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APPLICATION OF X-RAY FLUORESCENCE SPECTROMETRY IN ASSESMENT OF ULTRAFILTRATION MEMBRANE SURFACE CONDITION AT WATER PRE- TREATMENT UNITS OF THERMAL POWER PLANTS

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Abstract: *The objects of the study were the Doy Chemical hollow-fiber ultrafiltration membranes which were use for preparation of make-up water for the Novocherkasskaya Regional Thermal Power Plant (RTPP).*

We tried out a possibility of applying the X-ray fluorescence spectrometry to study the condition of the spent non-recoverable ultrafiltration membranes in order to identify the causes of their irreversible destruction. The ARL Quant'X X-ray fluorescence energy dispersive spectrometer of Thermo Scientific (USA) was used in the study.

Thin cuts of the Doy Chemical hollow-fiber ultrafiltration membranes were used in the experiments, which had worked for more than three years in the field conditions of the feed water of the Don River, Russia.

The analysis of the obtained samples spectra allowed us to assume that the membranes were irreversibly contaminated by iron bacteria. Basing on the conclusions made during the analysis of X-ray fluorescence spectra we developed and tested in field conditions one of the optimization variants for technological pretreatment scheme. This scheme enables a significant increase in the service life of ultrafiltration membranes, even when the feed water is heavily contaminated by bacteria. Field tests of the modernized technology were carried out at Novocherkasskaya RTPP during 2016-2018 and showed a significant increase in the service life of the membrane modules. At the same time, the quality of the filtrate, productivity and pressure drops at the cascades of ultrafiltration units fully corresponded to the normative values even in conditions of deteriorated quality of the feed river water.

It has been proved that aggressive regeneration of ultrafiltration membranes that have worked for a long time under the conditions of feed water having increased values of the total microbial number and high values of permanganate oxidation does not allow one to restore their initial state. In this case the main cause of ultrafiltration membranes contamination is iron, which is present in colloidal and bacterial forms in the pores and on the membranes surfaces. In the conditions of the Novocherkasskaya RTPP, in addition to timely flushing and chemical regeneration of ultrafiltration membranes, the necessity of organizing a preliminary treatment of the feed water with reagents having a prolonged bactericidal effect is accepted.

Keywords: *thermal power plants; water pre-treatment; water use; water regimes; water treatment units; water desalination; ultrafiltration membranes; X-ray fluorescence spectrometry; iron bacteria; water disinfection.*

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ПРИМЕНЕНИЕ РЕНТГЕНОФЛУОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ ДЛЯ ОЦЕНКИ СОСТОЯНИЯ ПОВЕРХНОСТИ УЛЬТРАФИЛЬТРАЦИОННЫХ МЕМБРАН ВОДОПОДГОТОВИТЕЛЬНЫХ УСТАНОВОК ТЭС

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Резюме: *Объектом исследования являлись половолоконные ультрафильтрационные мембраны производства Doy Chemical, использованные при подготовке добавочной воды для Новочеркасской ГРЭС.*

Опробована возможность применения метода рентгенофлуоресцентной спектрометрии для исследования состояния отработанных, не подлежащих регенерации, ультрафильтрационных мембран с целью выявления причин, приводящих к их необратимой деструкции. Исследования проводили с помощью рентгенофлуоресцентного энергодисперсионного спектрометра ARL Quant'X производства Thermo Scientific (USA).

В эксперименте были использованы тонкие срезы образцов половолоконных ультрафильтрационных мембран производства Doy Chemical, проработавших в производственных условиях более трех лет на исходной воде реки Дон.

Анализ полученных спектров образцов позволил предположить необратимое загрязнение мембран железобактериями. На основе выводов, сделанных при анализе рентгенофлуоресцентных спектров, разработан и опробован в производственных условиях один из вариантов оптимизации технологической схемы предочистки, позволяющий значительно увеличить срок службы ультрафильтрационных мембран, в том числе при значительном бактериальном загрязнении исходной воды. Производственные испытания модернизированной технологии проводились на Новочеркасской ГРЭС в течение 2016-2018 годов и показали значительное увеличение срока службы мембранных модулей. При этом качество фильтрата, производительность и перепады давления на каскадах ультрафильтрационных установок полностью соответствовали нормативным значениям даже в условиях снижения качества исходной речной воды.

Доказано, что проведение агрессивной регенерации ультрафильтрационных мембран, отработавших длительный срок в условиях исходной воды с повышенными значениями общего микробного числа и высокими значениями перманганатной окисляемости, не позволяет восстановить их исходное состояние. Основной причиной загрязнения ультрафильтрационных мембран в данном случае является железо, присутствующее в коллоидной и бактериальной формах в порах и на поверхности мембран. В условиях Новочеркасской ГРЭС помимо своевременных промывок и химических регенераций ультрафильтрационных мембран признана необходимость организации предварительной обработки исходной воды реагентами, обладающими пролонгированным бактерицидным действием.

Ключевые слова: *тепловые электрические станции; водоподготовка; водоиспользование; водные режимы; водоподготовительные установки; обессоливание воды; ультрафильтрационные мембраны; рентгенофлуоресцентная спектрометрия; железобактерии; обеззараживание воды.*

Introduction

In recent decades, membrane technologies for natural waters treatment have been increasingly widely used in the practice of water treatment of thermal power plants (TPP), due to their environmental friendliness, high quality of water purification, compact size of units and the possibility of their full automatization [1–6]. Ultrafiltration membrane units successfully replace multi-stage technological schemes, which include clarifiers. This allows one to avoid the deposition of contaminants by reagent methods and, consequently, to exclude the formation of precipitation of high humidity. This circumstance is extremely important, since efficient dewatering of precipitates involves the use of additional reagents and finishing dehydration units.

The main disadvantages of ultrafiltration methods for water pre-treatment are the membranes high cost, the significant consumption of wash water, and the sensitivity of membranes to the impact of certain specific impurities present in natural waters that can cause their irreversible destruction. Therefore, we believe that it is important to use highly informative methods for analyzing the surface condition of membranes, which allow one to predict possible negative changes of the membrane condition in the presence of certain impurities in the feed water.

Energy dispersive X-ray fluorescence spectrometry (EDXRF) was chosen as one of the methods for obtaining objective information about the surface condition of the spent ultrafiltration membrane. This method allows simultaneous recording the entire range of energies of the secondary (characteristic) radiation from the sample [7–9]. Fluorescence radiation is decomposed into the spectrum using Si-based semiconductor detectors that record all radiation from the sample and convert it into electrical pulses, forming a spectrum in the form of relationship between the number of pulses and the energy of each element. Further, the spectra are processed by mathematical methods and statistical analysis, allowing obtaining quantitative and qualitative data.

According to our data, the EDXRF method has not yet been applied for assessing the condition of spent ultrafiltration membranes used at the pre-treatment stage at water treatment facilities of thermal power plants. We have chosen this research method as it has certain advantages, namely the relatively low requirements for sample preparation and the possibility of analysis in wide range of concentrations.

Problem statement

In recent years, at PJSC OGK-2 Novocherkasskaya Regional Thermal Power Plant (RTPP) ultrafiltration clarification is used as a water pre-treatment technology, which was introduced by the specialists of NPK Mediana-Filter. Initially, the technological scheme of water treatment included the direct supply of raw water after preliminary mechanical filtration to ultrafiltration units. However, this technology resulted in reduction of the filter cycle and premature failure of the membranes. Therefore, as an experiment, a technology for preliminary disinfection of raw water by chlorine-containing reagents was developed, successfully tested on stand-alone modular units by the specialists of NPK Mediana-Filter under the direct supervision of the head of the chemical workshop of PJSC OGK-2 Novocherkasskaya RHPP S.E. Lysenko.

This article presents the EDXRF study of the surface condition of the spent ultrafiltration membranes, which were operated according to the technology without preliminary disinfection of water. In addition, a detailed description is given of an improved technological scheme of ultrafiltration, implementation of which has shown positive results.

Experimental technique

The surface conditions of ultrafiltration membranes were studied at the Platov South-Russian State Polytechnic University using the ARL Quant'X X-ray fluorescence energy dispersive spectrometer from Thermo Scientific (USA). The device has the following characteristics:

- Silicon-lithium detector with electric cooling;
- Measurements sensitivity is in the range from 0.0001 to 100%;
- The measurement time for one element is from 10 to 60 seconds;

- Adjustable size of the X-ray beam from 1 to 10 mm.

The thin cuts of samples of hollow-fiber ultrafiltration membranes from Doy Chemical, which had worked under real conditions for more than three years at the feed water of the Don River were used in the experiments. Slice No. 1 is the initial sample in dry condition; slice No. 2 is the sample subjected to soaking for 48 hours in distilled water; slice No. 3 is the sample in contact with a 4% solution of citric acid for 48 hours with continuous shaking and subjected to subsequent washing with distilled water for 6 hours.

Unfortunately, according to the terms of supply for the membranes, it is impossible to obtain a sample based on a "fresh" membrane (before its commissioning) to perform a comparative analysis. Therefore, the EDXRF method was used to study samples based on membranes decommissioned due to the impossibility of restoring their original flow capacity, that is, the so-called "spent" membranes.

Before being placed in cuvettes, the slices, which contacted with liquids, were held in air for 10 min. To detect characteristic radiation, semiconductor solid-state detectors were used, the operation of which is based on ionization inside the semiconductor, the detector type is Si (Li).

The anode material of the analyzer tube is Rh (optionally Ag). The maximum radiation power was 50 W at voltage supplied in 1 kV increments in the range from 4 to 50 kV. The selectivity of the recording was provided by 7 filters and additional direct excitation of electrons. The maximum counting speed was up to 100,000 pulses per second with an optimal value of about 50,000. The radiation stability is 0.25% for 8 hours for the device sensitivity in the range from 0.0001 to 100%.

Experimental results

Quantitative and qualitative results of the conducted experiments are presented in Table 1 and Figs.1,2.

Table 1

Quantitative results of the initial sample study by X Energy dispersive X-ray fluorescence y

Oxides concentration, %		Element concentration, %	
SO_3	19.02	Sx	7.62
CI	4.92	CI	4.92
TiO_2	19.52	Ti	11.70
MgO	-	Mg	-
CaO	7.95	Ca	5.69
P_2O_5	6.29	Px	2.74
K_2O	25.65	K	21.29
Fe_2O_3	0.501	Fe	0.350
ZnO	0.400	Zn	0.322
Sb_2O_3	0.0850	Sb	0.0710
Al_2O_3	14.62	Al	7.74
MnO	0.956	Mn	0.740
WO_3	0.061	W	0.048
Br	0.0203	Br	0.0203
PdO	0.0097	Pd	0.0084

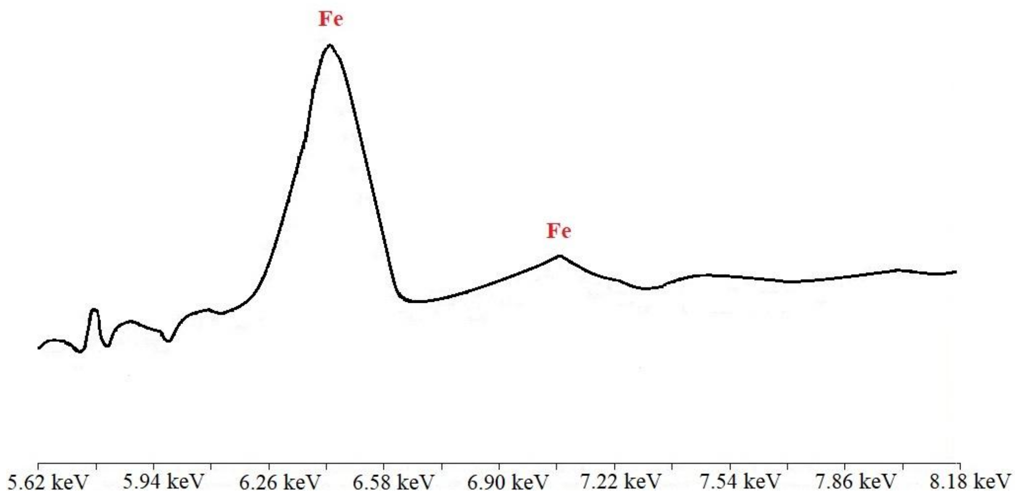

Fig. 1. X-ray fluorescence spectra of the initial sample of ultrafiltration membrane, fabricated using palladium filter.

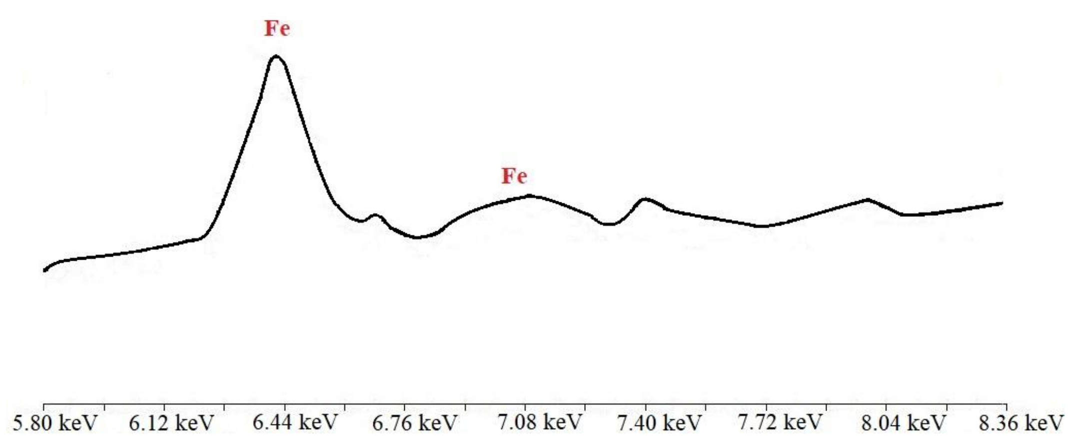

Fig. 2. X-ray fluorescence spectra of the initial sample of ultrafiltration membrane after chemical washing, fabricated using palladium filter

For the sample No.2, which was in contact with distilled water, no significant changes were revealed, so we can conclude that washing with water without the use of aggressive reagents does not lead to positive changes in the surface of the worked ultrafiltration membranes. Therefore, further studies were performed for the initial sample and sample No.3. The figures show the most characteristic parts of spectra for these samples.

Comparison of the spectra of the initial sample and the sample after aggressive chemical washing allows us to conclude that even chemical regeneration does not contribute to a fundamental change in the condition of the ultrafiltration membrane. In order to understand in more detail the reasons leading to an irreversible deterioration of the membrane, we consider the composition of the initial water entering the ultrafiltration unit (Table 2).

Table 2

Composition of the initial river water supplied to the ultrafiltration plant, according to the data from the chemical workshop of the Novocherkasskaya RHPP for 2014 - 2016

Characteristics	Meas. unit	Value
Total salt content	mg/l	500–1000
Particles percentage	mg/l	3–50
Iron concentration	mg/l	0.1–2.1
Permanganate oxidizability	mgO_2/l	3–32
Total stiffness	mg- equ/L	5–10
Alcalinity	mg- equ/L	2.3–4.5
Hydrosilicic acid concentration	mg/l	4–16
Oil products concentration	mg/l	0.05–1.1
pH		7.5–8.5
Temperature	^{0}C	7–34

Besides this, the increased values of the total microbial number were periodically recorded in the feed water. The presence of bacterial water pollution, together with high permanganate oxidizability, allows us to conclude that there is a bacterial film on the surface of the membranes [10, 11].

Analysis of the obtained spectra shows that the spent ultrafiltration membranes are characterized by the presence of iron, which remains even after acid chemical washing. Bacterial iron or iron bacteria are typical representatives of surface water bodies. Iron bacteria are represented, as a rule, by filamentous forms that can effectively be fixed on the surface of water treatment equipment, in particular on the surface of ultrafiltration membranes. In addition, iron oxides accumulate on the surface of bacterial cells, both as a result of absorption by ferrous bacteria of ferrous ions from the feed water, and as a result of oxidation of the bacterial film itself, accompanied by the deposition of insoluble ferric oxides and hydroxides. The absence of the effect of acid washing of the spent ultrafiltration membrane can apparently be explained by the fact that iron (III) hydroxide, which is a product of the activity of iron bacteria, under the proposed conditions of membrane regeneration forms a colloidal gel capable of accumulating in the membrane pores, reducing their cross-sectional area.

Thus, taking into account the increased permanganate oxidizability of the feed water and the high probability of bacterial contamination of ultrafiltration membranes, it was concluded that it is advisable to continuously disinfect water using sodium hypochlorite as a disinfecting reagent. To ensure the longest possible exposure time of free chlorine, the point of introduction of sodium hypochlorite, as a result of field experiments, was chosen in front of contact filters located in the technological scheme immediately before the ultrafiltration units.

Taking into account the transport lag from the point of introduction of sodium hypochlorite in the feed water pipeline to the point of control of free chlorine in the ultrafiltered water supply line to reverse osmosis plants (the location of reverse osmosis units in the process flow diagram is immediately after the ultrafiltration units), which is from 50 to 60 minutes, and inconstancy of chlorine absorption of the feed water, the selection of the optimal dose of sodium hypochlorite was carried out step by step with a dose change interval of not less than 1 hour.

The concentration of free chlorine at the inlet to reverse osmosis plants was monitored using the *Burkert* free chlorine control system, as well as by titration. For dosing of commercial sodium hypochlorite in a wide range of concentrations of active chlorine (from 20 to 190 g/l), a metering pump for the SEV-1 dosing station and the SEV-1 consumption tank were used.

Implementation of these technical measures had a positive effect on the condition of ultrafiltration units: the cartridges replacement time increased from 4 to 6 weeks, and during the inter-flood period it was about 8 weeks. The quality of the filtrate, productivity and pressure drops on the cascades of ultrafiltration plants during 2016–2018 never went beyond the regime charts.

Conclusions

Analysis of X-ray fluorescence spectroscopy data shows that even aggressive regeneration of ultrafiltration membranes that have spent a long time (more than 5 years) does not lead to restoration of their initial condition. This, possibly, is a consequence of exceedance of the critical transmembrane pressure during operation of the ultrafiltration unit, which causes irreversible mechanical changes in the structure of the membrane fiber. Taking into account the characteristics of the feed water, we can conclude that the main cause of contamination of ultrafiltration membranes, apparently, is iron, which is present mainly in colloidal and bacterial forms. Given the developed surface of ultrafiltration membranes, it can be assumed that the deposition and fixing of these forms of iron will occur both on the membrane surface and in its pores. As a result of these processes, the pore cross-sectional area of ultrafiltration membranes will decrease, causing a decrease in the flow through the membrane and, accordingly, an increase in transmembrane pressure, leading to its destructive changes.

Thus, based on the data of X-ray fluorescence analysis, we consider it expedient to carry out not only timely washing and chemical regeneration of ultrafiltration membranes, but also to organize preliminary disinfection of water entering the ultrafiltration unit, for example, by solution of sodium hypochlorite, which has a prolonged bactericidal effect.

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