Analysis of the step-by-step water purification of a combined water treatment plant at a heat and power complex

Vlasova A.YU.[1], Akhmetzyanova A.T.[2], Babikov O.E.[3]
Thermal and Nuclear Power Plants Department
Kazan State Power Engineering University
Kazan, Russian Federation
vlasovaay@mail.ru[1], 19aigul@gmail.com[2], olegsey1998@yandex.ru[3]

Abstract — For the functioning of heat and power complexes, demineralized water with certain standard indicators is needed, which are achieved due to the water treatment plants operation. The choice of water treatment method directly depends on the characteristics of the water source. It is possible to analyze the efficiency of water treatment according to the measured physical and chemical indicators at each stage of water treatment. The paper considers a combined water treatment plant, which includes membrane technologies and ion exchange. The article provides the analysis of the coolant indicators at each stage of the Kazan combined heat and power plant (CHPP-2) and Sterlitamak CHPP combined water treatment plants. Physical and chemical indicators were measured using titrimetric and spectrophotometric methods. According to the data obtained, the physicochemical indicators of water samples from certain water treatment stages exceeded the initial values by about three times. For the two considered power plants, recommendations are given to improve the water treatment units efficiency.

Keywords—Water treatment, membrane technologies, ion-exchange filters, reverse osmosis unit concentrate.

I. INTRODUCTION

Enterprises of the heat and power industry need a high quality heat carrier. The main requirements for water treatment are a decrease in the salts concentration in the purified water by tens of thousands of times. Such requirements are associated with the introduction of new installations, which require careful control of the coolant physicochemical parameters. Therefore, changes are being done to the water treatment system.

Currently, innovative technologies are used in the water treatment, which are aimed at increasing the production energy efficiency, reducing operating costs and harmful effects on the environment.

To date, most of the thermal power plants water treatment is carried out according to the "traditional" technology, with the use of clarification, filtration and ion exchange units. However, this technology has a number of disadvantages associated with the significant cost of reagents, the large size of the plant, the presence of highly mineralized alkaline and acid waste regeneration solutions, and the problems of their disposal [1], [2].

At existing and modernized water treatment plants at thermal power plants and other industrial enterprises of the Russian Federation, new problems arise related to the reduction in the consumption of source water and wastewater. Rising costs of fresh water use and wastewater discharges contribute to the water consumption reduction, reuse of wastewater, creation of low-waste, closed technologies, wastewater treatment technologies in most industrialized countries. Thermal power plants, which are characterized by minimal consumption of fresh water and wastewater discharge, are gaining increasing recognition in the world energy industry. In European countries, an operating license of the power plants is often issued on the condition that the water treatment scheme is completely drainless. And therefore, wastewater treatment is organized using a combination of membrane methods, ion exchanger and thermal desalination.

Since the second half of the 20th century, membrane technologies have been actively developed in water treatment, and today some enterprises use membrane or combined plants [3]. These technologies are resource-saving, since they are based on a physical separation process, without the use of chemical reagents, which means that the harmful impact on the environment is minimal. The most commonly used membrane processes are ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. Ultrafiltration and nanofiltration make it possible to remove coarse impurities, colloidal particles, and some organic impurities from water. At present, the field of membrane methods application in the energy sector is expanding. This is due to both their technological advantages and economic and environmental reasons. Existing membrane methods are constantly being improved, and the selectivity of ion-exchange membranes is increasing. The experience of their operation shows the best results in comparison with other methods for water treatment at thermal power plants.

Reverse osmosis is currently the most widely used of all membrane processes and it is used in 80-85% of all applications. The share of all other membrane processes accounts for only 15-20%, although their involvement is steadily growing.

Membrane methods have the following advantages:

1) the absence of phase transitions during the separation of impurities makes it possible to minimize the required energy consumption;

2) the impurities separation can be carried out at low water temperatures, which are determined by the membrane properties;

3) membrane processes are continuous (with the exception of membrane clogging cases);

4) membrane processes can be carried out without the chemical reagents dosing (if reagents are introduced, then in very small quantities);

5) devices for membrane processes are relatively simple and do not have moving parts. The amount of energy required for membrane processes usually exceeds 2-2.5 kWh/m^3 of filtrate [4].

The efficiency of membrane processes is determined by the membrane properties, which must match the following requirements: high selectivity, high specific permeability, resistance to the working medium action, invariability of characteristics during operation, sufficient mechanical strength, and low cost. The selectivity and specific permeability of the membrane depend on the materials and their structure, the concentration of impurities in the source water, temperature, pressure, hydrodynamic load.

Among membrane methods, ultrafiltration is rapidly developing and being introduced. Ultrafiltration technology is widely used in world practice to purify water from various surface water sources (rivers, reservoirs, lakes). Also, ultrafiltration technology is used in urban water supply system. The technology is constantly improving and becoming more competitive compared to traditional water treatment methods.

It cannot be argued that the use of membrane technologies completely excludes the use of chemical reagents. The flocculant dosing before ultrafiltration makes it possible to enlarge hard-to-remove small organic molecules (tannins, humic acids, fulvic acids), which give the water a yellowish tint. As part of complexes with flocculants, these compounds are successfully retained by the ultrafiltration membrane.

During the filtration process, the membrane pores become contaminated with deposits of concentrated impurities. Therefore, regular membrane washing with a reverse flow of purified water is required. Backwashing usually requires a pressure higher than the operating pressure.

Over the past decade, membrane technologies have been actively developed at thermal power plants in Russia for the treatment of make-up water for high-pressure and supercritical boilers, as well as make-up water for heating systems. The transition to membrane water treatment methods is also explained by the introduction of combined cycle gas turbine (CCGT) power plants. In Russia, the number of CCGT units put into operation is increasing every year. For the operation of a CCGT unit, a higher quality of water purification is required, and in order to achieve this, the water treatment scheme is changed. To achieve this goal, a mixed-bed filter with anion and cation exchange resins is used as an additional stage of water purification. This filter is able to reduce the residual salinity of demineralized water.

When using modern CCGT units, the problem of the organic substances presence arises in the water treatment cycle, which lead to biofouling, corrosion and, as a result, a decrease in the reliability and efficiency of the equipment operation.

In 2009, the JSC "All-Russia Thermal Engineering Institute" developed a standard [5], which gives the normalized values of the coolant quality indicators, taking into account the use of membrane methods of water purification and the use of polyamines in organizing the water-chemical regime at thermal power plants. Total Organic Carbon (TOC) was introduced into the standardized indicators of water quality [6].

The recognition that the presence of organic impurities in the coolant reduces the reliability of operation of heat and power equipment took place in 1985 at the International Water Conference, although even earlier this issue was actively discussed by the world community [7], [8]. At this time, the total organic carbon content of up to 8 mg / kg was allowed in the steam-water cycle of power plants [8]. We are aware of emergencies that led to serious damage to heat and power equipment caused by a high concentration of organic substances in the steam-water path [9], [10]. During thermolysis and hydrolysis in boilers, organic impurities are destroyed and turn into "potentially hazardous substances" [10]. These include not only potentially acidic, but also potentially alkaline and neutral agents, as well as substances that break down to carbon and create deposits on heating surfaces.

The content of organic substances in the source water is many times higher than the content of inorganic substances. They are very diverse in their composition and properties. At high temperatures, organic impurities can be modified and turn into substances potentially hazardous to the heating equipment. According to the nature of organic impurities that may be present in the studied water samples, according to chemical analysis, humic substances and some other organic molecules prevail. Humic substances have good solubility in water; their passage through ion-exchange filters and transfer with some vapor fractions occurs due to their thermal stability.

Water treatment plants optimization and combined technologies development are also associated with the tightening of requirements for feed water quality indicators. Water treatment at Kazan CHPP-2 and Sterlitamak CHPP includes a combined method using membrane technologies and ion-exchange filters. The main purpose of this article is to determine the treatment quality at each stage of water treatment. The degree of water purification was determined in the laboratory using titrimetric and spectrophotometric methods according to the physical and chemical water indicators.

II. MATERIALS AND METHODS

The water treatment system at Kazan CHPP-2 (Fig. 1) includes baromembrane technologies, followed by processing on ion exchange units. The source water enters automatic mesh filters with parallel reagents dosing, then the water enters the microfiltration unit. The clarified water is accumulated in clarified water tanks and fed to a reverse osmosis unit to obtain partially demineralized water. The clarified water in the reverse osmosis unit under pressure is divided into two streams: pure permeate and concentrate. After the reverse osmosis units, the partially demineralized water is passed through the calciners to the partially demineralized water tanks. Partially desalinated water is fed from the tanks to the ion exchange unit. Water demineralization by ion exchange method consists in successive filtration through H-cation exchange and then OH-anion exchange filters. In the H-cationite filter, the cations contained in the source water are exchanged for hydrogen, and an equivalent amount of acid is formed in the filtrate from the anions to which the absorbed cations were bound. On the OH-anion exchange filter, the acid anions formed during H-

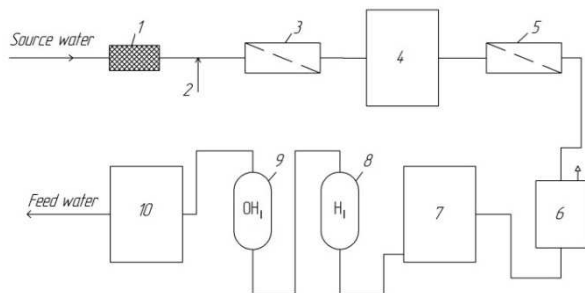cationization are retained by the anion exchanger, resulting in demineralized water.

Fig. 1. Kazan CHPP-2 water treatment scheme. 1 – mesh filters; 2 – reagents dosing; 3 – microfiltration unit; 4 – clarified water tank; 5 – reverse osmosis unit; 6 – calciner; 7 – partially demineralized water tank; 8 – H-cation exchange filter; 9 – OH-anion exchange filter; 10 – demineralized water tank.

In 2021, in the Republic of Bashkortostan, at the Sterlitamak CHPP, it was decided to reconstruct the water treatment plant by introducing membrane technologies and replacing the first stage ion exchange filters. Fig. 2 shows the water treatment scheme at the Sterlitamak CHPP before reconstruction.
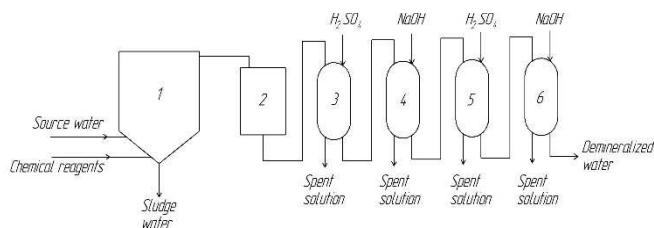

Fig. 2. Sterlitamak CHPP water treatment scheme before reconstruction. 1 – clarifier; 2 – mechanical filter; 3 – H-cation exchange filter of the first stage; 4 – OH-anion exchange filter of the first stage; 5 – H-cation exchange filter of the second stage; 6 – OH-anion exchange filter of the second stage.

The water enters the clarifier where chemicals such as milk of lime, coagulant and flocculant are dosed. Iron sulfate is used as a coagulant, and polyacrylamide is used as a flocculant. The clarified water enters the mechanical filter, where additional purification from the residual content of suspended particles takes place. The desalination unit consists of two stages of ion-exchange filters (H-cationite and OH-anionite), as a result of which demineralized water is obtained.

The need to introduce a combined water treatment plant is explained by a decrease in the load on the ion-exchange filters of the second stage, as well as a high consumption of chemical reagents and, as a result, the presence of a huge amount of wastewater with abnormal indicators. Spent regeneration solutions are quite rarely reused in the plant cycle and are subject to disposal by mutual neutralization to bring the pH value to a neutral value.

The modernized water treatment plant at Sterlitamak CHPP involves the replacement of cation and anion filters.

Modern membrane technologies are compact and automated, but expensive. A schematic diagram of the modernized water treatment plant is shown in Fig. 3. The pre-treatment stage includes a clarifier, followed by the passage of clarified water through a reverse osmosis unit and subsequent post-treatment on ion-exchange filters.
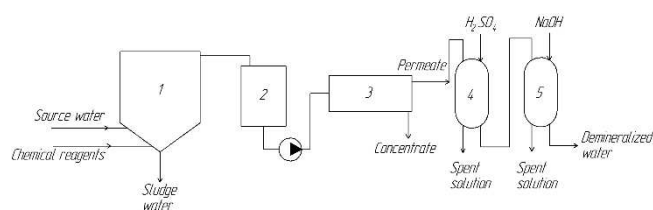

Fig. 3. Sterlitamak CHPP water treatment scheme after modernization. 1 – clarifier; 2 – mechanical filter; 3 – reverse osmosis unit; 4 – H-cation exchange filter; 5 – OH-anion exchange filter.

The use of the reverse osmosis method in the feed water treatment for steam boilers makes it possible to reduce the amount of consumed reagents (acids, alkalis, common salt) by 90% and at the same time get rid of wastewater containing these reagents [11]. Modern reverse osmosis membranes, in addition to salt ions, also retain organic molecules, silicates, which makes reverse osmosis extremely efficient and promising in the energy sector.

The selected water samples were analyzed for the following indicators: pH, electrical conductivity, total salt content, iron content Fe^{3+}, permanganate oxidizability, alkalinity, total hardness and chloride content, total absorption spectrum in the wavelength range of 190-800 nm. Sampling at each water treatment stage was carried out in accordance with the requirements of GOST 31942-2012. The permanganate oxidizability, alkalinity and hardness were determined by the titrimetric method. To determine the rest of the indicators, a Hanna HI 991300 conductometer and a Shimadzu UV-1800 spectrophotometer were used.

The titrimetric method is a quantitative analysis in which the content of a substance is determined by accurately measuring the volume of a reagent solution (titrant) that reacts chemically with the substance to be determined.

The Hanna HI 991300 conductometer is a portable waterproof device with a remote electrode for determining three indicators: hydrogen index (pH), electrical conductivity, total salt content. The principle of the conductometer operation is based on measuring the electric current strength that has arisen when the electrode is immersed, the measured indicators are displayed on the screen of the device.

Spectrophotometric analysis allows you to determine the spectral dependence of the absorption degree depending on the degree of absorption, transmission, optical density and concentration of the solution by various types of electromagnetic radiation: visible, infrared and ultraviolet. The principle of the spectrophotometer operation is based on the ability to determine different biological substances using electromagnetic radiation reflected or transmitted through them in the optical range by their ability to reflect different wavelengths. The Shimadzu UV-1800 is a dual-beam device where one beam hits the object under test and the other beam hits the sample, then the intensity results between the two light paths are compared. The research results are displayed on a personal computer using UV Probe software package. The presence of a built-in USB interface and USB control function makes it easy to connect a personal computer to the spectrophotometer. The software package has several operation modes: photometric, spectral, kinetic and quantitative. By combining different operation modes, you

can get a comprehensive result for the studied sample. Using a spectrophotometer, the following indicators were determined: iron (Fe^{3+}), chlorides, and spectral scanning in the wavelength range from 190 to 800 nm was performed. The UV-1800 spectrophotometer uses a high-performance Czerny-Turner monochromator with a holographic diffraction grating. The monochromator provides high measurement sensitivity and extremely low stray radiation (0.00005% at 340 nm) at high resolution (0.1 nm).

The following samples were taken as the test medium: source water, water after the mesh filter, outlet from the microfiltration unit, outlet from the reverse osmosis unit, concentrate after reverse osmosis unit, outlet from the H-cation exchange filter, outlet from the OH-anion exchange filter.

III. RESULTS AND DISCUSSION

The selected water samples were prepared and analyzed according to the following methods:

- Guidance document 52.24.495-2005. Hydrogen index and electrical conductivity of waters. Methodology for performing measurements by the electrometric method.

- GOST 4011-72. Drinking water. Methods for measuring the mass concentration of total iron.

- GOST R 55684-2013. Drinking water. Method for determining permanganate oxidizability.

- GOST 31957-2012. Methods for determining alkalinity and mass concentration of carbonates and hydrocarbonates.

- GOST 31954-2012.

Sample analysis results are presented in Table 1.

According to the results of the analysis, it can be seen that the measured water quality indicators after the mesh filters are slightly reduced.

At the next purification stage (microfiltration unit) there is an increase in the total salt content, electrical conductivity, content of iron ions, chlorides, and an increase in permanganate oxidizability. This is due to the coagulant dosing before the microfiltration unit. It is worth focusing on the indicator of permanganate oxidizability, which almost doubled. This indicator shows the organic substances presence (organic acids, phenols, humic substances, nitrogen-containing compounds, carbohydrates). A significant content of organic substances leads to a decrease in steam quality, the formation of coke-like deposits on the surfaces of heat transfer equipment, and also leads to rapid water foaming. The organic substances decomposition when water is heated leads to the formation of carbonic acid, which lowers the pH and thereby increases the corrosion rate.

When operating membrane technologies, it is necessary to carefully purify water from organic substances, colloid particles, heavy metals and hardness salts. If these requirements are not met, problems arise during the membrane units operation. This leads to the expensive membranes destruction and a reduction in their operating period by 2-3 times.

The water that has been purified on the reverse osmosis unit is characterized by a decrease in the values of the measured indicators. The quality indicators of reverse osmosis concentrate samples exceeded the initial water indicators by

about three times. These changes are logical, according to the method of water treatment. The final purification stage is the use of H- and OH- ion exchange, in order to prepare demineralized water, as can be seen from the measurement results. The use of the ion-exchange desalination method is optimal at a low salt content (less than 400 mg/dm^3).

TABLE I. WATER QUALITY INDICATORS AT EACH STAGE OF THE KAZAN CHPP-2 WATER TREATMENT PLANT

Water samples	pH	EC, mS	TSC, ppt	Fe^{3+}, mg/l	mg O_2/l	Alkali-nity, mg eq/l	TH, mg eq/l	Cl^-, g/l
Source water	7.50	0.3	0.15	0.156	0.034	2.5	6.9	0.013
Water after the mesh filter	6.59	0.4	0.12	0.098	0.013	1.5	7.2	0.054
Outlet from the microfiltration unit	6.73	0.44	0.22	0.113	0.021	1.3	8.0	0.068
Outlet from the reverse osmosis unit	7.0	0.20	0.12	0.168	0.014	1.45	8.1	0.063
Concentrate after reverse osmosis unit	7.1	1.55	0.78	0.210	0.064	2.9	30.4	0.243
Outlet from the H-cationite filter	6.43	0.02	0.01	0.162	-	0.15	-	0.004
Outlet from the OH-anion exchange filter	5.57	0.02	0.01	0.142	-	0.1	-	0.006

The technology of water treatment at Sterlitamak CHPP differs from Kazan CHPP-2 in that preliminary purification is performed using a clarifier and a mechanical filter. Such combinations are rare and are an intermediate result, before the complete modernization of the water treatment plant and the transition to the use of membrane technologies. The reason for this is the excess of indicators for the content of organic substances. For example, according to the results of the analyzes shown in Table 2, it can be seen that the content of organic substances measured by the method for determining the permanganate oxidizability decreases slightly after the clarifier and mechanical filter.

TABLE II. WATER QUALITY INDICATORS AT EACH STAGE OF THE STERLITAMAK CHPP WATER TREATMENT PLANT

Water samples	pH	EC, mS	TSC, ppt	Fe^{3+}, mg/l	mg O_2/l	Alkali-nity, mg eq/l	TH, mg eq/l	Cl^-, g/l
Source water	8.41	0.35	0.17	0.07	1.65	3.9	4.7	0.230
Water after the clarifier	10.5	0.41	0.24	0.06	1.36	0.75	1.7	0.210
Water after the mesh filter	10.1	0.37	0.21	0.03	1.11	0.71	1.6	0.190
Outlet from the reverse osmosis unit	7.5	0.25	0.14	0.01	0.7	0.3	0.1	0.033
Concentrate after reverse osmosis unit	7.7	1.55	0.78	0.05	2.5	2.9	3.5	0.243
Water after OH-anion filter of the second stage (demineralised)	7.77	0.07	0.05	0.005	0.3	0.014	0.002	0.002

Although such a trend is not observed after the ultrafiltration unit, organized using membrane technologies.

When using membrane methods, the content of organic matter is reduced, except when the unit must be shut down for flushing due to membrane units clogging. The combination of clarification technology with reverse osmosis is complicated by organic fouling of membranes. In turn, this leads to frequent flushing of the membranes, which reduces their service life and entails high capital costs. Therefore, the use of reverse osmosis is usually combined with ultrafiltration. The analysis also shows that the reverse osmosis concentrate has an excess in all indicators.

IV. CONCLUSION

In this article, an analysis of the coolant was carried out at each stage of the Kazan CHPP-2 combined water treatment plant. During laboratory studies, the main physical and chemical indicators using titrimetric and spectrophotometric methods were determined. These results made it possible to establish that the water at Kazan CHPP-2 after microfiltration and reverse osmosis units contains organic substances, as evidenced by the measured permanganate oxidizability index. The reasons for the organic substances presence may be insufficient membranes cleaning or the expired period of their operation. For the Sterlitamak CHPP, where pre-treatment is organized using a clarifier and a mechanical filter, followed by reverse osmosis purification, a slight decrease from the initial value of organic substances in clarified water is typical. This indicates an increased load on reverse osmosis and requires more frequent flushing of membrane units. As a result, the consumption of washing compositions increases and the service life of the membranes is reduced. During the experiment, the reverse osmosis concentrate from two power plants was analyzed. According to the data obtained, the physicochemical indicators exceeded the initial indicators by about three times. In order to reduce the wastewater volume and more effectively save water resources at the pre-treatment stage, it is recommended to treat wastewater in a settling tank. To reduce the wastewater volume after the reverse osmosis unit, it is recommended to soften it on an H-cation exchanger filter loaded with a low acidity cation exchanger with carboxyl functional groups -COOH. This filter must be included in a closed circuit for the reuse of regeneration solutions.

REFERENCES

[1] A.Yu. Vlasova, N.D. Chichirova, A.A. Chichirov, A.A. Filimonova, S.M. Vlasov, "Resource-saving technology for neutralization and purification of acidic and hard highly mineralized liquid wastes of the ion-exchange water treatment plant of TPP", Water and ecology, No. 2, pp. 3-17, 2017.

[2] A.A. Panteleev, V.F. Ochkov, S.S. Gavrilenko, "Schematic and technological solutions for water treatment plants based on integrated membrane technologies for combined cycle thermal power plants", Energy saving and water treatment, Vol. 4, No. 90, pp. 11–16, 2014.

[3] V.S. Frenkel, "Membranes Technologies: past, present, and future (in the North American example)", Water supply and Sanitarian appliances, No. 8, pp. 48-54, 2010.

[4] L.S. Sterman, V.N. Pokrovsky, "Physical and chemical methods of water treatment at thermal power plants", Moscow: Energoatomizdat, p. 328, 1991.

[5] VGB-Standard. Feed Water, Boiler Water and Steam Quality for Power Plants, 3rd ed. (VGB Power Tech, Essen, 2011).

[6] A.A. Filimonova, E.K. Arakelyan, A.A. Chichirov et al., "Physicochemical Analysis of Organic Impurities in the Coolant of Combined Heat and Power Plants Equipped with Combined-Cycle Power Installations", Therm. Eng., Vol. 67, pp. 314–319, 2020.

[7] Proc. Int. Water Conf., 46th Annual Meeting, Pittsburgh, PA, Nov. 4–7, 1985 (Eng. Soc. West. Pa., Pittsburgh, PA, 1985). https://www.yumpu.com/en/document/read/11613116/the-international-water-conference-eswp.

[8] G.V. Slavinskaya, V.F. Selemenev, "Organic Substances As a Factor Complicating The Conditioning Of Industrial And Drinking Water", Sorption And Chromatographic Processes, Vol. 2, pp. 297–302, 2007.

[9] O.I. Martynova, T.N. Petrova, O.S. Ermakov, A.A. Zotov, "The Behavior Of The Products Of Thermolysis Of Organic Substances In The Two-Phase Region: Boiling Water Equilibrium Saturated Steam", Thermal Power, Vol. 6, pp. 8–11, 1997.

[10] A.G. Pervov, A.P. Andrianov, E.A. Telitchenko, "Influence of biological pollution on the operation of reverse osmosis and ultrafiltration membrane elements", Critical technologies. Membranes, Vol. 21, No. 1, pp. 3-18, 2004.

[11] V.E. Kosmodamiansky, A.M. Mamedova, "Reverse osmosis in the schemes of deep desalination of additional water at thermal power plants", Energy saving and water treatment, No. 5, pp. 5–8, 2010.