INTRODUCTION

Iron constitutes about 5% of all solid crust. That is why, this metal can be found in almost all surface and groundwaters. Natural waters contain various elements from different rocks with which water comes into contact during its migration. These rocks include sand, gravel and clay materials which contain a large number of ferrous compounds. This leads to the formation and accumulation of iron in water. Iron in natural waters can be in the form of divalent and trivalent ions, colloids of organic and inorganic origin, such as Fe(OH)$_2$-, FeS, Fe(OH)$_3$-, complex compounds with humates and fulvic acids, as well as in the form of a fine suspension. Sources of water supply, as a rule, are surface and groundwater, the qualitative and quantitative indicators of which are determined by the natural conditions of origin and by the level of anthropogenic load. Water quality, depending on the application, is regulated by state standards and other regulations. In recent decades, practically all surface waters in Ukraine have been intensively polluted due to the increasing anthropogenic load resulting from the discharge of insufficiently treated water, surface runoff from agricultural lands, industrial sites and urban areas, etc. Some regions of Ukraine are characterized by high iron content in natural waters [Khilchevskyi et al. 2018, Linnik et al. 2012, Linnik et al. 2018].

The content of iron compounds in surface and groundwater depends on the geological, climatic, landscape and hydrological features of the region. The peculiarities of surface and groundwater formation on the territory of Ukraine are

ABSTRACT

As a result of the anthropogenic activity and the continuous increase in the scale of water consumption, surface and groundwater, which are sources of freshwater, have been degraded. Today, most water sources have high iron content. Contamination of groundwater with iron and other metals can occur due to the development of ore deposits and the operation of quarries. The existing technologies solve this problem only partially. Ions of heavy metals are toxic and dangerous for living organisms, including human beings. In this regard, it is important to develop effective methods of water treatment of various pollutants. Today, pollution of water bodies with iron ions has reached a critical level. This creates a problem for many regions not only in Ukraine, but also far beyond its borders. The problem is urgent and needs to be solved. When the pH value in water is less than 6.8–7.0 and the concentration of iron is high, it is advisable to use a combination of a number of methods with the introduction of reagents in order to perform deep purification. The reagent method of deironing is implemented by treating the source water with a suspension of lime water Ca(OH)$_2$. This approach allows deironing water effectively, but its implementation is accompanied by the formation of a large amount of sludge, which must be disposed of. An effective way to dispose of such precipitates is their use as a chemical additive in the production of cement, which was confirmed by the conducted research.

Keywords: low-waste technology, water treatment, removal of iron, reagent methods, lime, hardening time properties of cement, normal density, compressive strength properties.
affected both by natural conditions and by the effect of anthropogenic load. The qualitative and quantitative indicators of these waters vary significantly in time and area of distribution [Hryhorenko 2019, Khatri et al. 2015, Khatria et al. 2017]. It was found that drinking water is one of the factors contributing to the accumulation of iron in the human body. The waters of many groundwater aquifers in Ukraine have a high iron content, which ranges from 0.5 to 30 mg/dm³ and even more, but more often up to 5 mg/dm³ [Shevchenko et al. 2013].

Prolonged consumption of water with high iron content leads to liver disease, increases the risk of heart attacks, adversely affects the central nervous system and reproductive function, promotes allergic reactions, and blood diseases [Fazzo et al. 2017, Flannigan et al. 2015, Vardhan et al. 2019]. Therefore, excess iron in drinking water is a dangerous impurity [Jaishankar et al. 2014, Khadse et al. 2015]. The increase in color and turbidity of tap water may be caused by the presence of total iron. Prolonged stay of water in the water network and reducing the concentration of oxygen in it contribute to this process. Steel pipes are the most common in the water supply networks of Ukraine, the duration of reliable operation of which is not sufficient. Insufficient reliability of pipelines negatively affects the efficiency of the system and the quality of drinking water. Pollution of drinking water in the pipes of the water supply network occurs due to a sudden change in the movement of water in it or a change in its chemical composition. In the first case, the perturbation of sediment and its transition into the volume of drinking water take place. The second reason causes the dissolution of the solid part of the sludge, which facilitates its perturbation, the transition to the volume of drinking water and transportation to consumers. In addition, the high iron content gives the water an unpleasant taste, odor, and is the reason for shortages in the paper, textile, food and cosmetics industries. Glandular bacteria and growths can form in pipes as well as heat exchangers, reducing the cross-section of the pipes [Chaurasia and Srivastava 2020, Vorobyova et al. 2019].

Thus, the high iron content in surface and groundwater requires mandatory deironing, i.e. it is necessary to take a set of measures to reduce the iron content. Thus, this is an important economic, environmental and social problem, which has scientific, theoretical and practical significance. This is one of the priority areas in providing the population with pure water [Trus et al. 2019a]. Iron is removed from natural waters with methods that can be divided into two main groups: reagent-free (physical) and reagent. The process of oxidation of Fe²⁺ to Fe³⁺ is accompanied by precipitation of Fe(OH)₃, with its following filtration. This method is quite simple. The choice of oxidizer depends on the cost of the oxidizer and the amount of water for purification [van Genuchten and Ahmad 2020]. The process of ion exchange has numerous advantages such as low cost, simplicity of implementation, and recovery of components during resin regeneration. However, in the region of high concentrations, a decrease in the efficiency of the process is observed due to the “clogging” of the resin [Dabrowski 2004, Shkolnikov 2012].

Sorption materials can purify water from iron even at low concentrations [Biela and Kucera 2016, Hu et al. 2020, Trus et al. 2019b]. The direction of biosorption materials has been developed [Halysh et al. 2020a, Halysh et al. 2020b]. The effectiveness of materials based on calcium carbonate depends on pH, the presence of organic substances and other cations. This method allows one to reduce the concentration of iron to the values lesser than MPC [Wang et al. 2019, Wang et al. 2013]. Water filtration through sand, crushed coal constitutes an inexpensive method for groundwater treatment [Ellis et al. 2000, Vries et al. 2017]. Capillary materials are quite effective in water purification from iron ions and this direction is quite new for today [Radovenchyk et al. 2021].

The advantages of the electrocoagulation process are the absence of the waste chemical reagents and the high efficiency of the process [Gubari et al. 2021]. However, this method is quite energy consuming [Hashim et al. 2017, Trus et al. 2020a, Vasudevan et al. 2009]. Aeration is the method which does not require the use of chemical reagents for water purification and can be effectively applied for water with iron concentration of more than 5 mg/dm³ [Pleasant et al. 2014]. Biological methods are used to purify water from various sources. However, they need to be carefully studied experimentally for the selection of a biological agent [Aziz et al. 2020, Hu et al. 2012]. Membrane methods for water deironing are widely used [Trus et al. 2020b]. They allow removing both dissolved and
colloidal iron from water, providing a high degree of purification. However, membrane methods are not very often used for deironing due to the high cost [Choo et al. 2005, Kasim et al. 2017].

A method of oxidation with oxygen from air can be considered the simplest, cheapest and most environmentally friendly way to remove iron from natural waters. During the deironing groundwater, aeration is also can be used to increase the efficiency of the process [Korchef et al. 2009]. During the deironing of surface waters, coagulation with aluminum sulfate is performed after chlorination, liming and precipitation. In the process of water purification, sediments are formed, which must be disposed of [Trus et al. 2021, Martínez-Cruz et al. 2021]. The development of effective methods for the disposal of sludge formed during water deironing will help to create low-waste water deironing technologies.

MATERIALS AND METHODS

Materials

The objects of the study were the solutions with initial concentrations of total iron 10–100 mg/dm$^3$, which simulate natural waters, waters of centralized supply systems, washing waters and sediments of iron hydroxide formed in the process of water deironing.

Removal of iron ions from water

The solution in the amount of 0.5 dm$^3$ was poured to the flask with the volume of 1 dm$^3$ and left for a certain period of time. The residual iron concentration was determined every 2 hours. During removal of iron ions by liming, a 5% solution of lime water was dosed into the aqueous solution, stirred and left for precipitation. Then, the samples were filtered and the residual iron concentration was determined. The spectrophotometric method for iron ions determination [Li et al. 2013] was used to estimate its initial and equilibrium concentrations in solution. The efficiency ($Z$) of iron ions removal was calculated by the formula:

$$Z = \frac{C_0 - C_f}{C_0} \cdot 100, \%$$  \hspace{1cm} (1)

where: $C_0$ – initial concentration of iron, mg/dm$^3$; $C_f$ – final concentration of iron, mg/dm$^3$.

Sludge processing

During water deironing, a precipitate is formed, which was disposed of after dehydration as a chemical additive in the composition of I-500 cement. In order to study the physical and mechanical properties of cement, normal density, hardening time, compressive strength and water removal coefficient were determined. The precipitate formed as a result of water purification was Fe(OH)$_3$ hydroxide, which was added into the cement in the amount of 0.5–2.5 wt.% by co-mixing the components in a laboratory ball mill for 10 minutes.

RESULTS AND DISCUSSION

Removal of iron ions from water

In groundwater, which is a source of water supply, the concentration of iron can reach 1–10 mg/dm$^3$. Deironing of water using aeration methods involves the subsequent filtration of water on granular loads. The loose precipitate of iron hydroxide should be periodically removed by backwashing with water. The concentration of iron in the washing water can reach 50–100 mg/dm$^3$. Therefore, it was interesting to study the deironing of water at a concentration range of 10–100 mg/dm$^3$.

The residual concentration of iron without the adding of reagents decreases sharply in 1–2 hours. Further precipitation slightly reduces the concentration of iron. The residual concentrations of iron are quite high. The removal efficiency of iron ions is 91%, 78% and 85% for initial iron concentrations of 10, 50 and 100 mg/dm$^3$, respectively, after 10 hours of precipitation. Iron can occur in the form of suspended, colloidal and dispersed impurities that have the same charge, and this leads to intermolecular repulsive forces. Therefore, it is necessary to treat water before deironing to reduce the charge of impurities to zero values.

Lime was chosen as the reagent due to its low cost. It is an effective reagent in water treatment processes, which allows adjusting the pH, effectively softening the water and carry out its deironing [Gomelya et al. 2014]. Deironing of water by using the reagent method consists in the transfer soluble forms of iron into sparingly soluble. Liming is used to remove iron (II) sulfate. The added lime reacts first with ferrous sulfate (II):

$$FeSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Fe(OH)_2$$  \hspace{1cm} (2)
Then, iron (II) hydroxide is oxidized to Fe(OH)$_3$. During water aeration and subsequent treatment with lime, the processes that occur are described by the following reaction:

$$4\text{Fe(НСО}_3\text{)}_2 + 8 \text{Ca} \text{(OH)}_2 + \text{O}_2 \rightarrow 8\text{CaCO}_3 \downarrow + 4\text{Fe(OH)}_3 \downarrow + 6\text{H}_2\text{O} \quad (3)$$

If the amount of oxygen contained in the water is insufficient for oxidation, chlorination or aeration of the water is carried out simultaneously with liming. From Figure 1, it can be seen that the treatment of water with lime can intensify the processes of deironing. The most effective removal of iron occurred in the first 10–30 minutes.

Under industrial conditions, water is first aerated in a cooling tower, in the pallet of which a lime solution is introduced, then the coagulation and precipitation of most of the iron compounds in a settling tank equipped with thin-layer modules take place, followed by the removal of fine
suspension by filtration. Pre-aeration is used to enrich the water with oxygen and remove part of the free carbon dioxide, the presence of which may reduce the estimated doses of reagents.

**Sludge processing**

In order to study the possibility of disposal of sludge, additives up to 5 wt.% are allowed to add to the cement composition of type I. Therefore, the precipitate was introduced into the composition of the cement in an amount of 0.5, 1.0, 1.5, 2.0, 2.5 wt.%. The effects of sludge formed during water purification on normal density, hardening time, water removal coefficient and compressive strength at the age of 2 and 28 days are shown in Fig. 2–5.

Application of additives to the composition of cement in amounts of 0.5–2.5% does not cause the change in water removal coefficient and normal density of cement (Fig. 3, 4). The beginning of hardening time is 43, 40, 39, 38 and 37 minutes for 1, 0.5, 1.0, 1.5, 2.0 and 2.5% of the introduced additive, respectively. The end of hardening is increased from 140 to 150–157 min without additives and with the introduction of additives in the amount of 0.5–2.5% (Fig. 2). The strength of cement increases from 100 to 105 and from 100 to 100.7 at the age of 2 and 28 days, respectively, which allows us to recommend an additive to the application in cement composition in amounts up to 2.5% (Fig. 5).

Thus, the developed technology is an environmentally friendly technology, which allows...
deironing water efficiently with subsequent disposal of the formed sludge.

CONCLUSIONS

The water deironing processes was studied with lime as the reagent. During liming of water with initial concentrations of iron 10, 50 and 100 mg/dm$^3$ for 2 hours, the concentrations decreased to 0.9, 8.0, 12.0 mg/dm$^3$, respectively. During oxidation in air without the use of reagents, the concentrations were significantly higher and reached 2.0, 28.0 and 30.0 mg/dm$^3$. At the initial concentration of 10 mg/dm$^3$ after 8–10 hours of precipitation during liming, a decrease in iron concentrations to values of lower MPC (0.2 mg/dm$^3$) was observed. It was shown that with the introduction of sludge into the composition of cement in amounts of 0.5–2.5%, water removal coefficient and normal density of cement do not change. The beginning of the hardening time decreases from 43 to 40–37 minutes, and the end of hardening increases from 140 to 150–157 minutes without additives and with the introduction of additives in the amount of 0.5–2.5%. The strength of cement with the sludge increases from 100 to 105 at the age of 2 days and from 100 to 100.7 at the age of 28 days. Therefore, the physicochemical characteristics of cement do not deteriorate, which allows us to recommend the application of additives in the composition of cement in amounts up to 2.5%. This will contribute to the creation of low-waste water deironing technologies.

![Fig. 4. Effect of additives consumption onto normal density of cement](image1.png)

![Fig. 5. Effect of additives consumption onto compressive strength of cement](image2.png)
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