Development of a new technological scheme for water purification from iron

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Abstract. Drinking water is the most valuable resource for human life and for the existence of all life on Earth. Scientists predict that about half of the world's population will experience water shortages by 2030 [1]. Purification of fresh water from contamination to the required quality standards is one of the most demanded engineering tasks. Taking into account the prevailing hydrogeological conditions, the removal of dissolved iron from the water of underground horizons is more in demand. Iron removal technology includes the use of oxidizing agents: oxygen, chlorine, potassium permanganate and ozone. It is ozone, due to its high oxidizing potential - 2.07 V, that has become worldwide in industrial water treatment systems, where it is generated using a corona discharge. But in water purification systems of low productivity, up to 1000 l/h, ozone is practically not used, due to the high cost of such generators. The Sterlight SBQ-OZ lamp was proposed as an alternative for ozone generation. According to the manufacturer's data, the lamp can produce ozone in a concentration of 1.59 to 2.82 mg/l when an air flow of 141.5 to 28.3 liters per hour passes through it. A new technological scheme was developed for deferrization of water in a stream using ozone generated by an ultraviolet lamp or a block of lamps. The installation contains an injector, an improved mixing chamber with a bottom inlet of the ozone-air mixture with Pall rings, a sand-gravel filter, an ultraviolet sterilizer lamp. The design feature was that small doses of ozone produced from the air under the influence of ultraviolet radiation with a length of 185 nm oxidized the iron dissolved in water. As a result of the tests carried out, the iron content in the source water was reduced from 2.58 mg/l to 0.02 mg/l, which is 10.0 times lower than the maximum permissible values of the EU sanitary requirements and 15.0 times lower than the maximum permissible values of sanitary requirements of the Russian Federation and the USA. It has also been noted that iron oxidation is significantly improved in the presence of 10% STIROX catalyst based on total backfill.

1. Introduction
Drinking water is the most valuable resource for human life and for the existence of all life on Earth. Scientists predict that 47% of the world's population will experience water shortages by 2030 [1].

When purifying water from underground water sources, the main problem is the removal of dissolved ferrous iron. Many existing methods of deferrization based on the oxidation of iron, with further precipitation of hydroxide on the surface of clarifier filters, are widely used in practice. Oxygen in the air, chlorine, chlorine dioxide, potassium permanganate, hydrogen peroxide and ozone
are used as oxidants [2]. The effectiveness of an oxidizer is determined by its oxidative-electrochemical potential, expressed in volts. The highest oxidizing potential is possessed by ozone - 2.07 V [3].

Ozonation is used in various technological water treatment schemes. An effective water treatment, based on the combined effect of oxygen and ozone on the water of a polluted city reservoir is popular nowadays. After 5 months of operation of SCAVENGER™ units, the concentration of dissolved oxygen increased by 68%, while the concentration of heavy metals decreased significantly - aluminum by 65%, chromium by 35%, lead by 46%, magnesium by 20%, molybdenum by 40%, iron by 32%, cobalt 26% [6].

Ozone is used to improve the speed and quality of coagulation in water purification [7].

Often, acidic and soft groundwater contains a high content of organic substances - humic acids, which interfere with the oxidation of dissolved iron. To remove it, pre-aeration with ozone is used with further filtration through a sand-anthracite backfill. In this case, iron hydroxide is formed on the grains of the backfill, which is a catalyst for the oxidation reaction. Quality indicators are achieved through aeration alone. The best technology results have been achieved when the sand-anthracite filter operates as an adsorption filter [8].

In the practical use of water deferrization systems, air oxygen is most often used as an oxidizing agent. Air oxygen enters the treated water using various methods of pressure and non-pressure aeration. One of the supply methods is the use of small-sized oil-free compressors. The quality of the compressors has noticeably decreased in recent years, which forced the search for new ways of supplying oxygen to the treated water. The use of injectors did not always make it possible to provide the necessary oxidation potential of the air mixture, which was limited by the technical capabilities of the injector itself. It is possible to increase the oxidizing potential of the air by passing air before introducing ozone into the injector through an ultraviolet (UV) lamp-generator, using, for example, UV ozone generators from Sterlight S8Q-OZ. According to the manufacturer's data, the lamp can produce ozone in a concentration of 1.59 to 2.82 mg/l with an airflow of 141.5 to 28.3 liters per hour passes through it [5].

The mechanism of action of ozone can be described using direct oxidation, oxidation by radicals - indirect oxidation, ozonolysis and catalysis. Ozone is unstable and decomposes quickly. The half-life of ozone in water or air depends on temperature [4].

Ozone is formed from an oxygen molecule under certain conditions, when an oxygen molecule can dissociate - decay into two separate atoms. Such conditions in nature are provided by electrical atmospheric discharges and by exposure to solar ultraviolet radiation. In this case, atomic oxygen cannot exist independently and an ozone molecule is formed. The ozone molecule is fragile, therefore it is unstable and prone to self-destruction.

In water treatment systems, due to the instability of the molecule, ozone is produced directly on site using silent corona discharge generators or ultraviolet emitters. The concentration of ozone in the resulting ozone-air mixture is very different. When using corona discharge generators, the ozone content can reach up to 20 grams per one cubic meter of the mixture [4]. Under ultraviolet radiation, the concentration reaches 2.82 grams of ozone per cubic meter of the mixture [5]. It can be seen from the data presented that the efficiency of silent corona discharge generators is much higher, which led to their high distribution in practical water treatment. The more completely, efficiently it mixes and dissolves in the treated water, the less it needs to be produced to solve the set technological problem. Today, ozone generators and devices for deferrization of water based on ultraviolet radiation are used in water treatment systems at small water treatment plants and in domestic use, since they are less expensive and their use is safer. The required performance of the equipment for its generation largely depends on how effectively the ozone supplied to the water is used.

The known system of deferrization of water by the American company Triple O Systems, Inc is based on ultraviolet generation of ozone [9]. The technology provides for mixing the ozone-air mixture with purified water using an injector and feeding it to the input of the technological chain, where the components are mixed with the original purified water. Water treatment technology provides
The main disadvantages of the system are the complexity of the design and increased energy consumption associated with additional hydraulic pressure losses from the movement of the ozone-air mixture along the recirculation loop.

Deferization device based on ultraviolet ozone generation [10] contains a housing in which a bactericidal lamp is coaxially placed in a protective quartz cover. The reactor vessel is equipped with a feed water supply pipe, at the inlet of which an ejector is installed, and with a treated water outlet pipe. At the location of the radiation source on the inlet side, the cavity between it and the inner surface of the quartz cover is connected to the ambient air, and from the outlet side it is connected to the suction part of the ejector. The disadvantage of the device is that it operates exclusively on clear water without dissolved iron compounds that can oxidize and precipitate under the influence of ozone. From the sediment, the treated water will become opaque and will absorb hard disinfecting radiation.

Natural and artificially created materials that catalyze the oxidation reaction are often used as a filter material in water treatment systems. Natural catalytic materials are varieties of manganese oxides. A layer of manganese oxide is specially applied to artificial filtering materials. Inert materials such as quartz sand, hydroanthracite are also used [2].

For over 75 years, Pyrolox, a natural manganese dioxide catalyst produced in the United States of America, has been widely used. Pyrolox oxidizes hydrogen sulphide, iron and manganese and their insoluble compounds are retained in the feed and subsequently removed during backwashing. The use of additional chemicals during regeneration is not required. Pyrolox can be used for aeration, chlorination, ozonation and other post-treatment methods in cases where the source water contains high concentrations of contaminants. The disadvantages of using Pyrolox include the high density of the material - 2.0 g / cm³, therefore it is very important that the washing of the filters ensures sufficient expansion of the layer - 30 ... 50% and complete removal of the sediment. This is the only way to ensure a long service life.

For water filtration, FILOX-R is used - a specially processed and sieved natural ore with a content of 75 ... 85% of manganese dioxide, oxidizing even in high concentrations hydrogen sulfide, iron, manganese and retaining their insoluble compounds in the feed with subsequent removal during backwashing. The use of additional chemicals during regeneration is not required. The disadvantages of using FILOX-R in water treatment systems are the same as for Pyrolox.

The filtering material of the Pyrolusit brand is used for the same purposes as Pyrolox and FILOX-R [2]. The advantages of Pyrolusit include a lower bulk density of 1.0 ... 1.2 g / cm³, therefore using this system is simpler than when working with Pyrolox and FILOX-R.

The data on the effectiveness of pyrolusites used as a filter bed are given in the work of A. Ovchinnikov and V. Bocharnikov [11]. According to the authors, deferrization of water by filtration through a sand load is not advisable, since the iron content in the purified water exceeds the maximum permissible concentration, regardless of the filtration rate. To obtain the required result, filtration is recommended to be carried out on filters with a zeolite load at a speed of $V = 10-15$ m / h, or through pyrolusite.

The high bulk density and high cost of pyrolusites restrain their widespread use in water treatment systems. Experts and scientists are looking for ways to reduce the proportion of natural catalysts in the complex filling of the deferrization filter. The urgent problems of finding the optimal ratio of quartz sand and pyrolusite, as the closest natural filtering materials in the composition of the water treatment system, and of increasing the oxidizing potential of the oxidizing agent used are posed.

A typical deferrization system, as a rule, includes an aeration unit consisting of a compressor or an injector and a mixing chamber, as well as a deferrization filter, the complex filling of which consists of quartz sand with a fraction of 0.8 ... 1.2 mm and pyrolusite with a fraction of 0, 4 ... 1.2 mm. The ratio of filling materials depends on the filtration rate and on the contamination of the source water and is 50 ... 90 percent of quartz sand and 10 ... 50 percent of pyrolusite. Our practical experience of 18 years shows that the average content of pyrolusite in deferrization systems is 35 ... 40 percent in the total volume of the filter backfill. With this composition of the backfill, the washing speed is 40 ... 60 m / h,
which leads to abrasion of pyrolusite into a finer fraction and the removal of the dust-like fraction of the filtering bed. Minimizing the amount of pyrolusite in the total volume of the filter bed will significantly reduce the initial cost of the filter, reduce operating costs for backwashing the filter material, and reduce the carryover of the pyrolusite dust fraction.

The purpose of the scientific research is to increase the efficiency of the water deferrization process by developing a new technological scheme for water purification with a throughput of up to 1000 l/h.

To achieve this goal, it is necessary to solve the following tasks:
- to develop a water deferrization system based on ultraviolet ozone generation without the use of expensive ozone generators, a filter with a complex filling;
- to develop a new design of the mixing chamber to improve the mass exchange of the ozone-air mixture with the treated water;
- to determine the rational arrangement of the elements of the water treatment system and the optimal proportion of pyrolusite in the filter backfill.

2. Object of research, methods and research findings

To improve the quality of water purification from dissolved iron and to reduce the cost of the water treatment system, a technological scheme has been developed (Figure 1), which provides for the use of ready-made components from world manufacturers [RF patent No. 274093].

![Diagram of a unit for deferrization of water based on an ozone-air mixture](image)

In order to determine the effectiveness of the use of ultraviolet lamps for generating ozone in water treatment systems for removing dissolved iron with a concentration of up to 1.0 mg/l, an installation was created containing an ultraviolet ozone generator, an injector 3, a mixing chamber 4, a sand-gravel filter 5, a second ultraviolet a lamp for disinfection of water and the destruction of residual ozone 6. The design feature of the device is that small doses of ozone produced from the air under the influence of ultraviolet radiation with a length of 185 nm oxidize iron dissolved in water, and the destruction of possible residual ozone under the influence of ultraviolet irradiation with the length of
254 nm at the end of the processing line makes it possible to carry out the oxidation process to the end.

Water from a well with an iron content of 0.82 mg/l and a pH value of 7.8 was used as the initial water. The water quality was determined in an accredited laboratory of sanitary epidemiological surveillance in the Kostroma region of Russia.

According to the results of processing, the following data were obtained at the outlet after cleaning: when using only air oxygen, the concentration of iron at the outlet was 0.05 mg/l, when using an ozone-air mixture, the concentration of iron was 0.02 mg/l.

A high ozone content was noted in the sensory control of the waste excess gas downstream of the mixing chamber. Since ozone occurs only in the form of a solution in air or oxygen, it will be fair to assume that when the ozone-air mixture is passed through water, it will be redistributed between two solvents - air or oxygen and water. In this case, the ozone distribution coefficient $K_r(T)$ is experimentally determined - the ratio of the ozone concentration in water $C_w$, mg/l at a fixed temperature to the ozone concentration in the ozone-air mixture $C_g$, mg/l, at the same temperature and pressure [12]:

$$K_r(T)= \frac{C_w}{C_g}.$$  

It is known that ozone dissolves better at lower water temperatures, and decomposes faster when the water temperature rises. An increase in the saturation pressure promotes its dissolution. Compared with oxygen, ozone has a solubility of about 10 times. For example, at a water temperature of 20 °C, the $K_r(T)$ coefficient for oxygen is 0.0333, and for ozone it is 0.21 ... 0.38. The maximum concentration of ozone in water depends on the ratio of the amount of the supplied ozone-air mixture and on the amount of treated water, when the concentration of ozone in the ozone-air mixture depends on the quality of water, its temperature and saturation pressure, as well as on the duration of the saturation process [12].

In order to improve the mass exchange of the ozone-air mixture with the treated water, a new design of the mixing chamber 4 (Figure 2) has been developed, containing Pall rings and a tubular distributor from a standard water filtration system, which allows the ozone-air mixture to be dispersed into the treated water with a bubble size of up to 2 mm.

To test the system with a new mixing chamber, a water treatment unit was placed in the Yubileiny non-profit garden community in the city of Kostroma.

The initial underground water contained 2.93 mg/l of iron, the pH value was 7.9, and the dissolved ammonia content was 1.5 mg/l. The supply of raw water for purification was 421 l/h, the consumption of purified water was 453 l/h. Air and ozone-air mixture was fed through injector 3 with a flow rate of 110 l/h into mixing chamber 4. After mixing, 32 liters of ozone-air mixture per hour were dissolved in water, the rest 78 l/h were discharged into the atmosphere.
Figure 2. Diagram of a unit for deferrization of water based on an ozone-air mixture with its improved mixing with the treated water:

1- air supply regulator; 2- ultraviolet lamp S8Q-OZ; 3-injector; 4-chamber mixing with Pall rings; 5-filter of deferrization; 6-ultraviolet lamp S8Q-PA2; 7-flow regulator; 8-air separating valve ARI; 9-filter with carbon cartridge

According to the test results, the iron content in water after purification using air oxygen as an oxidizing agent was 1.02 mg/l, when using an ozone-air mixture - 1.16 mg/l.

To increase the generation and supply of ozone, one more ultraviolet lamp was additionally installed - an ozone generator 2 according to the scheme shown in figure 3. The experimental conditions were the same.
Figure 3. Diagram of the unit for deferrization of water with an ozone-air mixture with its improved mixing with the treated water and two ultraviolet lamps (ozone generators):
1- air supply regulator; 2- ultraviolet lamp S8Q-OZ; 3-injector; 4-chamber mixing with Pall rings; 5-filter of deferrization; 6-UV lamp S8Q-PA2; 7-flow regulator; 8-air separating valve ARI; 9-filter with carbon cartridge; 10-water meter; 11-gas meter

According to the test results when using air oxygen as an oxidizer, the iron content in the water after purification was 0.49 mg / l; when the ozone-air mixture was generated by one ultraviolet lamp - 0.68 mg / l and 0.84 mg / l during operation of two ultraviolet lamps, which is better than the indicators obtained in previous experience. During operation, a catalytic film of iron hydroxide formed on the sand bed, and accelerated the oxidation process. The organoleptic control of the water showed a high value of gaseous ammonia.

The deterioration of the oxidation of dissolved iron is associated with the activity of gaseous ozone in relation to gaseous ammonia, which is confirmed by the studies presented in [13].

To confirm the proposed provisions, tests were carried out on source water with a lower ammonia content at the water treatment plant of the Shuvalovo joint-stock company in the Kostroma region. An experimental water treatment unit for iron removal based on an increased yield of the ozone-air mixture worked according to the same scheme (figure 3).

The initial water contained 2.58 mg / l of dissolved iron, 0.5 mg / l of ammonia, pH 7.7. The temperature of the treated water ranged from 9 to 10.8 degrees Celsius. The water consumption at the inlet to the unit was 423 l / h, at the outlet from the system - 450 l / h. The supply of the ozone-air mixture through the injector was 107 l / h. 27 l / h of the ozone-air mixture was dissolved in water, the rest of the mixture was discharged in the form of excess gas through the air-separating valve after the mixing chamber.

The iron content in the water after purification by oxidation only with atmospheric oxygen was 1.08 mg / l; when using the ozone-air mixture generated by two ultraviolet lamps it decreased by 4.32 times and amounted to 0.25 mg / l. After 60 minutes of operation, the iron content at the outlet increased.

In order to stabilize the process of reducing the concentration of iron in water, the contact time of
the oxidizer with water was increased by installing one more mixing chamber 4 in series (Figure 4).

Figure 4. Iron removal system based on increased yield of ozone-air mixture with improved mixing with water, and with an increased contact time with treated water:
1- air supply regulator; 2- ultraviolet lamp S8Q-OZ; 3-injector; 4-chamber mixing with Pall rings; 5-filter of deferrization; 6-ultraviolet lamp S8Q-PA2; 7-flow regulator; 8-air separating valve ARI; 9-filter with carbon cartridge; 10-water meter; 11-gas meter

The unit also contained two ultraviolet lamps (ozone generators) 2 operating in parallel, an injector 3, two successive mixing chambers with Pall rings and a bottom distributor 4, a sand-gravel filter, an ultraviolet lamp for water disinfection and the destruction of residual ozone 6.

According to the test results, the iron content in the purified water after 60 minutes of the unit operation increased and amounted to 1.23 mg / l.

To test the effect of the amount of the ozone-air mixture supplied to the water, an oxygen generator was connected to the inlet of the ultraviolet ozone-generating lamps, which made it possible to increase the oxygen content in the air from 20 to 40 percent. The water consumption at the inlet in the experiment was 467 l / h, at the outlet - 507 l / h. Ozone-air mixture supply was 157 l / h, and it dissolved in water up to 40 l / h. Experiments have shown that the iron content in purified water has decreased from 1.23 to 1.05 mg / l, which is insufficient according to the condition of the maximum permissible concentration - 0.3 mg / l [15, 16].

To test the effect of the filtration rate of the components of the ozone-air water mixture on the purification parameters, two sand-gravel filters were installed in parallel in order to reduce the filtration rate (Figure 5).
Figure 5. Iron removal system based on increased yield of ozone-air mixture with improved mixing with water and reduced filtration rate:
1- air supply regulator; 2- ultraviolet lamp S8Q-OZ; 3-injector; 4-chamber mixing with Pall rings; 5-filter of deferrization; 6-ultraviolet lamp S8Q-PA2; 7-flow regulator; 8-air separating valve ARI; 9-filter with carbon cartridge; 10-water meter; 11-gas meter

With a decrease in the linear filtration rate by half - from 7 m3 / h to 3.5 m3 / h, the iron content in the purified water was 0.46 ... 0.51 mg/l at a water flow rate of 485 ... 510 l/h, which is higher than the maximum permissible values for drinking water.

In order to improve the efficiency of the developed water treatment system (Fig. 3), pyrolusite "Stirox" was added to the sand filling (Figure 6) - 5%, 10% of the total backfill volume. The test results are presented in the table.
Figure 6. Iron removal system based on increased yield of ozone-air mixture with improved mixing with water and with filtration on sand and gravel backfill with 10% addition of pyrolusite (a and b), c - with two mixing chambers in JSC "Shuvalovo" of the Kostroma region:
1- air supply regulator; 2- ultraviolet lamp S8Q-OZ; 3-injector; 4-chamber mixing with Pall rings; 5-filter of deferrization; 6- ultraviolet lamp S8Q-PA2; 7-flow regulator; 8-air separating valve ARI; 9-filter with carbon cartridge; 10-water meter; 11-gas meter
Table 1. Influence of pyrolusite content in the filling composition on water quality.

| Index                  | Backfill composition | Quartz sand 100% | Quartz sand 90% Stirox -10% | Quartz sand 95% Stirox -5% |
|------------------------|----------------------|------------------|----------------------------|---------------------------|
| Filtration rate, m / h |                      | 7                | 7                          | 7,4                       |
| Content iron in purified water, mg / l | 1,23                | 0,02             | 0,19                       |

The use of pyrolusite in the amount of 5 ... 10% of the backfill makes it possible to reduce the iron content in the purified water by 6.47… 61.5 times in comparison with the use of only quartz sand as a backfill. According to the results of the tests carried out, the iron content in water after cleaning using 10% Stirox from the filling volume was 0.02 mg / liter, which is 10 times lower than the maximum permissible values for the most demanding iron removal systems in the world, in the EU [14] and 15, 0 times lower than the maximum permissible values of sanitary requirements of the Russian Federation [16] and the United States [15].

3. Research findings

1. A new technological scheme has been developed for deferrization of water in a stream using ozone generated by an ultraviolet lamp or a block of lamps. The installation also contains an injector, an improved mixing chamber with a bottom inlet of the ozone-air mixture with Pall rings, a sand-gravel filter, an ultraviolet sterilizing lamp. The design feature was that small doses of ozone produced from the air under the influence of ultraviolet radiation with a length of 185 nm oxidizes the iron dissolved in water, and the destruction of possible residual ozone under the influence of ultraviolet radiation with a length of 254 nm at the end of the processing line makes it possible to carry out iron oxidation process to the end.

2. Iron oxidation is significantly improved in the presence of 10% STIROX catalyst based on the total backfill. The iron content in the water after purification is 0.02 mg / l at a water flow rate of up to 1000 l / h and at the initial iron content of not more than 2.5-3.0 mg / l, and at the presence of ammonia in the initial water up to 0.5 mg / l. This is 10.0 times lower than the maximum permissible values of the sanitary requirements of the EU and 15.0 times lower than the maximum permissible values of the sanitary requirements of the Russian Federation and the United States.

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