

CHEMICAL OXIDATION OF FERROUS IRON IN AQUEOUS SOLUTIONS AND GROUNDWATER SAMPLES

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Abstract. Several groundwater samples from southern Estonia containing 2–3 mg/L ferrous iron were treated with ozone and hydrogen peroxide. The results of the study indicated that these powerful oxidants might be successfully used in groundwater treatment for removal of ferrous iron. Subsequent coagulation and filtration enabled to reduce the total iron content in water to 0.04–0.08 mg/L, which fully meets the Eurostandard requirements (0.2 mg/L).

Key words: groundwater, ferrous iron, oxidation, ozone, hydrogen peroxide, filtration, removal.

INTRODUCTION

High iron content in groundwater of several districts in Estonia (especially in southern Estonia) is one of the most difficult problems in using groundwater for potable water supply.

The original concentration of dissolved total iron in Estonian groundwater is usually in the range 0.05–2.0 mg/L, in some cases up to 4–5 mg/L. In case of significantly higher iron content (>5 mg/L and more) local iron corrosion of the pipelines should be suspected.

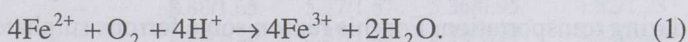
High iron content in groundwater is, of course, not only Estonian problem, it occurs world-wide. Iron and manganese are present in natural waters in their most reduced, and most soluble, forms: Fe^{2+} and Mn^{2+} . They enter groundwater under the reducing conditions existing in waters that have not been

exposed to atmospheric oxygen for long periods or in zones having active anaerobic bacterial populations. Part of the soluble iron and/or manganese can be in the form of quite stable humic and fulvic acid or colloidal silicon acid complexes. These complexes are generally oxidizable only by stronger reagents (chlorine, ozone, hydrogen peroxide, sodium hypochlorite, potassium permanganate, etc.).

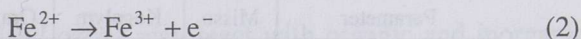
According to the Estonian Drinking Water Standard [1] the iron concentration in drinking water must not exceed 0.1, 0.3, and 1.0 mg/L for the quality classes "excellent", "good", and "satisfactory", respectively. The guideline of the EU standard (which has no classes) is 0.2 mg/L.

To meet the guidelines of excellent and good drinking water or the EU standard an effective iron removal technology is needed.

To remove iron it has to be oxidized to the state +3 to form insoluble ferric hydroxide. According to [2, pp. 168–196] the basic oxidation reaction can be written as



This reaction is favoured by an acidic medium, and the standard potential E_0 for the reduction half-reaction



is $E_0 = 0.78 \text{ V}$.

The main step for iron removal is its oxidation from the state +2 to the state +3. Aeration is obviously the most economical oxidation method. However, this method is generally recommended only for waters with a high iron concentration (>5.0 mg/L) and whose pH is over 6.0 after aeration. Moreover, iron should not be excessively chelated with organic matter or silica. Unfortunately, it often is.

According to Stumm [3], the kinetically limiting step for iron removal using atmospheric oxygen at pH around 7.0 is the rate of the oxidation reaction. Oxygen diffusion becomes limiting at pH greater than 8.0. The flocculation step can also become limiting at higher pH values.

Information on the ferrous iron oxidation and removal available from literature concerns mostly its oxidation with atmospheric oxygen at ambient temperatures, which are higher than those of typical groundwater [4].

It was expected that besides the temperature the reaction product of iron oxidation, a ferric hydroxide precipitate, might also play a role in the reaction. Both acceleration and retardation of the reaction with the addition of ferric hydroxide were reported [4]. It was pointed out that among many types of ferric hydroxide only $\gamma\text{-FeOOH}$ can be an effective catalyst [4].

Data on the impact of other chemical constituents of the initial groundwater (pH, content of bicarbonate and other metals as possible catalysts) as well as of stronger oxidants (ozone, hydrogen peroxide, etc.) at lower temperatures (<10°C) are clearly insufficient.

Hydrogen peroxide can be especially active in iron oxidation and removal cases as $\text{Fe}(\text{OH})_3$ catalyzes both the oxidation reactions it participates in and its own breakdown (Fenton reagent) [2].

This paper presents the results of a study of the kinetics of ferrous iron oxidation with air and with ozone at different bicarbonate concentrations and with hydrogen peroxide at different temperatures and pH levels.

EXPERIMENTAL

Oxidation experiments were carried out with different groundwater samples from southern Estonia (Misso, Orava, Lusti, Kaerepere) and, for comparison, from Kogalym, Siberia. The main parameters of four samples from Estonia and one from Kogalym are given in Table 1. It can be seen that all samples had quite a low ferrous iron (Fe^{2+}) content, which is obviously due to oxidation with air during transportation. For this reason some ferrous sulphate was added before the experiments to bring the initial ferrous iron concentration up to 3.5–4.0 mg/L.

Table 1. Main parameters of the groundwater samples studied

Parameter	Misso	Kogalym	Orava	Lusti	Kaerepere
pH	7.45	6.73	7.24	8.04	7.2
Alkalinity, mg-eq/L	4.4	2.0	2.8	5.5	6.0
Acidity, mg-eq/L	—	—	0.35	—	1.78
Hardness, mg-eq/L	8.0	2.0	4.9	10.5	14.4
Fe_{tot} , mg/L	2.91	2.98	2.02	2.16	0.08
Fe^{2+} , mg/L	0.12	0.05	0.68	0.73	0.08
Ca^{2+} , mg-eq/L	—	—	0.13	—	0.17
Cl^- , mg/L	1.52	2.97	0.79	—	—

— Not determined.

For the oxidation experiments a bubble column with a volume of 0.6 L kept at a constant temperature was used. To avoid premature oxidation of the ferrous iron with oxygen dissolved in the water the sample was bubbled through with a nitrogen flow before the experiments.

When preparing the model solutions with the initial ferrous iron content of 3.5–4.0 mg/L all the necessary chemicals were introduced into the reactor continuously bubbled through with nitrogen, and the moment of the introduction of the ferrous sulphate solution served as the starting point of the reaction.

After oxidation the water samples were filtered through a sand filter (sand fraction of 0.25–0.5 mm) for the removal of ferric hydroxide.

Iron (ferrous and ferric) was analysed according to [5], hydrogen peroxide according to [6], and dissolved ozone was determined using the method presented in [7].

RESULTS

The results of ferrous iron oxidation in five different groundwater samples using ozone, hydrogen peroxide, and for comparison oxygen of air at 5°C, are presented in Table 2. The highest ferrous iron removal efficiency (98–99%) was achieved by ozonation with the following filtration.

Table 2. The results of Fe^{2+} removal from groundwater samples

Technique	$\text{Fe}_{\text{tot}}/\text{Fe}^{2+}$				
	Misso	Kogalym	Orava	Lusti	Kaerepere
Initial sample (IS)	2.91/0.12	2.98/0.05	2.02/0.68	2.16/0.73	0.08/0.08
IS + Fe^{2+}	6.33/3.42	8.88/5.9	5.37/3.35	5.36/3.2	4.52/3.86
IS + Fe^{2+} + H_2O_2 (1 : 1)	6.33/0.34	8.88/1.01	5.37/0.94	5.36/0.9	4.52/0.94
IS + Fe^{2+} + H_2O_2 + filter	0.09/0.05	5.81/0.1	0.05/0.05	0.06/0.06	0.15/0.05
IS + Fe^{2+} + O_2	–	8.88/1.65	5.37/1.67	5.36/0.95	4.52/1.23
IS + Fe^{2+} + O_3	–	8.88/1.23	5.37/1.23	5.36/0.94	4.52/0.02
IS + Fe^{2+} + O_3 + filter	–	5.97/0.1	0.07/0.05	0.05/0.05	0.15/0.02

– Not investigated.

It is well known that dissolved ozone may react with organic and inorganic compounds in water directly or through the chemically very active $\cdot\text{OH}$ radicals formed as a result of molecular ozone decomposition [8]. It is also known that the $\cdot\text{OH}$ radicals are passivated by the carbonate and bicarbonate ions, which are quite natural constituents of groundwater.

To study the impact of bicarbonate ions on the ozonation of ferrous iron experiments with the model solutions were carried out at different bicarbonate concentrations: 0, 35, 100, and 350 mg/L HCO_3^- (Fig. 1). The curves in Fig. 1 clearly indicate that with increasing bicarbonate ion concentration in water the

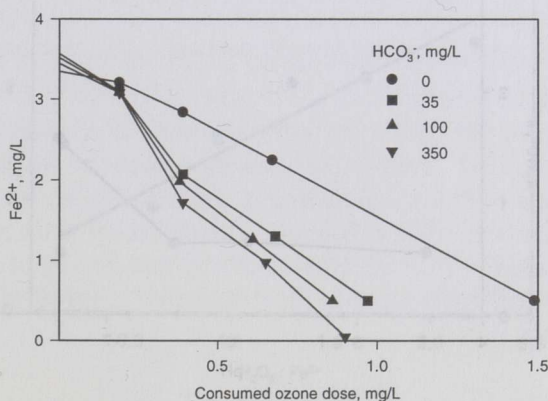


Fig. 1. Ozonation of ferrous iron in model solutions containing different amounts of HCO_3^- at 5 °C.

reaction of ferrous iron oxidation by ozone is accelerated, which means that the molecular ozone plays the key role in this reaction.

The same iron removal efficiency (98–99%) was achieved during oxidation with hydrogen peroxide at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 1:1 and with subsequent filtration (see Table 2).

Oxidation of ferrous iron with hydrogen peroxide presents even greater interest from the point of view of practical application due to its relative simplicity and lower capital/operational costs compared to ozonation. This was the reason why this process was investigated in greater detail. In both ozonation and H_2O_2 treatment, the decrease in the ferrous iron concentration in the solution can be described by the first order kinetics with the correlation coefficient $r \geq 0.990$. Figure 2 illustrates the pH-dependence of ferrous iron oxidation rate expressed by the first order rate constant k_1 (s^{-1}). It can be seen that when pH is in the range 4.5–6.5 it has almost no impact on the oxidation rate, but from 6.5 upwards a further increase in the pH value leads to a significant acceleration in the ferrous iron oxidation rate.

By varying the bicarbonate concentration in water in the same way as in the ozonation experiments we ascertained that the ferrous iron oxidation rate with H_2O_2 was almost proportional to the bicarbonate concentration (Fig. 3).

Figure 4 illustrates the impact of temperature on the ferrous iron oxidation rate at $\text{pH} = 7.5$. An increase in temperature by 10°C (from 5 to 15°C) accelerates the oxidation reaction almost 3 times. In addition, the oxidation rate changes proportionally to the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (Fig. 5).

For comparison ferrous iron was oxidized also with atmospheric oxygen (Table 2 and Fig. 6). The process proceeded several times slower than ozonation and hydrogen peroxide oxidation, and the efficiency of ferrous iron removal did not exceed 72%. Increase in the bicarbonate concentration from 0 to 350 mg/L accelerated the oxidation rate remarkably (Fig. 6).

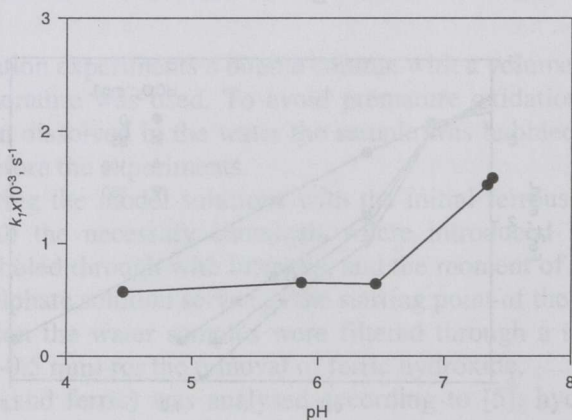


Fig. 2. Rate constant of ferrous iron oxidation (by hydrogen peroxide 1:1) vs. pH in an aqueous solution at 5°C .

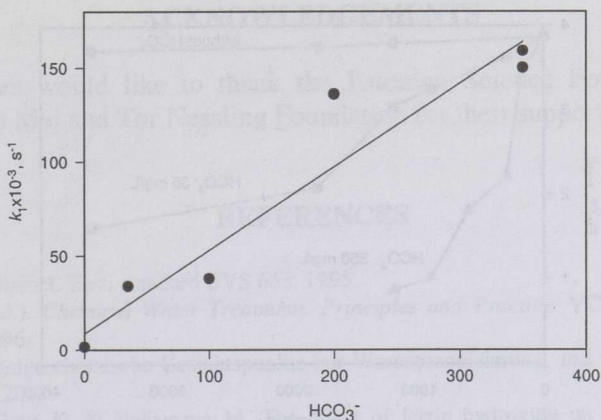


Fig. 3. Rate constant of ferrous iron oxidation (by hydrogen peroxide 1:1) at 5°C vs. HCO_3^- content in water.

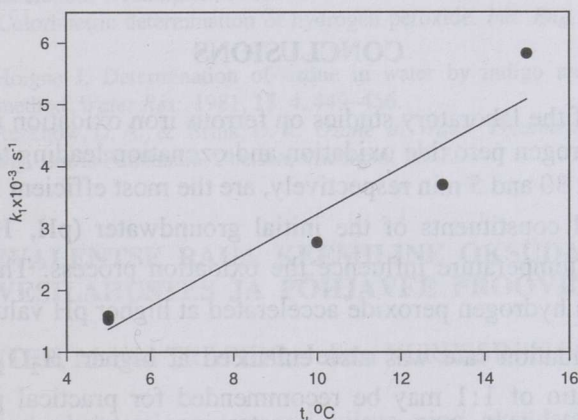


Fig. 4. Rate constant of ferrous iron oxidation (by hydrogen peroxide 1:1) vs. temperature in an aqueous solution at pH = 7.5.

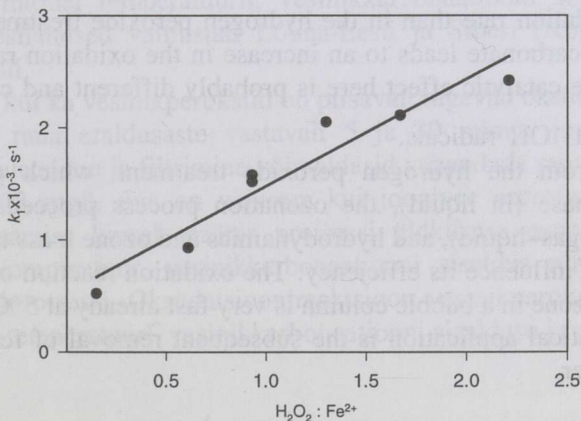


Fig. 5. Rate constant of ferrous iron oxidation at 5°C vs. Fe^{2+} and H_2O_2 ratio (mM/mM) in an aqueous solution at pH = 7.5.

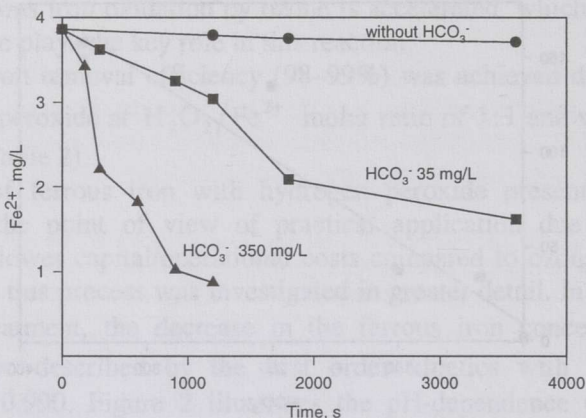


Fig. 6. Oxidation of ferrous iron at 5 °C with air at pH = 7.5.

CONCLUSIONS

The results of the laboratory studies on ferrous iron oxidation in groundwater showed that hydrogen peroxide oxidation and ozonation leading to 98–99% iron removal in about 30 and 5 min respectively, are the most efficient methods.

The chemical constituents of the initial groundwater (pH, HCO_3^- content, etc.) as well as temperature influence the oxidation process. The oxidation of ferrous iron with hydrogen peroxide accelerated at higher pH values and HCO_3^- content. The oxidation rate was also enhanced at higher $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios. However, the ratio of 1:1 may be recommended for practical purposes, as it enables to achieve >90% of ferrous iron oxidation at an entirely acceptable rate.

In ozonation both pH and HCO_3^- concentration have less impact on the ferrous iron oxidation rate than in the hydrogen peroxide treatment. Increasing the content of bicarbonate leads to an increase in the oxidation rate with ozone too; however, the catalytic effect here is probably different and connected with the passivation of $\cdot\text{OH}$ radicals.

Differently from the hydrogen peroxide treatment, which proceeds in a homogeneous phase (in liquid), the ozonation process proceeds in a heterogeneous system (gas–liquid), and hydrodynamics and ozone mass transfer are the main factors that influence its efficiency. The oxidation reaction of 3–5 mg/L of ferrous iron by ozone in a bubble column is very fast already at 5 °C and the main problem for practical application is the subsequent removal of ferric iron from the ozonized water.

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REFERENCES

1. Eesti Standardiamet. Eesti standard EVS 663. 1995.
2. Roques, H. (ed.). *Chemical Water Treatment. Principles and Practice*. VCH Publishers, New York, 1996.
3. Stumm, W. Einige chemische Gesichtspunkte zur Wasserozonisierung. *Ind. Eng. Chem.*, 1956, **18**, 201–207.
4. Tamura, H., Goto, K. & Nagayama, M. The effect of ferric hydroxide on the oxygenation of ferrous ions in neutral solutions. *Corrosion Sci.*, 1976, **16**, 197–207.
5. *Standard Methods for the Examination of Water and Wastewater*. 17th edn. American Public Health Association, Washington, 1989.
6. Eisenberg, H. Colorimetric determination of hydrogen peroxide. *Ind. Eng. Chem.*, 1943, **15**, 5, 327–328.
7. Bader, H. & Hoigne, J. Determination of ozone in water by indigo method and submitted standard method. *Water Res.*, 1981, **15**, 4, 449–456.
8. Langlais, B., Reckhow, D. A. & Brink, D. R. *Ozone in Water Treatment – Application and Engineering*. Lewis Publishers, Chelsea, Michigan, 1991.

KAHEVALENTSE RAUA KEEMILINE OKSÜDATSIOON VESILAHUSTES JA PÕHJAVEE PROOVIDES

Rein MUNTER, Marina TRAPIDO, Jelena VERESSININA ja Juha KALLAS

On määratud oksüdatsiooniprotsessi kiirus ning oksüdatsiooni aste kahevalentse raua oksüdeerimisel õhuhapnikuga, osooniga ja vesinikperoksiidiga vesilahustes mitmel temperatuuril, vesinikkarbonaatiooni sisaldusel ning pH väärtusel. Vesilahused valmistati Lõuna-Eesti ja Siberi (Kogalõmi) põhjavee proovide baasil.

Nii osoon kui ka vesinikperoksiid on piisavalt tugevad oksüdeerijad, et tagada 98–99%-line raua eraldusaste vastavalt 5 ja 30 minuti jooksul. Vesilahuse järgnev koagulatsioon ja filtrimine võimaldasid vähendada raua üldsisaldust vees kuni 0,04–0,08 mg/l, mis on väiksem kui joogivee eurostandard (0,2 mg/l). Osooni kasutamise korral määras protsessi üldkiiruse osooni massiülekande kiirus. Vee temperatuur, vesinikkarbonaatiooni sisaldus ning pH mõjutavad oksüdatsiooniprotsessi. Oksüdatsioonireaktsioon vesinikperoksiidiga ning osooniga kiireneb temperatuuri, vesinikkarbonaatiooni sisalduse ja pH kasvuga.