Abstract

As part of the work, an alternative environmentally friendly technology for water treatment of natural waters was proposed and tested, based on the combined use of hydrodynamic water treatment and ultrafiltration on ceramic membrane filters. The hydrodynamic characteristics of the treated water flow have been determined to achieve the maximum intensification of the oxidation processes of ferrous iron and manganese ions without the use of additional air ejection. The modes of hydrodynamic treatment of natural waters with additional air ejection were selected. The possibility of associated removal of highly corrosive admixture of dissolved hydrogen sulfide from natural waters and a decrease in the total hardness of the treated water has been established. The high efficiency of membrane tubular filters in the processes of removing dispersed impurities has been confirmed.

Keywords: Water purification, deferrization, hydrodynamic treatment, ultrafiltration, ceramic membranes

1. INTRODUCTION

Much attention has always been paid to the issues of industrial water treatment, and at present the problem has not lost its relevance. Depending on the requirements for the quality of the water used, vary. So, for example, for the operations of electrochemical coatings, fully demineralized water is required, and the operation of heating equipment (heat exchangers, water heating systems) requires mandatory softening of water.

Water coming from centralized water supply systems often does not meet high requirements and requires significant additional treatment. That is why the majority of enterprises of the metallurgical complex on the territory of the Russian Federation use water of artesian origin for make-up purposes.

Regardless of the place of operation of the artesian well, the water quality is quite high, it is bacterially not contaminated and has relatively low concentrations of inorganic salts Fe, Mn, Ca, Mg, Sr [1]. That is why artesian water is more preferable for water treatment processes, both from an economic and a technological point of view.

A prerequisite for the reliable and economically justified operation of the reverse osmosis system is the removal of iron and manganese compounds from the compounds, since during processing these compounds can pass from a justified form to an undissolved one, causing serious damage to membrane equipment.

In addition to the effect on the iron and manganese compounds on membrane elements, Fe^{2+} ions can intensify the corrosion processes of technological equipment, which can lead to its failure. (Figure 1). Metal losses associated with corrosion, according to various estimates, reach 12% of the volume of all metal structures [2]. The appearance of the pumping equipment of an artesian well with a high level of equipment utilization is shown in Figure 1. The average pump service life according to the passport is 5 years, while after 2 years the pump (Figure 1) failed.
Along with Fe²⁺ compounds, natural water contains accompanying Mn²⁺ impurities, which can cause blockage of pipes and significantly reduce the heat exchange characteristics of technological equipment. The presence of hardness salts in natural waters also has a negative effect on the heating surfaces of heating equipment, forming hard-to-remove Ca and Mg compounds on the surface.

The compounds listed above, contained in natural water, are currently not removed in the process of reagent oxidation (ozonation, chlorination) followed by the removal of colloidal particles on polymer filters [3-5].

High reagent costs, the complexity of the service system and the size of treatment facilities dictate the need to search for new highly effective methods for removing iron and manganese compounds from water.

Recently, more and more information about the prospects of using non-reagent methods of deferrization and demanganation based on hydrodynamic and cavitation processes has been encountered [6-7]. The combination of hydrodynamic treatment in combination with filtration of non-ceramic porous membranes was especially effective [8].

The main purpose of this work is to assess the possibility of using hydrodynamic water treatment in the processes of purification of artesian water from iron and manganese compounds for the heat engineering needs of a metallurgical enterprise.

2. RESEARCH MATERIALS AND METHODS

To assess the effectiveness of the process of water purification from dissolved iron and manganese compounds, a hydrodynamic oscillator was used, developed at the Department of Innovative Materials and Corrosion Protection of the Russian University of Chemical Technology, DI Mendeleev (Figure 2).
This device uses the energy of the flow of water passing through it, with the creation of stable cavitation resonance phenomena in it. The presence of this effect is due to the exact internal geometric characteristics of the GDGK device, coupled with certain hydrodynamic characteristics of the treated water flow supplied by the pumping equipment used. Due to the presence of tangential channels, when the flow of the supplied water swirls inside the working chamber, a vacuum zone arises, which makes it possible to eject air directly into the working chamber of the GDGC device or (if it is necessary to increase the oxidation state for a single treatment) an ozone-air mixture.

The use of a GDHC device promotes the insoluble state of Fe\(^{2+}\) Mn\(^{2+}\) compounds due to their oxidation, allows efficient oxidation of various substances (hydrogen sulfide, organic substances), and helps to reduce the total hardness of water by changing the ratio of hydrocarbonates and carbon dioxide. The insoluble compounds formed during processing are effectively removed from water during filtration through ceramic membrane elements with a pore size of 0.07-0.2 μm (Figure 3) [9].

The process of regeneration of the filtering surface of the ceramic membrane element is carried out in a counter-current mode with previously purified water. Such a technical solution allows to fully automate the technology of artesian water purification.

The determination of the content of metals in water before and after treatment was carried out on an AASA2 atomic absorption spectrometer with gas atomization (Akvilon, Russia).

The content of iron (Fe\(^{2+}\)) and manganese (Mn\(^{2+}\)) compounds was determined on a portable DR 900 spectrophotometer (HACH, USA).

The object of the study was artesian water from the territory of the metallurgical production of the Moscow region used for the needs of heating and recycling water supply.

3. EXPERIMENT RESULT AND DISCUSSIONS

At the first stage of the experiments, the fundamental possibility of oxidizing iron compounds using the hydrodynamic device described above was investigated. Data on the change in the concentration of iron compounds Fe\(^{2+}\) are presented in Table 1.

| Indicator       | Residual concentration, mg / l |
|-----------------|--------------------------------|
| Source water    | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
| Iron Fe\(^{2+}\)| 0.65     | 0.12    | 0.05    | <0.01   | <0.01   | <0.01   |
| Manganese Mn\(^{2+}\)| 0.13     | 0.07    | 0.06    | <0.05   | <0.05   | <0.05   |

Table 1 Efficiency of removal of iron and manganese compounds from the model water solution
From the data presented in Table 1, it can be concluded that even with a single treatment of water using a hydrodynamic device, it is possible to reduce the concentration of Fe$^{2+}$ by 75%, and with repeated treatment (water recycling), the concentration of Fe$^{2+}$ decreases to the level of the standard for drinking and industrial water. One-time water treatment allows to reduce the manganese content in water by 50%, while the repeated water treatment also brings the manganese content to the standard level. The residence time of the treated water in the hydrodynamic device is less than 1 sec, the linear velocity is > 25 m*s$^{-1}$.

Based on the data on the similarity of the behavior of iron and manganese compounds during hydrodynamic treatment and an extremely low concentration of manganese, further analytical control was carried out only by the content of iron ions, as the most critical parameter.

It is known that during storage in the open air, iron can spontaneously oxidize and fall to the bottom. Evaluation of the effect of hydrodynamic treatment on the rate of iron oxidation was carried out by changing the concentration of Fe$^{2+}$ in water before and after treatment in air. The data on the change in the concentration of Fe$^{2+}$ in the initial and treated water in the hydrodynamic device are presented in the graph in Figure 4.

![Graph showing change in Fe$^{2+}$ concentration](image)

**Figure 4** Change in the concentration of Fe$^{2+}$ in the source and treated water

From the data of the graph in Figure 4, it can be concluded that the hydrodynamic treatment of water makes it possible to increase the rate of oxidation of iron compounds by almost 8 times.

Data on changes in the chemical composition of artesian water during hydrodynamic treatment in combination with filtration on a ceramic membrane filter are presented in Table 2.

| Indicator          | Residual concentration, mg / l | Standard [10] |
|--------------------|-------------------------------|---------------|
| Source water       | After processing              |               |
| Iron total         | 1.38                          | 0.14          |
| Iron Fe$^{2+}$     | 1.11                          | 0.11          |
| Manganese          | 0.17                          | < 0.05        |
| Rigidty,           | 6.77                          | 5.89          |
| Suspended substances | 5.8                     | < 0.1         |

**Table 2** Chemical composition of artesian water before and after treatment
From the data presented in Table 2, it can be concluded that hydrodynamic treatment of water in combination with microfiltration processes on ceramic membranes allows removing iron compounds from artesian water with an efficiency of up to 90%, but also significantly reducing the content of manganese, hardness and suspended solids [10].

4. CONCLUSION

As part of the work done, the effectiveness of the application of the hydrodynamic treatment method in the processes of deferrization and demanganation of artesian water used for the heat engineering needs of a metallurgical enterprise in the Moscow region was assessed.

It was found that a single treatment of artesian water allows more than 75% to reduce the concentration of dissolved forms of iron and 50% of manganese compounds. It has been proven that in the process of passing water through a hydrodynamic device, not only direct oxidation processes occur, but the processes of indirect oxidation of iron compounds are intensified during exposure to the open air.

An extended study of the chemical composition of artesian water before and after hydrodynamic treatment (in combination with microfiltration on ceramic membrane elements) allows you to effectively remove iron and manganese compounds from water, and also helps to reduce the total hardness and minimizes the content of suspended solids.

The results obtained will significantly simplify the instrumental scheme of the water treatment process, completely abandon the use of reagents, which will significantly increase the economic feasibility of the artesian water purification process.

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