THE IMPACT OF FLUCTUATIONS OF TEMPERATURE ON HYDROCHEMISTRY OF COOLING RESERVOIR

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ABSTRACT

In this paper, we examined the effect of temperature fluctuations on the hydrochemistry of the cooling reservoir of Ekibastuz Power Plant-1, located in the Pavlodar region of the Republic of Kazakhstan. Cooling steam turbines is carried out with water cooling reservoir, created on the basis of Zhankeldy salt lake. Therefore, the distinguishing feature of cooling reservoir is unusual thermal regime, which affects the hydrochemistry, hydrobiology, hydrology, morphometry of reservoirs, causing undesirable processes, such limescale, biological growth of aggregates, eutrophication etc. All these factors dictate the urgent need to assess the impact of hydraulic and power construction on water bodies and the development of measures to optimize the use and maintenance of favorable conditions for the functioning of ecosystems.

Keywords: hydrochemistry, cooling reservoir, hydrochemical regime

INTRODUCTION

Temperature of the water reservoir is one of the most important factors for the hydrochemistry of the reservoir and life processes in organisms [1]. An important stage in the study of reservoirs, especially reservoirs - coolers, is the period of its formation, when intensive process at the interface "water - bottom sediments" and active intake of all mobile compounds from soil, bedrock and soil into water, resulting their concentration in bottom layer. The speed of distribution of the compounds accumulated in the water layer depends on the water temperature, depth, and level of mixing of water masses. In absence of mixing can accumulate different materials of inorganic and organic origin, released from soil and flooded plants, in bottom layers. In this regard, there is often a decrease of pH and dissolved oxygen.

In the period of formation, intake of various substances occurs not only in the leaching of rocks and soils, silts, but also due to the processes of microbiological degradation of soils and plants. Therefore, at this stage it is difficult to determine which processes dominate in the formation of regime of reservoir. However, they all tend to ultimately lead to enrichment of water by nutrients. For this reason, the quality of water of reservoirs during it formation might be unsatisfactory by various indicators, which is especially important to be considered by water users. Moreover, intake of certain substances (in particular, manganese) from sediments can affect the development of algae. The appearance of manganese in water can also causes interference in water treatment. Higher concentration of metal ions and anions of weak and strong mineral acids and organic acids may lead to precipitation of salts in technical water systems of Power Plant, especially in systems of cooling of condenser turbines.

STUDY AREA

Cooling reservoir created on the basis of washed salt lake Zhankeldy in the Pavlodar region of Kazakhstan by filling with water Irtysh-Karaganda channel (now channel Satpayev). The area of cooling reservoir of Ekibastuz Power Plant-1at the normal water level (158.5 m) is 19.5 km^2 and an average depth is 4.6 m, with maximum near the 8.5 m. The total project capacity of the station equal to the 4 million kW energy. The circulating water consumption for cooling of turbine condensers of Ekibastuz Power Plant-1with 8 energy units, each with a capacity of 500 thousand kW, is 120 m^3/s. Refill water of cooling reservoir of Ekibastuz Power Plant-1with water from Irtysh-Karaganda channel, as a rule, carried out every month (except winter period) in the amount of 2.0-16.0 million m^3 [2]. The inflow of water in the broad gully Zhankeldy in cooling reservoir of Ekibastuz Power Plant-1 is 0-1.05 million m^3. The catchment area of the basin is almost 240 km^2. The chemical composition of the water Irtysh-Karaganda channel characterized by stability of ionic and mineral composition. Limits of variation of total mineralization constitute 134-295 mg/l, and its maximum attained in the winter and autumn seasons. The symbol of water by Alekin remain constant (C_{II}^{Ca}).

The climate of the study area is continental with long severe winters and short hot summers. The average annual temperature is +3.3 ^{0}C in winter with strong winds and low snow cover, which reaches 10-20 cm (maximum is 52 cm). According to the meteorological station of Pavlodar city the average annual air temperature in July is +21.2 ^{0}C; -47 ^{0}C is absolute minimum in January. Because of its geographical location, this area is characterized by a deficit of moisture: average annual precipitation is 231-249 mm.

Industrial water supply of Ekibastuz Power Plant-1 is carried out on the reverse pattern, with cooling of circulating heated water in the turbine condenser in the cooling reservoir. It was first performed at a shallow depth in nature combined scheme of surface discharge of heated water in the turbine condenser and chilled water intake bottom.

Length of abductor open channels defined by modeling of conditions to ensure the most cost-effective plant operation in large-scale models.

Warm water is distributed over the surface of the reservoir, which is cooled again and enters the intake, thus closing the cycle. The water supply for hydraulic ash produced by gravity spillway conduits of wastewater tract. On water treatment and boiler water channel feeding the heating system water is supplied from the Irtysh - Karaganda channel gravity conduits, as circulating water cannot be used for chemical water treatment due to its high salinity reaching 600-1000 mg/l.

MATERIALS AND METHODS

The investigation of cooling reservoir of Ekibastuz Power Plant-1 was carried out from its formation and in a steady hydrochemical regime (since 1978 to 2004) [2]. In the first years of existence of cooling reservoir the water samples are taken every ten days and in the future - seasonally. To study the hydrochemical regime of cooling reservoir water and sediment sampling was carried out at the intake structures at the site of discharge of warm water on the surface of the waters, and in the bottom layer, as well as feeding channels with sampling according to [3].

In addition, over the years conducted surveillance regime of unstable components of the chemical composition of water reservoirs with sampling every 2 hours for 1-2 days. Subsurface sampling produced by the Molchanov sampler, model GR-18, and by the device for sampling major monoliths of soil TM-0.025 or Petersen corer the sediments and soil samples are collected.

The determination of pH was done according [4]. Determination of calcium ions was carried out titrimetrically and was based on the formation of Ca^{2+}-ions with Murexide hardly dissociating crimson compound. During the titration calcium ions are bind by Trilon B in even less dissociating complex, and Murexide colors alkaline solution in violet. Method of the determination of magnesium ions based on the titration of magnesium ions by Trilon B in the presence of eryochrom black in the same solution, in which Ca^{2+}-ions were bound in the complex by Trilon B in the presence of Murexide, the color of which is to be destroyed with hydrochloric acid beforehand. During titration, the color of the solution changes from red through purple to blue [5].

Analysis of carbonate and hydrocarbonate ions was done by direct titration. During the titration of water, containing ion of CO_3^{2-}, hydrochloric acid with phenolphthalein indicator, CO_3^{2-} -ion is transferred to the ion HCO_3^-, and half of carbonate ions are titrated. During further titration by acid with methyl orange, complete decomposition of first formed during titration and contained in the water HCO_3^--ion occurs.

To identify the process of carbonate sedimentation from the water of the reservoir 2 sedimentometers (special vessels of 1 liter volume) were established in the areas of water intake and discharge at a depth of 5 m from the surface during the period from the 20th May to the 12th September, 2004. The precipitate formed on the walls and bottom of reservoir were analyzed by X-ray. The analysis carried out a DRON-05 diffractometer on the copper radiation with a nickel filter. Decoding of the X-ray results was performed by comparison with the reference.

During the study period organized 74 expeditions and analyzed about 2000 water, soil and sediment samples collected from cooling reservoir.

RESULTS AND DISCUSSIONS

In the first two years of the cooling reservoir of Ekibastuz Power Plant-1, the temperature condition is not very different from natural. After putting into operation all eight units the temperature conditions significantly changed (the last unit was put in 1984). In winter the ice cover on the reservoir is absent, there is only the ice edge near the eastern, southern and western coasts.

The "active zone", where the cooling of waste water occurs, is approximately 40% of the area. During the heat flow is its rapid cooling (-2.7^{0}C) per kilometer. Deadlock zones and whirlpools occupy the entire shallow part (about 60% of all land area). Total homothermia of the flow is observed at a distance of 1.5 - 2.0 km from the water intake gallery. In the waters of the reservoir under the influence of wind on the surface is more intense mixing of flow than in calm weather. According to the data of automatic stations of stream measurements, wind speeds over 10 m/sec mixes the surface layer up to 2 m depth. The increasing of the capacity of station up to 2.0 MW resulted to increasing in area of spreading of the heat flow, to decreasing in the area of deadlock zones and whirlpools [2].

The water temperature in the release area exceeds natural temperature on 6-10^{0}C (Table 1). On certain days at work of all TPP units discharge water temperature rises to 39.0-43.0^{0}C. A similar thermal regime persists in subsequent years (Table 2).

Table 1 - Dynamics of seasonal temperatures in thermal and not-heated zones of the reservoir of Ekibastuz Power Plant-1

Zones of reservoir	Seasons			
	Winter	Spring	Summer	Autumn
Thermal zone	9.1-19.2	16.3-26.7	21.0-33.6	11.5-30.2
Not-heated zone	2.0-9.9	5.8-19.9	18.2-25.8	4.5-23.4

Discharge of heated water in the reservoir has a significant impact on all processes occurring in it, including hydrochemical processes. Reaction rates would also change over time, which is reflected in the content of many of the components of the chemical composition.

Discharged water temperature in summer is 1.3÷2.0 times higher than the temperature of the water at the water intake, in spring - 1.7÷4.4, in autumn - 1.4÷32.0, and in winter - in 6.7÷125 times. Heating of the bottom layers of water and soil can reach up to 28^0 C in summer and in winter up to 14^0 C. Abrupt changes in water temperature have a negative impact on the elements of the ecosystem of the pond. So O.V. Rubtsova found that if water is heated to 30 ° C toxicity of heavy metals such as Cu, Zn, Cd for some species of macrobenthos increases 2÷4 times and becomes lethal to them [6]. Analysis of heavy metals in the water of reservoir indicates that in the heating zone the concentration of Pb is on average 16 times higher than in not-heated areas; 1.8 times - the concentration of Cu; 1.4 times - the concentration of B and Sr; 1.2 times - the concentration of Al and Ba; 1.1 times - the concentration of Mn, Zn, Cd. However, in certain seasons reverse pattern for Mn, Cu, Zn, Sr, Al and Ba was observed. This is due to the fact that during water flowing through the cooling system, sorption of these elements on the walls of the condenser tubes and formations of crystals or amorphous inorganic substances (autochthonous and allochthonous origin), contained in water, occurs.

Table 2 – Limit values of the water temperature of the reservoir – cooler of Ekibastuz Power Plant-1 in a multi-year cycle, ^{0}C

	Winter	Spring	Summer	Autumn	The average annual increase of t^0, in the number of times
1979	0.1-4.0	-	-	-	-
1980	-	1.0-4.0	17.5-25.0	1.0-12.0	4.7
1981	1.0-14.0	3.5-15.5	22.0-32.5	0.5-16.0	10.6
1982	0.2-17.0	12.0-21.5	19.0-33.5	3.0-16.0	19.1
1983	-	14.0-28.0	22.0-31.5	1.2-22.0	5.8
1984	2.0-19.2	5.8-26.7	18.2-33.6	4.5-30.2	5.7
1985	2.0-16.0	8.0-23.5	21.0-32.5	-	4.1
1986	0.5-18.0	10.0-26.0	21.0-35.5	-	13.4
1987	0.5-18.5	8.0-20.5	25.0-43.0	-	13.8
1988	3.0-20.0	-	-	-	-
1989	0.4-12.0	7.5-22.5	20.0-40.0	10.0-26.0	9.4
1990	0.2-25.0	12.5-24.5	25.1-35.0	8.5-22.5	32.7
1991	0.4-11.8	14.2-23.8	19.6-38.8	15.3-21.8	8.6
1992	0.4-11.6	13.5-21.6	20.2 -37.1	-	-
1993	1.7-15.9	11.8-22.2	24.2-36.2	16.0-25.2	3.6
2004	1.0-12.0	9.0-24.0	24.0-38.5	13.5-25.3	4.6
2007	0.9-13.2	-	23.6- 37.6	14.0- 22.3	-

Analysis of sediment on the content of heavy metals in the same period showed that in the heating zone the concentrations of Fe, Mn, Zn, Cd is on average 12 times higher than in not-heated areas; 3-5 times - the concentration of Cu and Pb. In addition, the analytical determination indicates the presence of a local discharge of warm waters, the increasing of the concentration of the toxic components of the technological cycle (acids, oils).

Plotting the relation of the content of oil on the water temperature is possible to distinguish two areas (Figure 1). The first area is in the temperature range from 15 ^{0}C to 26 ^{0}C, there is a sharp increase in oil content (area of existence of high concentration up to 2.6 mg/l) in it. Equation of correlation of the concentration of oil on the temperature for this area is: $y=0.3418e^{0.071X}$ (where: y is the concentration of oil, mg/l; x is temperature, ^{0}C). This exponential dependence has the correlation coefficient equal 0.70. The second area is in the temperature range from 25 ^{0}C to 43 ^{0}C, there is a very slow increase in the concentration of toxicants (area of existence of low concentrations less than 0.5 mg/l) in it. The equation of a linear relation of oil product concentration on the temperature for this area is: $y=0.003x + 0.3365$. Correlation is estimated as weak, as r is equal 0.15.

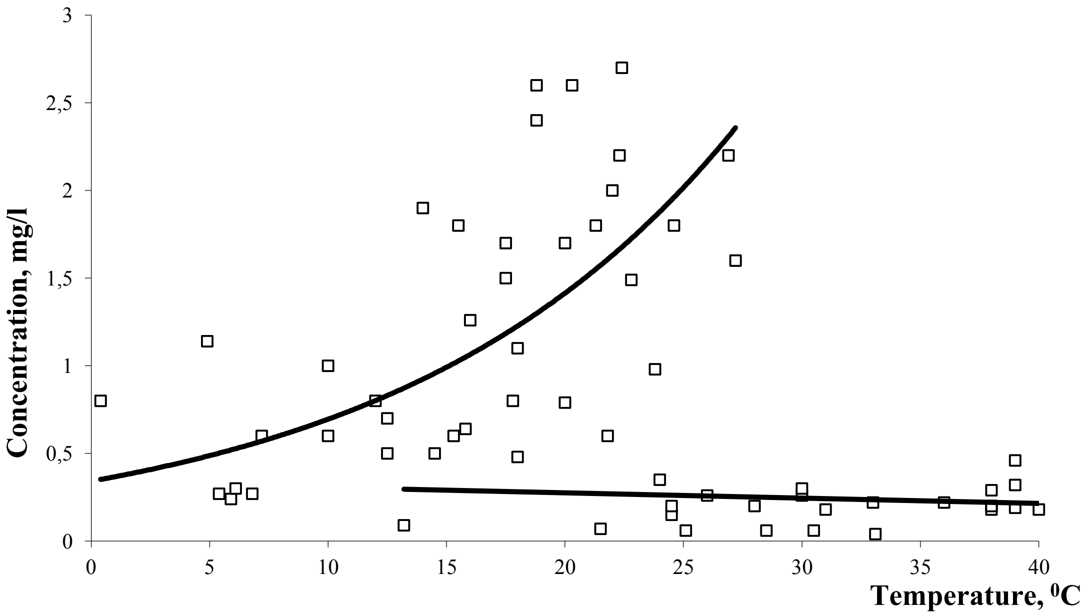

Figure 1 - The dependence of the oil content in the water on temperature of cooling reservoir Ekibastuz Power Plant-1

Sharp fluctuations of water temperature not only during a year, or a season, but even a day affect on the behavior of other components of the chemical composition, such as gases, nutrients and organic matter. Due to the decrease of the solubility of gases (O_2, CO_2) for heating of water at the thermal area of the reservoir would expect a significant worsening of the oxygen regime. However, the amount of dissolved O_2 at the discharge of warm water from Power Plant, e.g., in 1983, 1984, varies within 7.1÷12.0 mg/l, and at water intake area - 6.0÷11.2 mg/l. Increasing of the oxygen content (although slightly) indicates that the discharge of warm water circulation has a positive effect on the gas conditions. The same phenomenon was observed by the authors [7] in other reservoirs. This phenomenon is due to the release of O_2 at more intensive photosynthesis and aeration of the water masses under the influence of turbulent flow of water.

Investigation of the influence of temperature on the regime and dynamics of organic matter and nutrients, non-metals clearly revealed the following regularity. On heating areas content of NH_4^+, F, Br and I is always less than in not-heated areas (in 1.1÷2.0 times); NO_3^- concentration and permanganate oxidation is higher (in 1.1 - 18.9 times); almost constant concentration of NO_2^--ions, and the concentration of Fe, P, Si and B in different seasons of the year is or increased (in 1.1 - 1.6 times), or decreased (in 1.1 - 1.9 times). The elevated concentrations of nitrate ions and values of permanganate oxidation in heated water are explained by intensive processes of nitrification and decomposition of organic matter. The latter fact leads to the formation of NH_4^+-ions. Fluorides, bromides and iodides and boron compounds are likely to precipitate or transformed in the cooling system.

Investigating water on the water intake areas and waste water on the content of major ions, pH, the amount of supersaturation of water by calcium carbonate (S/St), the following trend is clearly visible. Waste water is depleted by Ca^{2+}-ions (18 out of 22 cases) for 0.1÷1.00, HCO_3^- (in 11 cases) for 0.1-0.9 mmol/l eq. Increasing of temperature of water and its flow in the cooling system of turbine promotes the dissociation of hydrocarbon-ions, formation and increasing of the concentration of carbonate-ions (in 18 cases) for $1.5 \div 31.4 \cdot 10^{-6}$ mol/l. Favorable conditions for the saturation and supersaturation of water by calcium carbonate are created. The value of S/St in the heating water in the majority cases (19 out of 22) is higher than in the water of the water intake for 0.13 - 4.15 units. Changes occurring in water content can be presented in the indexes for O.A. Alekin as follows:

a) water intake: $Cl_{III}^{Na} \rightarrow Cl, S_{III}^{Na,Ca} \rightarrow S_{II}^{Na} \rightarrow Cl_{II}^{Na} \rightarrow S_{II}^{Ca} \rightarrow Cl_{III}^{Na} \rightarrow Cl_{II}^{Na} \rightarrow C_{II}^{Mg} \rightarrow Cl_{III}^{Na,Ca} \rightarrow Cl_{III}^{Na}$

b) waste water: $Cl_{III}^{Ca} \rightarrow Cl, S_{III}^{Ca} \rightarrow S_{II}^{Ca} \rightarrow S_{III}^{Ca} \rightarrow S_{III}^{Ca} \rightarrow Cl_{II}^{Ca} \rightarrow Cl_{III}^{Ca} \rightarrow Cl_{II}^{Ca} \rightarrow Cl_{III}^{Ca} \rightarrow Cl_{III}^{Ca}$

Thus, the temperature fluctuation ultimately leads to a change in class, group or even type of water.

Decoding of bar diagrams for the three forms of $CaCO_3$ (calcite, aragonite, vaterite) and $Mg_3Ca(CO_3)_4$ (huntite), as well as for the studied sediments allowed us to conclude that from the water of reservoir of Ekibastuz Power Plant-1 chemogenic formation and sedimentation of calcium carbonate in the form of calcite occur. Moreover there was larger mass of salt on the water waste area (1.85 g) than on the water intake area (1.03 g). Crystal optical analysis of obtained precipitations has revealed the presence of crystals of chemogenic calcite in the form of rhombohedrons with a size of 0.004 cm, and detrital material (shells, chalk particles) containing calcium carbonate.

Heated waste water, having higher pH, CO_3^{2-}-ion concentration, supersaturation values, mix with water of reservoir and result to more intense hydrochemical processes leading to the formation of calcium carbonate. It should be noted that the thermal pollution itself is a potent factor, and in the reservoir - cooler of Ekibastuz Power Plant-1 it is superimposed by effects of level fluctuations.

CONCLUSION

The observed increasing of the temperature of the water of cooling reservoir of Ekibastuz Power Plant-1 is higher than environmental standards, is due to non-optimal operating conditions of energy engineering equipment and water bodies, which worsens the cooling capacity of the reservoir and ultimately causes economic damage.

To reduce the negative effects of the influence of Ekibastuz Power Plant-1 it is necessary to establish a system of control of wastewater discharges, ensure the reliability of operating modes of Ekibastuz Power Plant-1, the cooling reservoir and the realization of water protection activities.

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