{\text{дм}^3}$, $pH = 8,32$)	1121	16,18	1
		16,81	4
		15,54	5
Medium values		**16,18**	3
water 3 ($C_{Cl}^- = 71,8 \frac{\text{мг}}{\text{дм}^3}$, $C_{SO_4}^{2-} = 44,4 \frac{\text{мг}}{\text{дм}^3}$, $pH = 8,45$)	584	3,28	11
		4,35	9
		3,83	3
Medium values		**3,82**	4
water 4 ($C_{Cl}^- = 20,0 \frac{\text{мг}}{\text{дм}^3}$, $C_{SO_4}^{2-} = 27,7 \frac{\text{мг}}{\text{дм}^3}$, $pH = 7,7$)	525	0,67	8
		0,74	15
		0,60	13
Medium values		**0,67**	11
water 5 ($C_{Cl}^- = 54,2 \frac{\text{мг}}{\text{дм}^3}$, $C_{SO_4}^{2-} = 46,9 \frac{\text{мг}}{\text{дм}^3}$, $pH = 8,89$)	1460	0,74	7
		0,92	14
		0,54	14
Medium values		**0,73**	9

Fig. 2. Change in corrosion rate of brass L-68 depending on chloride content in cooling water ($pH = 7,7 - 8,9$)

The experimental data (Tab. 2., Fig. 2.) show that the chloride content in cooling water significantly affects the average corrosion rate of brass L-68. For example, at almost the same sulphate concentration in water (44,4 и 46,9

$\frac{mg}{dm^3}$) and roughly the same meaning pH(8,45 и 8,89) cCorrosion rate of brass in water at chloride concentrations 54,2 and 71,8 $\frac{mg}{dm^3}$ is equal 0,73 and 3,82 $\frac{mg}{m^2 \cdot hour}$ respectively. As a result of processing of experimental data in the program Mathcad 13, the equation of corrosion rate dependence on chloride concentration in cooling water was obtained:

$$\vartheta_{cor} = 7,64 \cdot 10^{-3} \cdot e^{0,077 \cdot C_{Cl^-}} + 1,47 \left(\frac{mg}{m^2 \cdot hour}\right).$$

It should be noted that the average quadratic deviation, when used for processing experimental data, was 4%.

Figure 3 shows the dependence of the mean corrosion rate of brass L-68 on the sulphate content of the cooling water. This figure shows that, as the sulphate content of cooling water increases, the corrosion rate of brass increases, but this dependence is less obvious than for the change in the corrosion rate of brass from the chloride content in cooling water. In this case, the change in the corrosion rate seems to be related not so much to the sulphate concentration but to the chloride content. Therefore, the corrosion rate of L-68 brass in the water may be more representative depending on the total content of chlorides and sulphates (fig. 4). This relationship shows that the corrosion-active anion content in cooling water is the determining factor influencing the corrosion rate of L-68 brass.
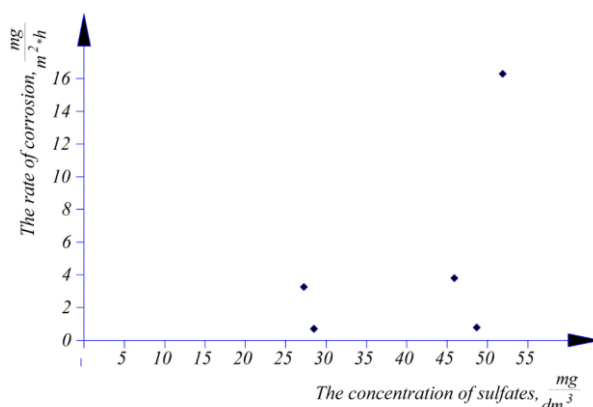

Fig. 3. Change in corrosion rate of brass L-68 depending on the sulphate content in cooling water
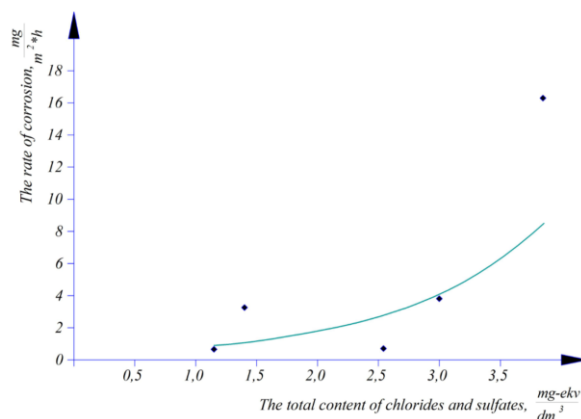

Fig. 4. Evolution of the corrosion rate of brass L-68 depending on the total chloride and sulphate content in cooling water.

As a result of processing of experimental data in the program Mathcad 13, the equation of corrosion rate dependence on the total concentration of chlorides and sulphates in cooling water was obtained:

$$\vartheta_{cor} = 9,496 \cdot 10^{-4} \cdot e^{2,535 \cdot \left(C_{Cl^-} + C_{SO_4^{2-}}\right)} + 0,155 \left(\frac{mg}{m^2 \cdot hour}\right).$$

This dependence is similar in form to the dependence of the corrosion rate of brass on the chloride content in cooling water, but the average square deviation for processing experimental data is 10.4%.

Figure 5 shows the dependence of the corrosion rate of brass in cooling water on dry residue. This relationship is similar to that of the variation in the corrosion rate of brass with the chloride content, but points are more dispersed.

Comparing the water quality and the results of the L-68 brass corrosion rate experiments, the following conclusions can be drawn:

- The most mineralized water 2, with the highest content of chlorides and sulphates, suspended substances and petroleum products, has the most corrosive activity.

- Water with the lowest impurity content and pH value (water 4), which is an additive water of one of the thermal power plants, has the least corrosion activity.

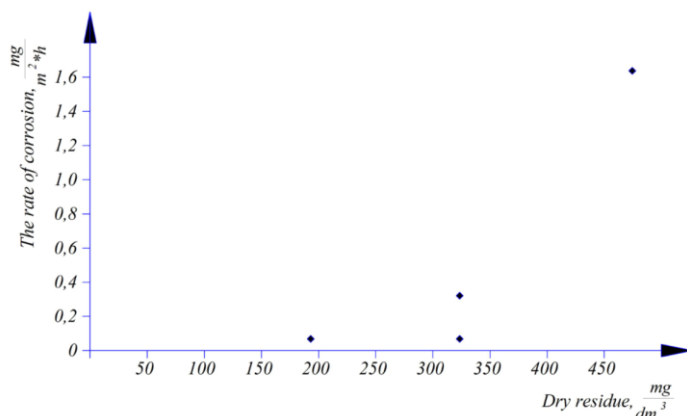- Sufficiently strong mineralized water 5 with the highest pH has low corrosion activity.

Fig. 5. Variation of corrosion rate of brass L-68 depending on dry residue of cooling water

4. Conclusions

Thus, cooling water was found to be more corrosive than additive water relative to brass L-68. The determining factor influencing the corrosion rate of brass L-68 is the concentration of chlorides and sulphates, that is, the content of corrosion-active anions: The obtained data are well consistent with the corrosion results of copper in water containing only chlorides or sulfates: effect of chlorides many times; exceeded the effect of sulfates.

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