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Applying Hydrogen Peroxide for Oxidizing Underground Water Iron

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Abstract

Oxidation of iron contained in underground low-mineralized cold waters of the Tyumen North has been studied for the case of an environmentally appropriate oxidizer such as hydrogen peroxide. The relationships for the residual content of iron depending on the concentration and the specific doze of the oxidizer have been obtained for performing the process within free volume as well as with loading a sandy filter. The results of the investigations were used for designing and constructing the underground water conditioning station with the productivity of 50 thousand m³/day at the Novy Urengoy.

Key words: underground waters, iron, hydrogen peroxide, water conditioning technology

INTRODUCTION

The oxidation of iron is one of the basic processes of underground water conditioning technology alongside with filtering through a granular layer.

The need for deironing of underground waters in using them for domestic and potable water supply is determined, first of all, by negative influence of iron compounds upon a human organism. Iron excess exerts a toxic effect on liver, spleen, brain. This factor strengthens inflammatory processes in organisms and results in the deficiency of some microelements (copper, zinc, etc.). The requirements for iron removal from water under using are determined not only by hygienic reasons, but also by a broad range of undesirable consequences of aesthetic, technical and economic character such

as traces on linen, utensils and household water-consuming equipment; corrosion and sediment in pipelines; fast failure of water-heating and water-softening systems.

Hydrogen peroxide in some cases has been applied abroad for oxidation of iron of mining, drainage and underground waters [1].

It should be noted that the processes of H₂O₂ decomposition with simultaneous oxidation Fe²⁺ to give Fe³⁺ and catalytic H₂O₂ decomposition caused by these ions, are investigated in sufficient detail [2–5].

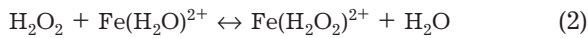
Fe²⁺ ions are oxidized by hydrogen peroxide according to a stoichiometric reaction

$$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (1)$$

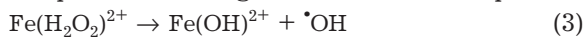
This reaction proceeds quantitatively under the excess of Fe²⁺ ions, whereas the excess of H₂O₂, results alongside with iron (III) oxidation in H₂O₂ decomposition with allocation oxygen evolution.

It is considered to be the case that the interaction of H_2O_2 with Fe^{2+} aqua ion results in the formation of $\dot{\text{O}}\text{H}$ radicals as a primary reactive species. However, the formation of the hydroxyl radical in this reaction represents only a special case of oxidation-reduction transformations of $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ complex intermediate.

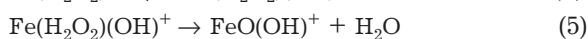
The primary act of interaction between Fe^{2+} with H_2O_2 consists in the replacement of one co-ordinated water molecule:



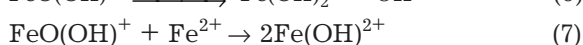
The formation of $\dot{\text{O}}\text{H}$ radicals in acidic media (so-called Fenton process) occurs as the result of the peroxo complex decomposition to give the products of single-electron transfer process:



At $\text{pH} > 3$ the iron (II) oxidation reaction rate increases, which could be connected with the dissociation co-ordinated water in the peroxo complex. The dissociation of hydrogen peroxide should result in the reduction of its oxidizing ability and, correspondingly, in decreasing the inner-sphere electron transfer reaction rate, whereas the dissociation of water would result in a considerable decrease of the oxidation-reduction potential of $\text{Fe}^{4+}/\text{Fe}^{2+}$ couple. Owing to this fact a possibility appears for the reaction of two-electron inner-sphere transfer with the formation of hydrolyzed ferryl ion [2]:

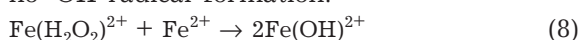


This species could participate either in the oxidation of water with the formation of OH radicals, or interact with the second iron ion without the formation of free radicals:

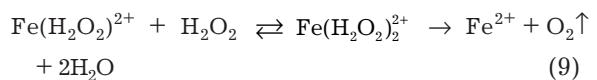


Owing to the reaction (5) occurring, the increase in the values of pH the acid-base equilibrium (4) is broken, and at $\text{pH} \geq 5.5$ the effective reaction rate constant of oxidation Fe^{2+} ceases to depend on the pH value [2].

Non-hydrolyzed $\text{FeH}_2\text{O}_2^{2+}$ complex and ferryl ion could interact with a "third particle" which can be presented, in particular, by the second iron ion. In this case the reduction of hydrogen peroxide to produce water occurs with no $\dot{\text{O}}\text{H}$ radical formation:



The second molecule of hydrogen peroxide can also manifest itself as "a third particle" *via* the interaction with peroxo complex (or ferryl ion) according to the mechanism of ligand substitution of a co-ordinated water molecule. As a result, a molecular (catalase) mechanism of H_2O_2 decomposition becomes possible to perform:



It is obvious that with the use hydrogen peroxide for underground water iron oxidation, all the reactions listed are quite likely to occur. The process becomes to a considerable extent complicated in subacidic environments wherein the formation of $\dot{\text{O}}\text{H}$ radicals is more probable, especially in the presence of organic impurities in water. Within neutral aqueous media, hydrogen donors interacting with ferryl ion, as well as traces of copper ions as co-catalysts for H_2O_2 decomposition reactions and for the oxidation of organic substances could participate in the mechanism of the process [2].

The process can also become complicated due to the formation iron (III) hydroxides. According to data from [3–5], the spontaneous H_2O_2 decomposition in the neutral aqueous media under aerobic conditions occurs on the surface of iron hydroxide microcolloid particles proceeding via non-radical mechanism. In this case the increase in the concentration of both Fe^{3+} ions, and Fe^{2+} ions results in the fact that the reaction rate of H_2O_2 decomposition process increases almost irrespective of pH value and hydrogen peroxide concentration. These factors cause the chemistry of water deironing process with the use of H_2O_2 to be complicated.

At the same time, the idea of using hydrogen peroxide as an environmentally safe oxidizer for purifying potable water from iron ions is of doubtless interest, especially in cases when traditional deironing methods are inefficient. The technology with the use of hydrogen peroxide was tested earlier in our work [6] as applied to underground waters of the Urengoy gas condensate field (GCF). The distinctive features of the composition of these waters consist in low values of water hardness (0.15–0.40 mg-eq/dm³), alkalinity (0.29–0.38 mg-eq/dm³) and water temperature (0.3–1.4 °C). The content of total iron amounts to 5.5–6.2 mg/dm³, includ-

ing Fe(II) amounting to 4.7–5.5 mg/dm³. Applying the classical methods for deironing water with such composition does not provide obtaining the normative content of iron in purified water.

EXPERIMENTAL

The laboratory-scale investigation we performed concerning the process of deironing the underground waters of the Urengoy GCF according to the H₂O₂ oxidation–filtering flow-chart, have confirmed a high efficiency of the method under consideration.

The work was carried out under conditions inherent in the operating water supply point of the Novy Urengoy waste disposal plants (WDP) within the autumn-winter time, at the minimal temperature of water under treatment.

At the first stage, the oxidation of iron (II) within free volume has been investigated. Water sampling for determining the residual iron was carried out in 1 min after entering the reagent.

At the second stage, the treatment of initial water with H₂O₂ was carried out immediately before the filtering through a laboratory-scale sand filter (*H* = 1.2 m, *d* = 0.8–1.6 mm). Without H₂O₂ use the filtering of initial water through the same sandy filter did not result in any considerable decrease of the content of iron ions in water.

RESULTS AND DISCUSSION

Figure 1 demonstrates the residual content of iron (II) in unfiltered water depending on the initial concentration hydrogen peroxide and on the specific doze of the oxidizer. One can see that the theoretical doze of the oxidizer (0.3 mg/mg) provides the oxidation of no more than 20 % of iron (II) in the initial water. To all appearance, it could be connected with the fact that in the reaction volume, alongside with oxidation of iron (II), there are catalytic H₂O₂ decomposition processes occurring. In order to reach the residual content of iron (II) equal of 0.2 mg/dm³ under these conditions (with no subsequent filtering) one should use a triple excess of the oxidizer.

Figure 2 demonstrates the residual content of the total iron in filtered water depending on the initial concentration of hydrogen peroxide and on the specific doze of the oxidizer. It is seen that employing the hydrogen peroxide as an oxidizer allows one to purify water to an almost complete extent from iron-containing compounds: the residual content of iron amounting to less than 0.1 mg/dm³.

The dependence of the residual content of total iron in filtered water on the specific doze of hydrogen peroxide demonstrates that when the basic part of the process occurs in the fil-

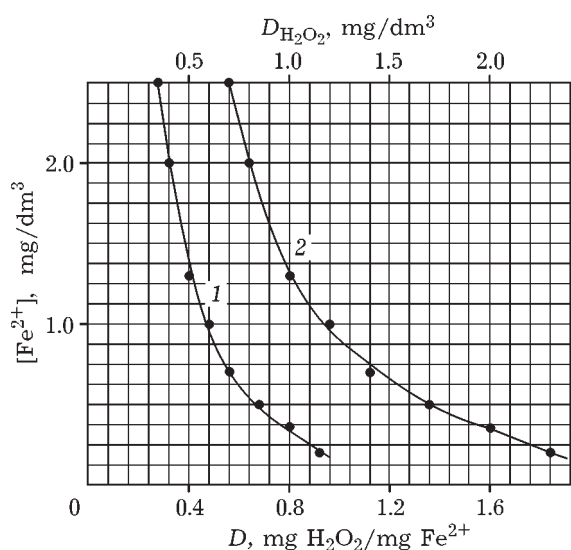


Fig. 1. Residual iron (II) content in unfiltered water depending on the initial concentration (1) and the specific H₂O₂ doze (2). [Fe²⁺]₀ = 5.0 mg/dm³, pH 6.2, T = 3 °C.

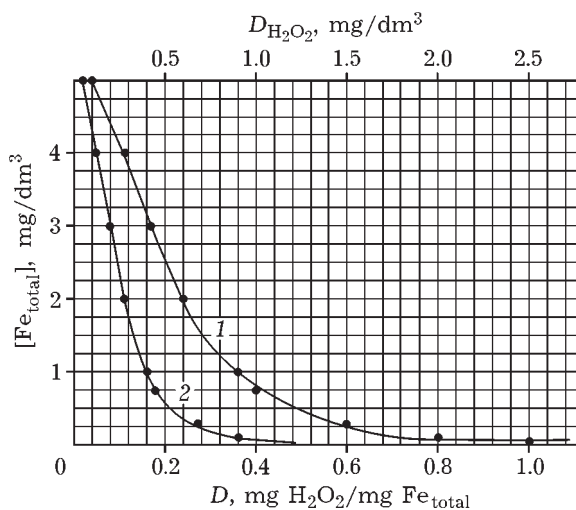


Fig. 2. Residual content of total iron in filtered water depending on the initial concentration (1) and the specific H₂O₂ doze (2). [Fe²⁺]₀ = 5.0 mg/dm³, pH 6.2, T = 3 °C.

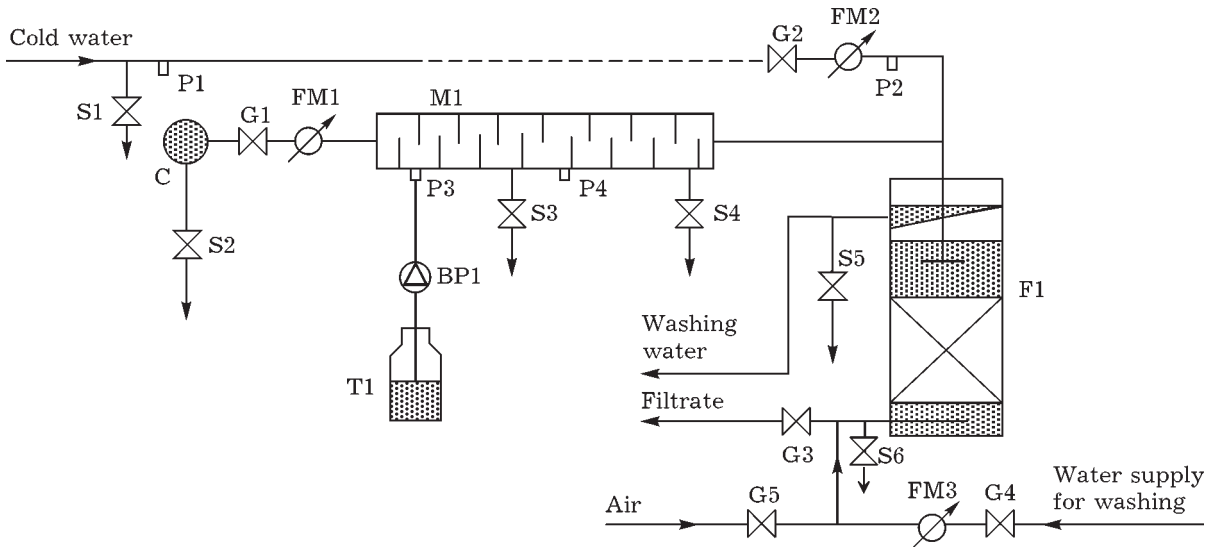


Fig. 3. Process flowsheet of the pilot installation: C – heated water collector; M1 – mixer; F1 – filter; FM1–FM3 – flowmeters; BP1 – batcher pump; T1 – tank with the reagent; S1–S6 – sampling stopcocks; G1–G5 – gates; P1–P4 – pipes for reagent input.

tering layer the reaction of iron (II) oxidation is prevailing. In order to obtain the residual content of total iron at a level of 0.05–0.10 mg/dm³ the excess of the oxidizer should not exceed 30 % with respect to stoichiometrical (calculated) doze.

The results obtained under laboratory conditions have been verified using a pilot installation with the productivity of 2.5 m³/h. The design of installation (Fig. 3) provided the possibility for processing both the initial (cold) water supplied from the distributive chamber of water-heating tanks, and heated water supplied from the distributive pipeline of the WTS filtering station (Novy Urengoy).

The oxidizer doze chosen is insufficient for the complete oxidation iron (II); the residual content of iron (II) before filtering varied within the range of 0.1–0.2 mg/dm³.

Data concerning the content of iron in water before processing and after filtering are presented in Table 1. It should be noted that the treatment of cold water has required for increasing the doze of hydrogen peroxide by 11.5 % on the average.

As it follows from the data presented, the temperature of the process does not influence the concentration of iron in filtered water. This fact allows one to reject heating before processing underground water, which heating is

frequently employed at water supply plants under the conditions of the Tyumen North.

The application of the technology proposed has improved to a considerable extent the organoleptic parameters of water quality (from 2 points to 1 point).

The results obtained have been used in performing the production project “Extending the WTS of the Novy Urengoy up to the productivity of 65.0 thousand m³/day”. The station has been accepted for permanent operation in December, 2007 after the reconstruction. The retention of iron in the purified water does not exceed 0.05 mg/dm³. Basing on the experience of starting-up and adjustment works as well as of trial operation, we have developed practical recommendations concerning the application of the technology proposed in designing the deironing stations of any productivity.

TABLE 1

Results of in-process testing the technology of potable water deironing in the Novy Urengoy

Water	Iron content, mg/dm ³			
	Initial		After treatment	
	Fe _{total}	Fe(II)	Fe _{total}	Fe(II)
Cold (+1 °C)	6.7–6.9	5.3–5.4	0.1–0.3	0
Heated (+6 °C)	5.8–6.1	4.6–4.7	0.1–0.3	0

CONCLUSION

The application of hydrogen peroxide for oxidation of underground water iron is of a great practical value, especially due to insufficient efficiency in employing classical methods. The results of laboratory-scale research and pilot tests under the conditions of operating water supply point, as well as operational parameters of reconstructed waste disposal plants of the Novy Urengoy have confirmed the technology proposed to be of a high efficiency; the results can be used for designing and reconstruction of water-supply waste disposal plants in the northern regions of Russia.

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