Investigation of bacterial contamination of a mixed-bed filter of a TPP water treatment plant by IR spectroscopy

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***Abstract* —During the operation of water treatment plants at thermal power plants with combined cycle gas turbines, colonies of microorganisms are formed, which negatively affect the operation of the equipment. The types and number of bacteria depends on the source of water supply, seasonality, and water-chemical regime. The aim of the research is to analyze and quantify the bacterial contamination of a mixed-bed filter in a laboratory setup. To determine the number of bacteria and the contamination of ion-exchange resins on the mixed-bed filter unit, the following methods were used: ATP luminometry with a System SURE Plus device, evaporation and separation of a mixture of substances under reduced pressure on an IKA RV rotary evaporator and infrared spectroscopy of substances (FTIR, Shimadzu). As a result of the research, data on the number of bacteria in water samples were obtained on a laboratory installation of a mixed-bed filter, a spectral analysis of the bacteria present in the regenerative solution was carried out. The number of bacteria was determined at each stage of research. On a laboratory installation of a mixed-bed filter, the process of development of microorganisms that reduce the performance of ion-exchange resins has been revealed.**

Keywords—thermal power plants, water treatment plants, water purification, mixed-bed filter, infrared spectroscopy, bacterial contamination.

I. Introduction

Thermal power plants (TPPs) are the largest consumer of natural water and the main sources of polluted wastewater discharge. Water is an irreplaceable resource for petrochemical and energy production. Water is used as a cooling agent for the final product, as a cooler for technological units and equipment, as a solvent for preparing reagent solutions, as a source of steam, as a source of condensate.

The production of chemically demineralized water at TPPs is a complicated process involving a complex of water treatment plants. Most of the water treatment plants at TPPs in Russia and the CIS countries were built in the twentieth century according to the traditional scheme. This scheme consists of a clarifier with liming and coagulation or only with coagulation, mechanical filters with appropriate loading, one or two desalination stages. Such a scheme is considered "classical" for water treatment to compensate steam and condensate losses in power units with drum boilers. One of the reasons for the prevalence of this scheme is the possibility of its application for the water purification of various qualitative composition (in terms of salt content and suspended solids). Over a long period of operation, water treatment plants built according to a similar scheme have received high wear. This caused high operating costs, significant consumption of reagents, and an increase in waste water discharge. These factors lead to the fact that TPPs become uncompetitive enterprises in modern market conditions.

Due to the reform of the energy sector in Russia and the emergence of government support programs – Power Delivery Contracts (PDC and PDC-2), the energy sector began to implement new cost-effective technological solutions for the generation of electricity and heat in tough market conditions – binary cycles based on combined cycle gas turbines (CCGT). Over the past 15 years, more than 100 CCGT units have been commissioned, however, they are equipped with imported equipment, which has to be adapted to the structure and equipment of domestic TPPs.

At foreign TPPs, binary CCGT units became widespread ten years earlier [1]. To date, both abroad and in Russia, considerable experience has been accumulated in the operation of CCGT units and their water-chemical regimes, which requires analysis.

Due to the introduction of combined cycle gas turbines at thermal power plants, the quality of the feed water of the waste heat boilers requires its more thorough preparation. Combined water treatment plants based on membrane and ion-exchange filters are becoming more widespread at CCGTs. To reduce the cost of modernization, existing water treatment plants are retrofitted with "tail" devices: electrodeonization or mixed ion exchange filters. During operation, filtering materials (membranes, ion-exchange resins) of water treatment plants are exposed to bacterial contamination [2-6]. The total number of bacteria ranges between 1,000,000 and 100,000,000 CFUs per cm^2.

The problem of biological contamination at thermal power plants is an urgent problem, despite the thorough water treatment. Biological contamination leads to various emergency situations and a decrease in the efficiency of heat and electricity production.

The types of bacteria contained in source water are diverse. The main types include: heterotrophic, mucus-forming, sulfate-reducing, iron-producing, acid-producing, fluorescent bacteria. The boundary between aerobic and anaerobic microorganisms is relatively arbitrary. Although bacteria that cannot grow in the presence of dissolved oxygen are usually considered obligate anaerobes, in practice, bacteria that do not grow on the surface of a solid or semi-liquid medium in air at atmospheric pressure are considered anaerobic.

Based on the analysis of literature data, the main types of bacteria that can be found in the source water and on the equipment of TPPs have been determined [7-10]. The results are presented in Table 1.

TABLE I. TYPES OF BACTERIA INVOLVED IN BIOCONTAMINATION.

<table>
<tr><th colspan="2">Type of bacteria</th><th>TPP equipment</th></tr>
<tr><td rowspan="2">Algae</td><td>Blue-green (Cyanobacterium, Synechococcus sp., Rhodoferax sp., Sphingomonas, Acidovorax, Pseudomonas sp., Lysobacter, Chroococcus, Phormidium, Pseudanabaena, Lyngbya sp., Nostoc insulare, etc.)</td><td rowspan="2">- water intake locks,
- cooling ponds,
- splash pools,
- catchment basins and cooling tower fills,
- water lines,
- steam turbine condensers,
- tanks and reservoirs of source water</td></tr>
<tr><td>Filamentous greens (Chlorella zofingiensis, Chlorella pyrenoidosa, Chlorococcum sp., Scenedesmus obliquus, Haematococcus pluvialis, Chlorella minutissima, Scenedesmus quadricauda, Neochloris oleoabundans, Botryococcus braunii, Scenedesmus AMDD, etc.)</td></tr>
<tr><td colspan="2">Heterotrophic bacteria (Sphingomonas, Pseudomonas, Bacillus, Herbaspirillum, Bosea, etc.)</td><td>- water intake locks,
- cooling ponds,
- splash pools</td></tr>
<tr><td colspan="2">Mucus-forming bacteria (Akkermansia muciniphila, Bacteroides thetaiotaomicron, Bacteroides fragilis, Ruminoccous gnavus, etc.)</td><td rowspan="5">- catchment basins and cooling tower fills
- water lines
- steam turbine condensers
- tanks and reservoirs of raw water
- clarification units
- mechanical filters
- microfiltration and ultrafiltration units
- reverse osmosis installations
- ion exchange units</td></tr>
<tr><td colspan="2">Sulfate-reducing bacteria (Desulfovibrio, Desulfotomaculum, DS. microbium, DS. bulbus, DS. bacter, Thermodesulfobactrium, Archaeoglobus, etc.)</td></tr>
<tr><td colspan="2">Iron-producing bacteria (Gallionella sp., Leptothrix sp., etc.)</td></tr>
<tr><td colspan="2">Acid-producing bacteria (Carnobacterium, Enterococcus, Lactobacillus, Aerococcus, etc.)</td></tr>
<tr><td colspan="2">Fluorescent Pseudomonas (Pseudomonas corrugata, Pseudomonas brassicacearum, Pseudomonas frederiksbergensis, Pseudomonas mandelii, Pseudomonas kribbensis, Pseudomonas koreensis, Pseudomonas mucidolens, Pseudomonas veronii, Pseudomonas antarctica, Pseudomonas azotoformans, Pseudomonas trivialis, Pseudomonas lurida, Pseudomonas azotoformans, Pseudomonas poae, Pseudomonas libanensis, Pseudomonas synxantha, Pseudomonas orientalis, etc.)</td></tr>
<tr><td colspan="2">Denitrifying bacteria (Thiobacillus denitrificans, Micrococcus denitrificans, Serratia sp., Pseudomonas sp., Achromobacter, etc.)</td><td>- sewer systems,
- sewage locks,
- wastewater tanks</td></tr>
</table>

At TPPs, bacteria can live not only on filter materials, but can also be found in water intake locks, cooling ponds, spray pools, cooling towers of various types, water pipes, steam turbine condensers, and storage tanks for liquid media.

Currently, several methods are used to prevent biological contamination. These methods include mechanical, physicochemical, electrochemical, acoustic, electromagnetic methods, etc.

Some TPPs use the ball cleaning method to mechanically remove biological deposits of the condenser tubes. High-efficiency ball cleaning systems are successfully operated at more than 40 TPPs in Russia: Astrakhan TPP-2, Berezovskaya TPP, Zainskaya TPP, Kashirskaya TPP, Konakovskaya TPP, Permskaya TPP, Ryazanskaya TPP, Troitskaya TPP, Cherepovetskaya TPP, Volzhskaya TPP-2, Naberezhno-Chelninskaya CHPP, Novosibirsk CHPP-5, Orlovskaya CHPP, Perm CHPP-9, as well as most CHPPs of OAO Mosenergo, etc.

The most common chemical methods are chlorination, ozonation, sodium hypochlorite and chlorine dioxide injection. These methods are effective, inexpensive, and easy to operate.

However, the use of existing chemical methods for the purification of ion-exchange resins from biological contamination is limited by the properties of ion-exchange materials. An increase in the concentration of additionally introduced oxidants (chlorine, oxygen, ozone, etc.) can lead to the destruction of the ion-exchange resin matrix.

Zsuzsa Kéki and colleagues studied the biological contamination of a water treatment plant at a TPP, which consisted of stages of pre-treatment, chemical desalination, and mixed-bed filters [11]. As a result of the research, it was found that the mixed-bed filter is subjected to high biological contamination, despite the fact that no biological contamination was found on H-cationic and OH-anion filters. In water samples from the mixed-bed filter, the number of bacteria was comparable to the samples of the source water and varied in the range of $2{\cdot}10^4$ - $8{\cdot}10^4$ CFU/ml. Biocides (Bronopol (Sigma, Germany), ProClin (Supelco, Germany), Kathon WT (Rohm and Haas, UK)) were tested in the study.

S.M. Abdelsalam et al. observed significant biological contamination on the surface of anion exchange resin from water treatment plants units at the Shoubra El-khiema and Damietta TPPs in Egypt [12]. Most of the bacteria belonged to Bacillus, which are relatively resistant to biocide treatment. During operation, ion exchange resins can decrease their exchange capacity earlier than their service life due to bacterial contamination. A high level of biological contamination negatively affects the operation of ion exchange filters, since microorganisms can reduce the exchange capacity of ion exchangers by up to 5% [13].

Murthy P.S et al. have studied ion exchange resins using scanning electron microscopy. The results showed that the granules of ion exchange resins were covered with noticeable organic deposits [14]. Also, the authors found the presence of cracks in the granules of the ion exchange resin, and the granules of the cation exchange resin were even partially destroyed due to biological contamination.

Water disinfection using biocides is an effective method only if the biocides are able not only to remove biofilms, but also further prevent the development of biofilms. The use of traditional biocides (chlorine, bromine, hypochlorite) mainly leads to the destruction of microorganisms in a certain period of time and does not solve the problem of biofilm formation.

N. Matsuda et al. studied the biological contamination of a water treatment plant with mixed-bed filters as the final treatment stage [15]. In contrast to the results of studies by previous authors, no bacteria growth on the surface of ion-exchange resins was found.This study also describes the effect of temperature on the behavior of bacteria viable in ultrapure water.

In Russia, insufficient attention is paid to studies of bacterial contamination of water treatment plants at TPPs. The rules of technical operation [16] do not standardize the total microbial number at water treatment plants.

In July 2020, researchers from the Kazan State Power Engineering University conducted industrial studies on bacterial contamination of feed water of the CCGT boilers of the Kazan CHPP-1 branch of JSC Tatenergo.

The water treatment plant at Kazan CHPP-1 is organized according to the following scheme: the initial Volga water is supplied from the water intake for heating. The water is heated to a temperature of 35±1°C in the winter in condensers, and in the summer in the built-in bundle and raw water heater. The heated water is sent to the chemical workshop for the first stage of water treatment on the AMO-600 magnetic apparatus. The next stage is preliminary water purification with clarifiers of the VTI-250I brand (liming, coagulation). Lime is dosed in excess, maintaining hydrated alkalinity in the limed water at least 0.1-0.3 mg-eq / dm^3, the pH value of limed water 10.1-10.3 at t=25°C. Ferrous sulfate $FeSO_4 \cdot 7H_2O$ is used as a coagulant for liming.

Lime-coagulated water after clarifiers is collected in two tanks and pumped to mechanical filters. Further, the water is directed to ion exchange treatment for the production of demineralized water.

Ion-exchange water treatment is implemented according to the scheme: H-cationite filters of the first stage, then the anionite filters of the first stage. After the anion exchange filters of the first stage, the water through the ejector-type calciners enters the tanks of partially demineralized water. Partially demineralized water from the tanks is pumped to the H-cation-exchange filters of the second stage, then to the anion-exchange filters of the second stage. After the anion exchange filters of the second stage, the demineralized part of the water enters the third stage of ion exchange desalination – mixed-bed filters with internal regeneration.

It was found that in the water samples taken after the mixed-bed filter, the number of bacteria is at a high level. At the outlet of the mixed-bed filter, the number of bacteria exceeded $6 \cdot 10^6$ CFU/ml. Most of the microorganisms are fixed on the surface of the equipment and about 10% are in the water environment. Bacterial contamination can be caused by a long mixed-bed filter regeneration cycle, slow water flow, stagnant zones and low quality of source water in summer.

For a deeper understanding of the process of bacterial contamination in a mixed-bed filter, a laboratory experiment was set up.

II. Materials and methods

During the laboratory research of the mixed-bed filter operation, a set of methods was used:

1) To determine the amount of biological contamination in the laboratory setup of the mixed-bed filter, the ATP-luminometry method was used with the System SURE Plus device. The luminometer records any ATP molecules in the water sample, which are formed not only by bacteria, but also by any organic matter. ATP is an organic molecule that is the main source of energy for living cells. This molecule plays a major role in the transfer of energy into the cell. The presence of ATP in a water sample indicates an insufficient degree of its purification and the potential for the formation and growth of bacteria.

A luminometer detects the presence of ATP by performing a chemical reaction between ATP and luciferin / luciferase, which causes luminescence. Luminescence is detected and measured with a luminometer. The luminescence intensity is directly proportional to the amount of ATP in the water sample. The luminometer displays results in relative light units (RLU). Luminescence resulting from the reaction of ATP and luciferin / luciferase is emitted as photons. The luminometer captures photons and displays the results directly to the RLU. The higher the luminescence intensity recorded by the luminometer, the higher the RLU value.

The RLU value may not match the CFU value. Since the luminometer records all the ATP, it is impossible to determine what the RLU is actually displaying: microbial ATP, residual ATP, or a combination of these indicators. Based on this, it cannot be argued that RLU is equal to CFU. Therefore, the luminometer cannot completely replace the test for microbiological purity.

2) Method of infrared radiation spectroscopy (IR-Fourier, Shimadzu). The method is based on the microscopic interaction of infrared light with a chemical through an absorption process that results in a set of ranges called a spectrum. For infrared spectroscopy, a Shimadzu IRAffinity- 1S apparatus was used. The principle of operation of the IRAffinity-1S spectrophotometer is based on the Michelson method: determining the path difference between the interfering beams when moving the mirrors in a two-beam interferometer. The radiation emitted by the light source passes through the aperture with the help of the collimator, the beam of rays is reflected, becomes parallel, and then is divided into two beams in the beam splitter at an angle of 30°. The beam splitter is a germanium film sprayed onto a potassium bromide (KBr) substrate. One beam is reflected from the fixed mirror, while the other hits the movable mirror. Then both beams are reflected back into the splitter. Each of the reflected beams becomes interfering as they pass through the splitter. The rays returning back are transmitted and reflected radiation. The transmitted radiation from the fixed mirror and reflected from the movable one are combined and intersected with each other, going to the collecting mirror. The fixed mirror has an auto-adjustment function that maximizes interference efficiency. The beam passed through the sample, installed in the centre of the cuvette compartment, is reflected by a collecting mirror and enters the detector, where it is determined in the form of an interferogram, representing a Fourier image of the recorded optical spectrum.

3) The method of inoculation in a Petri dish is one of the stationary methods of artificial cultivation of microorganisms on nutrient media.

4) Method of evaporation and separation of a mixture of substances under reduced pressure on a rotary evaporator IKA RV.

To determine the amount of biological contamination on the mixed-bed filter, laboratory studies were carried out on model solutions.

Model solutions were prepared from chemically pure hydrochloric acid 6% HCl with a mass fraction of 35-38%, chemically pure sodium hydroxide 4% NaOH with a mass fraction of 99%, and river water from the Volga, simulating the source water.

Laboratory studies were aimed at observing the dynamics of the process of contamination of ion exchange resins in contact with water that has artificially introduced bacteria.

The authors have created a laboratory setup (Fig. 1), which makes it possible to simulate the processes of operating modes of a mixed-bed filter with the water environment and regeneration with model solutions.

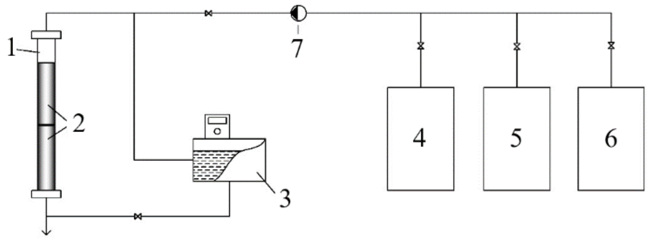

Fig. 1. Laboratory installation of a mixed-bed filter.
1 - magnetic water treatment unit; 2 - clarifier; 3 - clarified water tank; 4, 5
1 - ion exchange column; 2- monodisperse copolymer of styrene with divinylbenzene brands TOKEM-140 and TOKEM-840 in a ratio of 60/40; 3- liquid thermostat LOIP LT-108a; 4 - HCl block; 5 - NaOH block; 6 - distilled water; 7 - water pump.

TABLE II. PHYSICAL AND CHEMICAL INDICATORS OF WATER BY STAGES AT THE WATER TREATMENT PLANT OF KAZAN CHPP-2.

No.	Specifications	Value
1	Temperature range without external cooling, °C	+10 – +100
2	Temperature range, taking into account tap water cooling, °C	+5 – +100
3	Accuracy of temperature maintenance, °C	±0.1
4	Set temperature error, not more than °C	±0.2
5	Heater power, W	1900
6	Max flow rate, l / min	7.5
7	Pressure, bar	0.17
8	Bath volume, l	8
9	Working fluid	water, water-glycerin mixture

The laboratory setup consists of (1) an ion exchange column; (2) monodisperse copolymer of styrene with divinylbenzene brands TOKEM-140 and TOKEM-840 in a ratio of 60/40. To circulate the coolant and maintain a constant operating temperature, a LOIP LT-108a liquid thermostat (3) was used. The technical characteristics of the thermostat are presented in Table 2. For the "regeneration" mode, regeneration solutions (HCl, NaOH and distilled water) are supplied through the pump (7) from tanks (4), (5) and (6).

III. RESULTS AND DISCUSSION

By inoculation in a Petri dish for 48 hours at t=33°C, $1 \cdot 10^6$ CFU/ml of bacteria was grown. The resulting bacteria were placed in a solution simulating a heat carrier located in the tank of a LOIP LT-108a liquid thermostat. For four days, the process of operation and regeneration of a mixed-bed filter was simulated in a laboratory setup. The number of bacteria was determined at each stage of the experiment using a System SURE Plus luminometer with AQ100 Aquasnap Total ATP detectors every 10 hours [17,18].

Fig. 2 shows that at the beginning of the filter operation in the water sample, the content of bacteria decreased to $0.92 \cdot 10^6$ CFU/ml. This phenomenon caused the formation of biofilm on the walls of the ion exchange column. After 50 hours of operation, there was an increase in the number of bacteria in the water samples from the output of the mixed-bed filter. After 96 hours, the number of bacteria in the water sample was $1.3 \cdot 10^6$ CFU/ml. After 4 days, regeneration began at the installation simulating the operation of a mixed-bed filter. The first portion of the regeneration solution was taken for evaporation and separation of a mixture of substances under reduced pressure on an IKA RV rotary evaporator for subsequent infrared spectroscopy. After regeneration, the filter was washed with distilled water and samples were taken for ATP analysis.

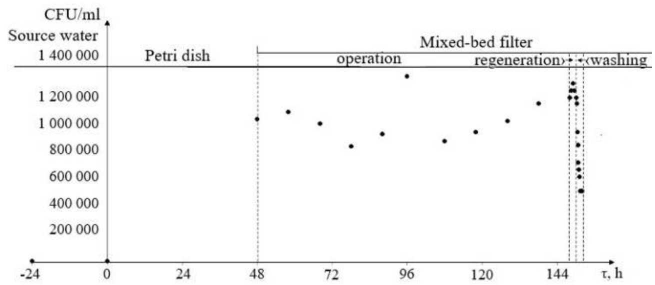

Fig. 2. Change in the number of bacteria on the mixed-bed filter.

During the regeneration of the ion exchange column, an increase in the number of bacteria in the sample can be noted due to the fact that the contaminants were washed out. But the distilled water sample also showed bacterial contamination. Accordingly, traditional mixed-bed filter regeneration does not provide complete purification. Under these conditions, it is possible that re-contamination may occur during operation, leading to the appearance of bacteria.

Infrared spectroscopy was used to determine the substances contained in the dry residue of the first portion of the regeneration solution.

To prepare solid samples, we used a widespread method of pressing tablets of the test substance with an alkali metal halide, KBr. Then the resulting mixture was pressed in a special PGR400 mold into a tablet with a diameter of 10 mm under a pressure of 10.5 t/cm^2.

The results of infrared spectroscopy of the first portion of the regeneration solution are shown in Fig. 3.

New absorption bands characterizing the stretching vibrations of the Fe-O bond in α-Fe_2O_3 in the range of 650- 450 cm^{-1} indicate the leaching of iron-forming FeO compounds from the installation. Low fluctuations in the range of 620-1000 cm^{-1} are explained by the presence of the SO_4^{2-} and SiO2 ionic compounds.

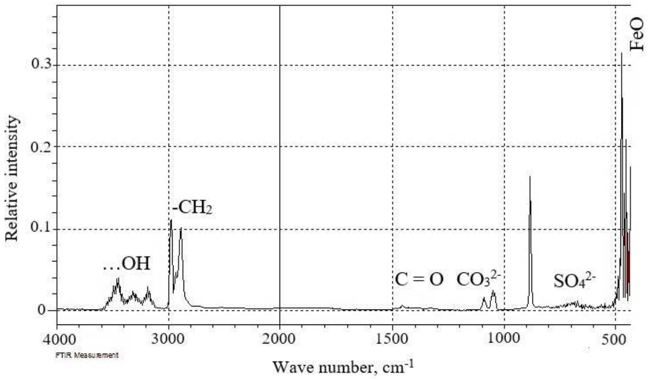

Fig. 3. Spectrogram of the first portion of the regeneration solution.

Salts of carboxylic acids and stretching vibrations of the C=O functional group were determined at 1000-1500 cm^{-1}. A series of pronounced peaks in the obtained spectrogram in the range of 1050-1100 cm^{-1} and 2800-3600 cm^{-1} indicate the presence of the hydrocarbon organic compounds group in the form of humic acids, tannins, proteins, fats, amino acids, fulvic acids, phenols, higher alcohols, aldehydes, as well as compounds secreted by microorganisms.

IV. Conclusion

The authors created a laboratory setup that simulates the "operation" and "regeneration" modes of a mixed-bed filter. Model solutions imitating the heat carrier of Kazan CHPP-1 made it possible to conduct a comprehensive study of biological contamination dynamics of ion-exchange resins at a laboratory unit. This helped to explain the results of the authors' previous study, in which significant biological contamination was observed in water samples after the mixed-bed filter. During the experiment, an increase in bacterial contamination was detected, the number of bacteria reached $1.3 \cdot 10^6$ CFU/ml. With further regeneration of the laboratory installation of the mixed-bed filter, bacterial contamination decreased. By the method of infrared radiation spectroscopy IR-Fourier, Shimadzu the content of substances in the dry residue of the first portion of the regeneration solution was determined. Based on the results of infrared spectroscopy, the presence of organic compounds in the range of 2800-3600 cm^{-1} was confirmed. The rules for the technical operation of power plants and networks of the Russian Federation do not standardize the total microbial number on ion exchange water treatment plants. The authors recommend to consider the possibility of continuous monitoring of the total microbial number and parmanganate oxidizability for the stages of water treatment plants at TPPs.To prevent bacterial contamination of the mixed-bed filter, it is possible to consider the possibility of installing additional chemical bactericidal / UV treatment of water before the filter, thermal treatment of water or changing the water-chemical regime at the stage of preliminary water purification before the ion exchange unit.

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