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KINETICS OF FERRUM(II) IONS OXIDATION BY AIR OXYGEN IN WATER IN HORIZONTAL ABSORBER WITH BUCKET-LIKE DISPERSERS

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Received: December 12, 2014 / Revised: February 23, 2015 / Accepted: July 15, 2015

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Abstract. The oxidation rate of ferrum(II) to ferrum(III) by air oxygen in water has been investigated in the horizontal absorber with bucket-like dispersers. The reaction order relative to Fe^{2+} and OH^- ions has been determined based on established dependencies of ferrum(II) ions concentration on dispersion time at their various initial concentrations and medium pH. It has been shown for the first time that at pH = 5.5–6.2 in water during oxidation of ferrum(II) ions an autocatalysis occurs due to the formed ferrum(III) ions.

Keywords: water treating, groundwater, ferrum(II), oxidation, horizontal absorber, bucket-like disperser.

1. Introduction

Ensuring humanity by quality drinking water is becoming an urgent global issue. A drinking quality of river water, which is the main source of water supply in Ukraine and many other countries, systematically decreases; its purification is difficult and expensive. As a result, the usage of groundwater defensed from land pollution and partially cleared by penetration through the filtering species is of great importance [1]. However, during penetration through the red-brown soils with limestone patches, reddish sandstone, *etc.*, water is enriched by the compounds of many chemical elements, in particular, compounds of ferrum(II), the content of which may achieve 30 mg/dm^3 and more [2]. The allowable content in tap water is 0.2 mg/dm^3 and 1.0 mg/dm^3 – for water from the wells and cappings [3]. The usage of such drinking water leads to the accumulation of hemosiderine in the liver, which destroys it and increases the risk of myocardial infarction [4].

Water is purified from Fe^{2+} ions *via* their oxidation, formation of sparingly soluble $\text{Fe}(\text{OH})_3$ and its further

removal from water. The main issue is the selection of oxidant, the cost of which determines the cost of treatment. In this respect the use of air oxygen as an oxidant for ions Fe^{2+} is of great interest. The main problem is creation and maintaining the sufficient concentration of dissolved oxygen in water, because oxygen is very poorly soluble in water [5]. Moreover, this solubility becomes smaller in the presence of dissolved salts.

Groundwater deferrization by air oxygen is accompanied by diffusive and kinetic phenomena because the process includes homogeneous and heterogeneous reactions. The total rate of the process is limited by the rate of air oxygen dilution in water and occurs in the diffusive area. Thus, at water pH of 6.7 in the open reservoir after 30 min of the process the deferrization efficiency is only 38 % [6]. If the process time is the same but air is bubbled through water layer the deferrization efficiency increases to 87 % [7]. Such high efficiency is achieved for 7 min using vacuum ejectors [8]. The effective mass exchange equipment provides the increased contact area between gas and liquid phases. Moreover, the increased rate of oxygen absorption promotes process transfer from the diffusive area into the kinetic one. However, while using vacuum ejectors and injection nozzles the great amount of energy is consumed. To decrease the energy consumption a mass-transfer apparatus ensuring high intensity of oxygen absorption may be used, for example horizontal absorber with bucket-like dispersers [9]. Its specific energy consumption is less by order compared with that of jet apparatuses. The peculiarity of the mentioned absorber is a creation of droplet high rate in the gas flow leading to the minimum thickness of immovable gas film around the droplet. Therefore, the resistance from the direction of the gas phase sharply decreases. Moreover, there is also a low

resistance from the direction of the liquid phase due to the great number of grinded droplets escaped from the disperser slits and so called “shock effect” – breaking of liquid droplets against apparatus wall or one against another [9]. Thus, in the case of using horizontal absorber with bucket-like dispersers the diffusion inhibition is sharply minimized and oxidation rate depends on the rate of the chemical reaction.

It is known [8] that Fe^{2+} oxidation is described by Eq. (1):



In accordance with Eq. (1) the reaction rate may be represented as Eq. (2):

$$-\frac{dC_{\text{Fe}^{2+}}}{dt} = k \cdot C_{\text{Fe}^{2+}}^n \cdot C_{\text{O}_2}^m \cdot C_{\text{OH}^-}^z \quad (2)$$

where k – rate constant; n, m, z – reaction orders relative to the corresponding components; $C_{\text{Fe}^{2+}}, C_{\text{O}_2}, C_{\text{OH}^-}$ – reagents concentrations, mol/m^3 .

The increase in oxygen absorption rate leads to the equality of its concentration in water to the equilibrium one and its constancy. It means that the reaction order relative to oxygen may be assumed as zero ($m = 0$) in the apparatus with bucket-like dispersers. To determine the dependence of the reaction rate on the concentration of Fe^{2+} ions and hydroxy ions it is necessary to know the reaction order relative to each of them.

There is no definite answer to the question about the reaction order relative to ferrum(II) ions – either of the first or the second order ($n = 1-2$). Concerning the reaction order relative to hydroxy ions – mainly it is close to 2 ($z = 2$). Therefore the aim of the work was to investigate the reaction rate of ferrum(II) oxidation and determine the reaction order relative to Fe^{2+} and OH^- ions.

2. Experimental

The investigations were carried out using the laboratory plant illustrated in Fig. 1.

The air by a compressor (1) was fed to the horizontal absorber (5) through a rotameter (3). The air amount was varied by a cock (2). Using a burette (4) 0.1N solution of NaOH was added. The medium pH was controlled by pH-meter (7) of 150-M type. At the outlet of absorber the droplets of dispersed water were trapped by a drop catcher (6) and returned back to the absorber. The absorber diameter was 0.5 m, its length was 0.3 m. A roller of 0.2 m diameter with two bucket-like dispersers was situated inside the absorber. According to [9] the optimum linear rate for dispersers was 10 m/s. The roller was set in motion by an electric motor (8).

The “model” water was prepared using distilled water. Before the experiments it was boiled to remove oxygen and definite amount of FeSO_4 solution was added. Water pH was established and controlled by introducing 0.1N NaOH. The initial concentration of Fe^{2+} ions was varied within 0.5–1.1 mol/m^3 ; water pH was 5.5–6.2. The experiments were carried out at 296 K under atmospheric pressure. The concentrations of Fe^{2+} ions were determined using a spectrometry method in accordance with ISO 6332:2003 and pH – using pH-meter 150M with combined electrode ESKL-08M 1.

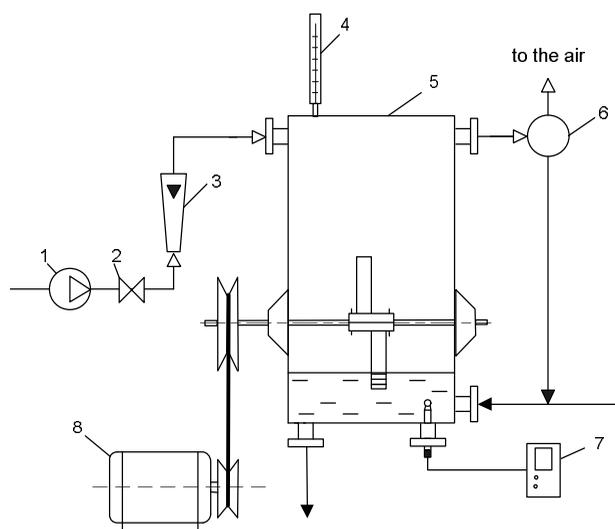


Fig. 1. The scheme of the laboratory plant for Fe^{2+} and OH^- ions oxidation by air oxygen in water: compressor (1); cock (2); rotameter (3); burette (4); horizontal absorber with bucket-like dispersers (5); drop catcher (6); pH-meter (7) and electric motor (8)

3. Results and Discussion

The change of Fe^{2+} ions concentration in time was determined using model water with the initial concentrations of Fe^{2+} ions 0.5, 0.7, 0.9 and 1.1 mol/m^3 . Water pH was 5.5, 5.7, 6.0 and 6.2. The dependence of Fe^{2+} ions concentration on time is represented in Fig. 1.

In the beginning the concentration of Fe^{2+} ions slightly decreases, then sharply reduces and in the end its change is miserable. At pH = 5.5 for the first 2000 s the concentration reduces from 1.5 to 0.8 mol/m^3 , for the next 1500 s – to 0.2 mol/m^3 and in the end of the process (not shown in Fig. 1) – from 0.2 to $0.3 \cdot 10^{-3}$ mol/m^3 . The general contact time is 10000 s.

To explain the low rate of Fe^{2+} ions oxidation in the beginning we carried out the additional experiments. The absorber was filled by water without Fe^{2+} ions and dis-

solved oxygen and then water was saturated by air oxygen. The experimental results are represented in Fig. 2.

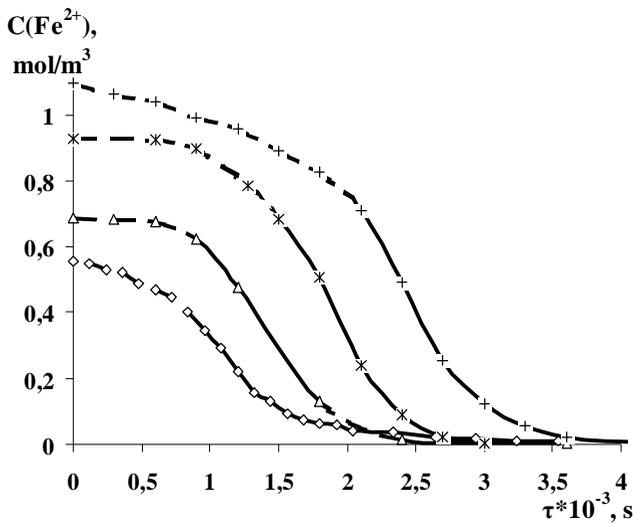


Fig. 1. Fe^{2+} ions concentration vs. contact time at pH = 5.5. The solution initial concentrations (mol/m^3) are: 1.1 (1); 0.8 (2); 0.7 (3) and 0.5 (4)

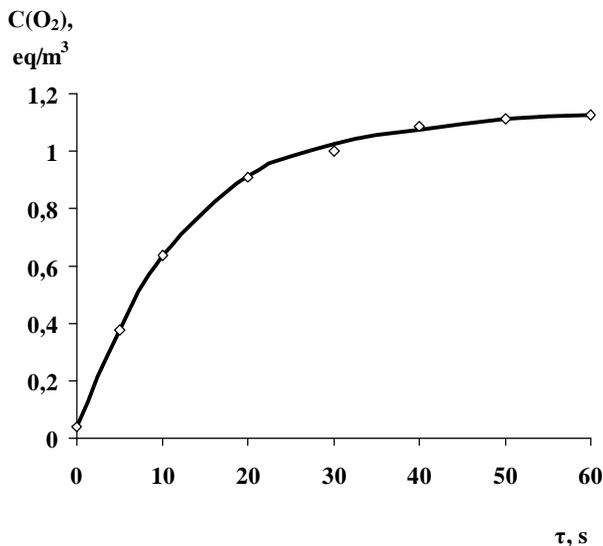
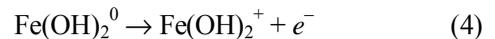
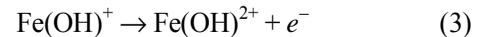


Fig. 2. Dissolved oxygen concentration vs. contact time

After 5 s the oxygen concentration in water was 0.66 eq/m^3 , that is equal to $\approx 80\%$ of saturation. The complete saturation is achieved quickly, after 20 s. It means that the low rate of Fe^{2+} ions oxidation in the beginning is not limited by the concentration of dissolved oxygen.

A lot of laboratory, factory and commercial tests prove the catalytic properties of ferrum(III) compounds over the surface of filtering material [5, 7]. Therefore it looks like the intermediate compounds (Eqs. (3) and (4))

are formed in the horizontal absorber with bucket-like dispersers at the start time [8].



To study the effect of formed ferrum(III) intermediate compounds on the reaction rate we carried out the special investigations.

We used two kinds of model water with the initial concentration of Fe^{2+} ions 0.9 mol/m^3 at pH = 5.7. The ferrum(III) compounds were added to one kind of water. Other parameters were the same as in the previous investigations.

Fig. 3 shows the dependence of Fe^{2+} ions concentration on contact time while adding ferrum(III) compounds and without them. In water with ferrum(III) compounds the oxidation rate is high but then it sharply decreases (curve 2). In the second case (without ferrum(III)) the shape of curve 1 is almost the same as the curve from previous investigations with Fe^{2+} ions concentration of 0.9 mol/m^3 and pH = 5.7. It is the confirmation that ferrum(III) compounds have catalytic reactivity not only over the surface of filtering material [5] but in water volume as well.

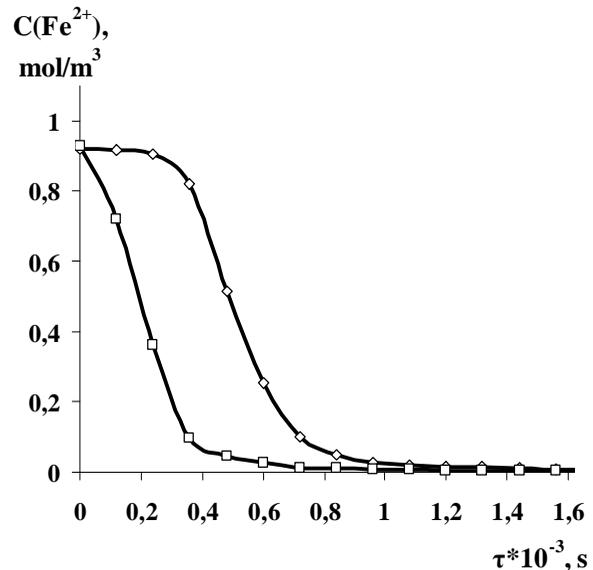


Fig. 3. Fe^{2+} ions concentration vs. contact time at pH = 5.7 and initial concentration of 0.9 mol/m^3 : without ferrum(III) compounds (1) and with ferrum(III) compounds (2)

Taking into account the autocatalytic character of Fe^{3+} ions action the reaction order of the oxidation reaction relative to Fe^{2+} and OH^- ions were determined using the kinetic curves without initiation period of the intermediate complexes, when Fe^{2+} ions concentration varies from 0.01 to 0.2 mol/m^3 . Within this range the concentrations of dissolved oxygen and ferrum(III)

compounds are more higher than those of Fe^{2+} ions. Thus, we assume the concentration of dissolved oxygen as a constant value without the influence on the reaction rate. The catalytic reactivity of ferrum(III) is also constant and does not affect values n and z .

The dependence of Fe^{2+} ions concentration on contact time in the disperser at different values of water pH is represented in Fig. 4. It is observed from Fig. 4 that at water pH = 6.2 the deferrization efficiency achieves 99.7 % after 2 min that confirms the high efficiency of the investigated disperser compared with vacuum ejectors.

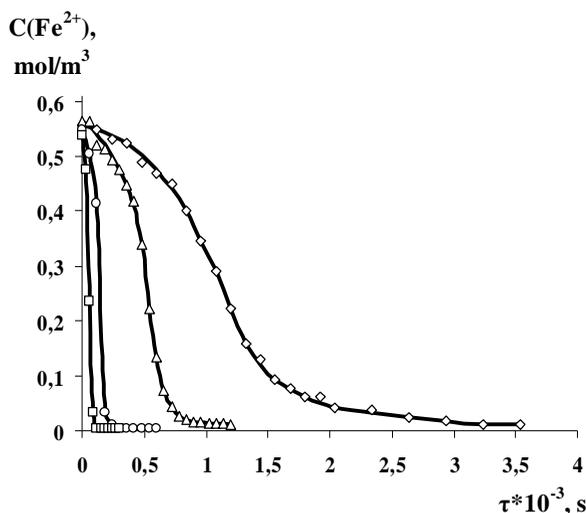


Fig. 4. Fe^{2+} ions concentration vs. contact time at pH: 5.5 (1); 5.7 (2); 6.0 (3) and 6.2 (4)

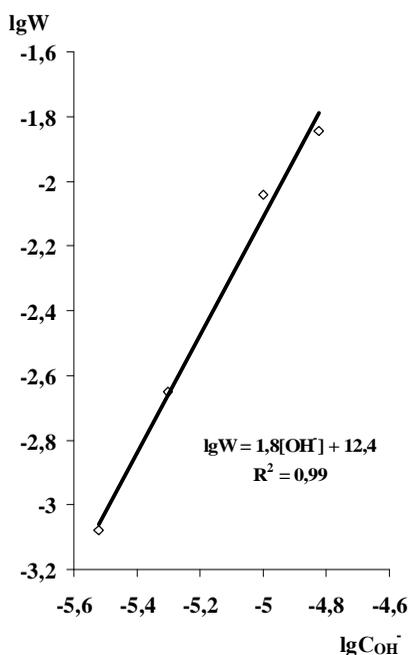


Fig. 5. Dependence of the logarithm of Fe^{2+} ions oxidation on the logarithm of OH^- ions concentration (Fe^{2+} ions concentration is 1.1 mol/m^3)

The curves (Fig. 5) obtained under the coordinates $\lg W - \lg C$ have the straight character (W – the reaction rate and C – OH^- ions concentration). The reaction order relative to OH^- ions is 1.9. The calculated value of the reaction order relative to Fe^{2+} ions is 0.7. Taking into account that the oxygen concentration is constant in the apparatus with bucket-like dispersers, the kinetic equation of Fe^{2+} ions oxidation has the form:

$$W = -\frac{dC_{\text{Fe}^{2+}}}{dt} = k' \cdot C_{\text{Fe}^{2+}}^{0.7} C_{\text{OH}^-}^{1.9} \quad (5)$$

where $k' = k \cdot C_{\text{O}_2}$

On the basis of the obtained results we determined k' , the value of which is hundred times higher than that in other apparatuses [11]. The obtained kinetic equation may be used for the calculations of groundwater purification from ferrum(II) compounds in the apparatus with bucket-like dispersers.

4. Conclusions

1. Oxidation of Fe^{2+} ions by air oxygen in water in the horizontal absorber with bucket-like dispersers at pH = 5.5–6.2 occurs in the kinetic area. The reaction order relative to Fe^{2+} ions is 0.7 and to OH^- ions – 1.9. During deferrization there is an excessive concentration of oxygen dissolved in water compared with that of Fe^{2+} and OH^- ions, therefore the reaction order relative to oxygen may be assumed as the zero one.

2. The obtained ferrum(III) compounds have the catalytic reactivity not only over the surface of filtrating material but in the water volume as well.

3. The use of the horizontal absorber with bucket-like dispersers allows to transfer Fe^{2+} ions oxidation from diffusion to kinetic area.

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**КІНЕТИКА ОКИСНЕННЯ У ВОДІ ЙОНІВ
ФЕРУМУ(II) КИСНЕМ ПОВІТРЯ У
ГОРИЗОНТАЛЬНОМУ АБСОРБЕРІ З
КОВШОПОДІБНИМИ ДИСПЕРГАТОРАМИ**

Анотація. Досліджено швидкість окиснення у воді йонів Феруму(II) до Феруму(III) киснем повітря у горизон-

тальному абсорбери з ковшоподібними диспергаторами. На основі встановлених залежностей концентрацій йонів Феруму(II) у досліджуваній воді від часу диспергування за різних їх початковому вмісту та рН визначено порядок реакції за йонами Fe^{2+} та OH^- . Вперше встановлено, що в об'ємі води за рН = 5,5–6,2 при окисненні йонів Феруму(II) має місце явище автокаталізу завдяки утвореним йонам Феруму(III).

Ключові слова: водопідготовка, очищення підземних вод, окиснення Феруму(II), горизонтальний абсорбер з ковшоподібними диспергаторами.

