

Contributions of homogeneous, heterogeneous and biological iron(II) oxidation in aeration and rapid sand filtration (RSF) in field sites

C. G. E. M. van Beek, J. Dusseldorp, K. Joris, K. Huysman, H. Leijssen, F. Schoonenberg Kegel, W. W. J. M. de Vet, S. van de Wetering and B. Hofs

ABSTRACT

In groundwater treatment, after aeration, iron(II) is precipitated in rapid sand filtration (RSF) by homogeneous, heterogeneous and biological oxidation. The contribution of homogeneous iron(II) oxidation may be calculated from equations and constants available in the literature. Heterogeneous iron(II) oxidation produces hydrous ferric oxides coated filter sand, resulting in a growing filter bed height, from which the contribution of heterogeneous iron(II) oxidation may be estimated. The complement is contributed by biological iron(II) oxidation. At present this contribution may also be estimated by *Gallionella* spp. counts by quantitative real-time polymerase chain reaction. Based on field data of drinking water treatment plants from the Netherlands and Belgium, it appears that at pH \approx 7.5 biological iron(II) oxidation is the main iron(II) removal process. At higher pH homogeneous iron(II) oxidation becomes dominant, while at lower pH heterogeneous iron(II) oxidation delivers a relevant contribution. The distribution of these oxidation processes is influenced by RSF operation such as presence of supernatant water, wet or dry (trickle) filtration, oxygen concentration, filter velocity, etc. Experience shows that the distribution between these three iron(II) oxidation processes may change over time. These results are important for RSF operation, iron sludge production, and fields like chemical well clogging.

Key words | aeration, drinking water, heterogeneous and biological iron(II) oxidation, homogeneous, rapid sand filtration (RSF)

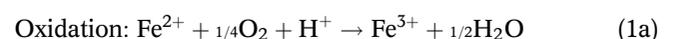
INTRODUCTION

In the treatment of anaerobic groundwater to drinking water in Western Europe, iron(II) is usually removed by aeration and rapid sand filtration (RSF) producing hydrous ferric oxides (HFO). Drinking water prepared in this way meets the legal limit of <0.2 mg/l iron, usually containing <0.05 mg/l iron. Recently, *Tekerlekopoulou et al.* (2013) reviewed this process.

In the oxidation of iron(II) to HFO, three processes may be distinguished (*Böhler 1999; van Beek et al. 2012*):

homogeneous (=flocculent) oxidation, heterogeneous (=adsorptive, autocatalytic, or contact) oxidation and biological oxidation.

Homogeneous iron(II) oxidation is characterized by the oxidation of dissolved iron(II) by dissolved oxygen, subsequent hydrolysis and precipitation of HFO:



C. G. E. M. van Beek (corresponding author)
B. Hofs
KWR Watercycle Research Institute,
PO Box 1072,
Nieuwegein 3430 BB,
The Netherlands
E-mail: Kees.van.Beek@kwrwater.nl

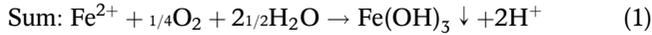
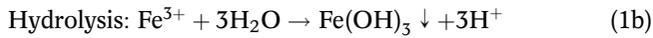
J. Dusseldorp
W. W. J. M. de Vet
Water utility Oasen,
PO Box 122,
Gouda 2800 AC,
The Netherlands

K. Joris
K. Huysman
Water utility Pidpa,
Desguinlei 246,
Antwerp 2018,
Belgium

H. Leijssen
F. Schoonenberg Kegel
Water utility Vitens,
PO Box 1205,
Zwolle 8001 BE,
The Netherlands

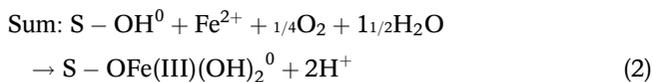
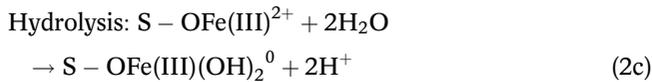
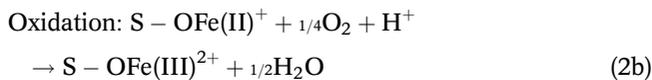
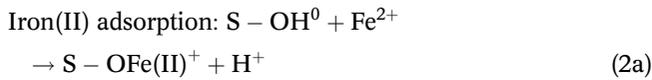
S. van de Wetering
Water utility Brabant Water,
PO Box 1068,
BC's-Hertogenbosch 5200,
The Netherlands

W. W. J. M. de Vet
Now at water utility WML,
PO Box 1060,
Maastricht 6201 BB,
The Netherlands



From Equation (1) it is clear that homogeneous oxidation is favored by a high oxygen concentration and a high pH. These conditions are achieved by very intensive aeration, as in aeration-degassing-towers. In this process HFO flocs will develop and accumulate in the aeration tank and/or in the supernatant water on top of the filter bed, and, as long as dissolved iron(II) is present also in the filter bed. The presence of this sludge on top of the filter bed makes regular backwashing necessary.

In heterogeneous iron(II) oxidation several steps may be distinguished: first adsorption of dissolved iron(II) by HFO surfaces (S-OH⁰: surface hydroxyl group), followed by oxidation of the adsorbed iron(II). The final step is hydrolysis of the adsorbed ferric iron:

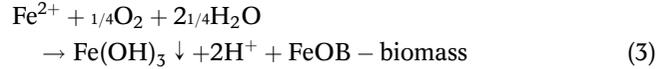


Equation (2) shows that for heterogeneous oxidation HFO-surfaces are necessary for adsorption. Consequently, this process will mainly occur inside the filter bed and the development of HFO precipitates on these surfaces will result in growing filter-grains. Consequently, heterogeneous iron(II) oxidation is characterized by an increase over time of the thickness of the filter bed.

Characteristic for heterogeneous iron(II) oxidation is that adsorption and oxidation may occur separated in

time. This phenomenon is advantageously applied in subsoil iron removal (SIR) (van Beek 1985).

Biological iron(II) oxidation may be represented as:



In natural systems this oxidation process generally occurs under rather special conditions: dissolved iron(II)-oxygen interfaces, generally characterized by variable iron(II) but low oxygen concentrations and slightly acid to neutral (5.5 < pH < 7.0) conditions (Emerson & Weiss 2004). Recently, it was shown that the combined presence of dissolved iron(II) and oxygen is the main prerequisite for biological oxidation by *Gallionella ferruginea* (Hanert 2006), a condition which is representative for RSF. Indeed, *Gallionella* spp. are generally present in RSFs (Mouchet 1992; Pacini *et al.* 2005; Qin *et al.* 2009) and their numbers were even determined in the pilot-plant trickling filters described below (de Vet *et al.* 2011).

Here we will derive the contribution of homogeneous, heterogeneous and biological iron(II) oxidation and precipitation in the treatment of anaerobic groundwater to drinking water by aeration and RSF under various conditions. We will do this with the help of data from full-scale operation water treatment plants (WTPs) and one pilot plant. These data are representative for usual operational field conditions and cover a wide range of groundwater chemistries.

As soon as the optimal conditions for each of these processes are available, it is possible to optimize WTPs with respect to iron(II) removal. Moreover, the results of this study are of relevance to other fields where iron(II) precipitation plays a role, like well clogging.

CALCULATION OF THE CONTRIBUTION OF EACH OXIDATION PROCESS

The rate equation for homogeneous oxidation may be represented as (Stumm & Morgan 1996):

$$\frac{d}{dt}[\text{Fe}^{2+}] = -k_1 \frac{[\text{Fe}^{2+}][\text{O}_2]}{[\text{H}^+]^2} \quad (4)$$

where k_1 represents the rate constant for homogeneous oxidation ($\text{mol.l}^{-1}.\text{sec}^{-1}$). This relation is generally accepted and applied (e.g. de Vet 2011, p. 226). After integrating Equation (4) at constant oxygen concentration and constant pH, and after inserting the appropriate initial condition, the fraction of iron(II) precipitated by homogeneous oxidation as a function of residence time may be calculated as:

$$\frac{[Fe^{2+}]_0 - [Fe^{2+}]}{[Fe^{2+}]_0} = 1 - \exp\left(-k_1 \frac{[O_2]}{[H^+]^2} \tau\right) \quad (5)$$

where $[Fe^{2+}]_0$ represents the concentration of iron in the abstracted groundwater (mol/l), $[Fe^{2+}]$ the concentration of iron leaving the filter bed (mol/l), and τ (sec) the total residence time of the treated water during aeration, in supernatant water and in the iron removal part of the filter bed. The iron removal part of the filter bed was estimated to be in single bed filtration the top half of the filter bed height (Štembal *et al.* 2005) and in double bed filtration the height of the first filter bed. If these conditions are not met, the resulting variation is usually small to negligible.

The value of k_1 appears very sensitive to temperature (Stumm & Morgan 1996) and water composition (Sung & Morgan 1980). Davison & Seed (1983) determined the value of k_1 in lake-water of 10°C . As the temperature of the abstracted groundwater in the Netherlands varies between

10 and 12°C , and the chemical composition of lake water is more or less similar to the chemical composition of groundwater used for the public drinking water supply, their value as determined at sub-atmospheric oxygen concentration has been used: $k_1 = 2.2 \cdot 10^{-15} \text{ mol.l}^{-1}.\text{s}^{-1}$.

Figure 1 shows the fraction of iron(II) oxidized as a function of pH for three residence times.

As in RSF a residence time of 10 minutes is considerable, this figure shows that under these conditions removal of dissolved iron(II) by homogeneous oxidation becomes incomplete to negligible at $\text{pH} < 7$ to 7.5 . However, Equation (5) is only valid at constant oxygen concentration and at constant pH. During oxidation of iron(II) oxygen is consumed and protons are produced, resulting in a shift of the relations in Figure 1 to the right. The magnitude of this shift depends on the concentration of iron(II) to be oxidized and the buffer capacity (Stumm & Morgan 1996, p. 885) of the treated water. The decrease in pH in the first filter bed, due to removal of iron(II) is usually not greater than 0.2 to 0.3 pH units, and a maximum of 0.5 units (personal communication, van den Akker 2015), while the decrease in oxygen concentration is usually not greater than 0.05 mmol/l . The influence of both of these changes on the fraction of iron(II) oxidized can be estimated from Figure 1.

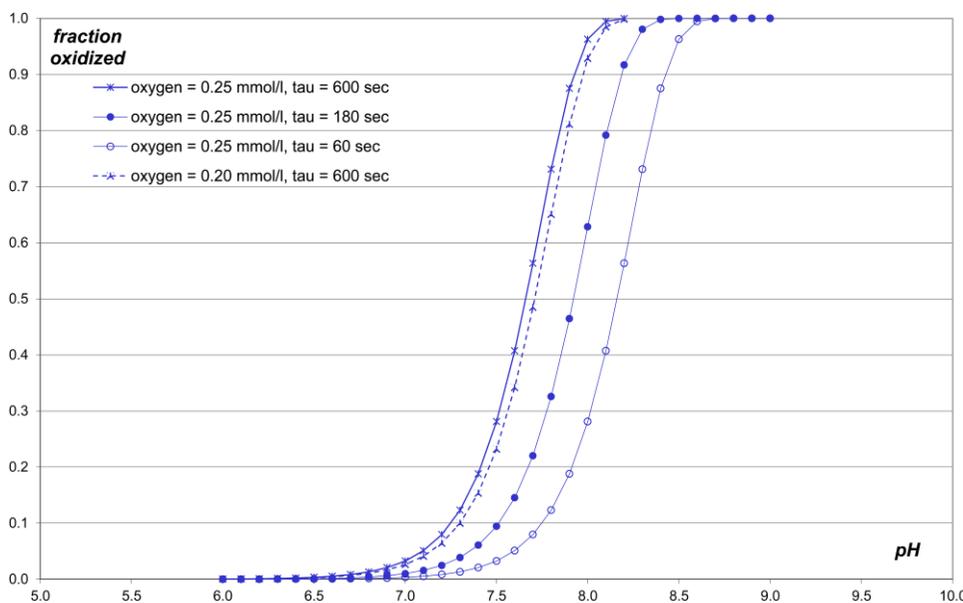


Figure 1 | Fraction of iron(II) oxidized by homogeneous oxidation as function of pH for three values of residence time and two values of oxygen concentration ($k_1 = 2.2 \cdot 10^{-15} \text{ mol.l}^{-1}.\text{s}^{-1}$).

The rate equation for heterogeneous oxidation may, in analogy to Sung & Morgan (1980) and Tamura *et al.* (1980), be represented as:

$$\frac{d}{dt}[Fe^{2+}] = -k_2 \frac{[S - OH^0][Fe^{2+}][O_2]}{[H^+]} \quad (6)$$

where k_2 represents the rate constant for heterogeneous oxidation ($l.mol^{-1}.sec^{-1}$), and $[S-OH^0]$ the adsorption capacity for iron(II) (mol/l). Integration of this equation yields:

$$\frac{[Fe^{2+}]_0 - [Fe^{2+}]}{[Fe^{2+}]_0} = 1 - \exp\left(-k_2 \frac{[S - OH^0][O_2]}{[H^+]} \tau\right) \quad (7)$$

However, Equation (7) is hard to use as there is no unanimous opinion with regard to the adsorption of iron(II) by HFO (Appelo & Postma 2005, p. 340; Hiemstra & van Riemsdijk 2007), and because the adsorption capacity is hard to estimate as there is no general relation between this capacity, or HFO surface exposure, and HFO content.

As already mentioned, heterogeneous iron(II) oxidation is characterized by bed height growth. By drawing up a balance between the total amount of iron supplied to the filter bed and the amount of iron bound inside the filter, the contribution of heterogeneous iron-oxidation to total iron removal is estimated.

If the WTP consists of several (parallel) filters, and all filters are operated identically, the mass of iron supplied per m^2 of filter bed per day equals:

$$m_{Fe, supplied} = \frac{Vc_{Fe}}{1,000A} \quad (8)$$

with $m_{Fe, supplied}$ mass of iron supplied ($kg Fe.m^{-2}.day^{-1}$), V total volume water treated each day (m^3/day), A total surface area of the filter bed (m^2), and c_{Fe} concentration of iron in abstracted groundwater (mg/l).

If all filter beds are not operated identically, the mass of iron supplied may also be calculated from the filter-flux and equals:

$$m_{Fe, supplied} = \frac{qc_{Fe}h}{1,000} \quad (9)$$

with q filter-flux ($m^3.m^{-2}.h^{-1}$) and h average number of operation hours per day (h/day).

The mass of iron removed by heterogeneous oxidation may be calculated from the bed-height-growth-rate as:

$$m_{Fe, removed} = \frac{10}{365} r_{bed} d_{coating}^{bulk} f_{Fe} \quad (10)$$

with r_{bed} bed height growth rate ($cm/year$), $d_{coating}^{bulk}$ bulk density of iron growth on filter grains (kg dry matter/ l material), and f_{Fe} iron content of filter grain coating ($kg Fe/kg$ dry matter).

Filter bed height may be measured conveniently over time. However, bed height growth may not only be governed by an increase in grain diameter, but may also be affected by other conditions. Occasionally, iron sludge may contain appreciable amounts of filter bed grains. Apparently, during back-washing filter bed material has been spilled over, resulting in an under-estimation of the bed height growth rate. Contrarily, bed height growth rate may also be over-estimated when fine sand (suspended matter) is delivered by one or more of the production wells. Both phenomena did not occur in the WTPs included in this study.

Filter beds may be back-washed in many ways: intensively or extensively with water, mixtures of water and air or alternately with water and mixtures of water and air, with varying velocities and with varying time-lengths. By intensive back-washing, HFO coated filter sand grains will be rubbing against each other and thereby losing a part of their coating. This loss will result in a too low estimate of the filter bed height growth rate. Consequently, all calculated contributions of heterogeneous iron(II) oxidation in iron(II) removal are actually minimum values.

The apparent density of the growth of the iron pellets has been determined by water utility Pidpa for WTP Grobbedonk as $1.22 kg/l$ bulk material, inclusive porosity, as an average of five analyses varying between 1.16 and $1.24 kg/l$ consisting of pure HFO pellets. This value is in good agreement with the range of 1.15 to $1.30 kg/l$ provided by the Residuals Management Cooperation (Dutch: Reststoffenuitvoering). The iron content of these grain-coatings has been determined by Pidpa as $0.428 kg Fe/kg$ dry matter. This value is somewhat below the range of values for iron-sludge

as determined by 'Reststoffenunie', which range from 0.45 up to 0.50 kg Fe/kg dry matter.

With respect to biological iron(II) oxidation, several studies have shown that *Gallionella* spp. are the dominant Iron Oxidizing Bacteria (FeOB) in RSF (de Vet et al. 2012). These organisms are strictly chemolithotrophic, which means that they are completely dependent for their energy on the oxidation of dissolved iron(II) by oxygen. This unique property allows the estimation of the role of biological iron(II) oxidation in total iron(II) removal. By drawing up an iron mass balance and a *Gallionella* spp. mass balance (calculated from the number of *Gallionella* spp. as determined by quantitative real-time polymerase chain reaction (qPCR)) over the RSF, the actual biomass yield (=dry weight (DW) of *Gallionella* spp. per unit weight of iron(II) oxidized) is determined. Values for the maximum biomass yield reported in literature equal 0.013 g DW/g Fe (Neubauer et al. 2002) and 0.006 g DW/g Fe (Lütters & Hanert 1989). By comparing the actual value for the biomass yield with these maximum values, the contribution of biological iron(II) oxidation to total iron(II) oxidation may be estimated. For details refer to de Vet (2011) and de Vet et al. (2011, 2013).

If no iron and/or *Gallionella* spp. mass balance is available, the contribution of biological iron(II) oxidation may be estimated as the complement of homogeneous and heterogeneous iron(II) oxidation.

As iron oxidizing bacteria (FeOB) need surfaces for their attachment, this process may only occur inside the filter bed. Over time the pores inside the bed will become clogged by biomass and by biologically produced HFO, making regular back-washing necessary.

RESULTS AND DISCUSSION

Distribution of oxidation processes under usual operational conditions

The contribution of the various iron(II) oxidation processes to iron(II) removal by aeration and RSF has been determined in WTPs under usual operational conditions.

In aeration and RSF many varieties may be distinguished (Böhler 1999; DVGW 2005; de Moel et al. 2006),

which are fine-tuned to the chemical composition of the abstracted groundwater to be treated. In this research four classes have been distinguished, see Table 1.

The resulting increases in pH in Table 1 are averages: the increase in pH not only depends on the intensity of aeration, but also on the buffer capacity of the aerated water.

Table 2 presents, besides a short summary of abstracted groundwater qualities, a summary of the contribution of the various iron(II) oxidation processes to total iron(II) removal for the distinguished classes of aeration and RSF for various WTPs, as estimated by the methods described.

Table 2 shows that the calculated contribution of homogeneous iron(II) oxidation to iron(II) removal is in line with theory: absent to negligible at pH < 7 to 7.5 and increasing with increasing pH. These calculated values are somewhat over-estimated, as the initial values for oxygen concentration and pH have been substituted in Equation (5) and the substituted retention times inside the filter are probably too large.

This table also shows that the contribution of heterogeneous iron(II) oxidation to iron(II) removal is relevant at low pH, with moderate aeration, and decreasing with increasing pH and increasing aeration. These values may vary somewhat, as for the calculation of this contribution unique values have been applied for bulk density (=1.22 kg/l) and iron content (=0.428 kg Fe/kg dry matter). In practice these values will probably vary somewhat between the various sites.

Table 1 | Classes of aeration and RSF distinguished in this research

Class	Description
I	Very intensive aeration, resulting in high pH and high oxygen concentration On top of the filter, supernatant water is present
II	Intensive aeration, resulting in medium pH and medium oxygen concentration On top of the filter, there is supernatant water
III	Moderate aeration, slight increase of pH and low oxygen concentration Some supernatant water. Compared to other types, usually higher filter velocity
IV	Very intensive aeration, resulting in high pH and high oxygen concentration Filtration of mixture of air and water (dry or trickling infiltration)

Table 2 | Estimated contributions of homogeneous, heterogeneous and biological iron(II) oxidation to iron removal in aeration and RSF ($k_1 = 2.2 \times 10^{-15} \text{ mol.l}^{-1} \cdot \text{sec}^{-1}$, $d_{\text{coating}}^{\text{bulk}} = 1.22 \text{ kg/l}$, and $f_{\text{Fe}} = 0.428 \text{ kg/kg}$)

Water treatment plant	Balen		Bunnik		Dalen		Grobbe-donk		Haaren		Groene-kan		Harderbroek		Herentals		Loosdrecht		Macharen		Veghel		Vlierdien	
	Pidpa	WMD	Vitens	WMD	Vitens	WMD	Pidpa	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD	Vitens	WMD
Chemical composition abstracted groundwater																								
pH	6.60	6.30	7.39	6.30	6.60	6.60	7.82	7.46	7.65	6.75	7.47	7.05	7.32	7.10										
Electrical conductivity, EC (mS/m)	31.0	44.7	44.0	47.3	39.9	34.4	26.6	59.5	65.6	45.9														
Alkalinity (mmol _e /l)	2.92	1.07	4.43	3.94	2.57	4.00	1.90	4.16	5.80	5.20														
Iron concentration (mg/l)	27	3.25	12	34.7	0.46	19.7	5.34	12	2.5	4.3														
Aeration and RSF class	III	I	I	III	III	I	I	II	I	III	II	III	I	I										
Calculation contribution iron(II) removal by homogeneous oxidation (%)																								
Oxygen concentration after aeration (mg O ₂ /l)	5	2	5.5	9	6.5	8.5	3	6.5	6	9														
pH after aeration	6.7	7.8	6.5	6.7	7.95	8.15	6.85	8	7.1	8.1	7.8													
Filter flux (m ³ /(m ² ·h))	18.4	10	11.8	5.5	7	9	8.1	8	14	8.8	7													
Residence time in aeration tower (min)	0	0	0	0	3	0	0	0	0	3	3													
Residence time in supernatant water (min) ¹	0.8	1.8	0.0	2.7	3.4	1.3	1.9	2.3	1.1	1.7	2.1													
Residence time in filter bed (min) ²	2.3	2.4	5.1	8.7	3.4	2.7	5.3	3.0	3.4	2.7	3.4													
Total residence time (min)	3.2 ^a	4.2 ^b	5.1 ^a	11.5 ^a	9.9 ^b	4.0 ^b	7.2 ^a	5.3 ^b	4.5 ^a	7.4 ^b	8.6 ^b													
Calculated contribution homogeneous oxidation (%)	0	46	0	1	95	94	0	76	2	99	72													
Calculation contribution iron(II) removal by heterogeneous oxidation (%)																								
Iron supply (kg Fe/(m ² bed area, day))	11.675 ^c	0.355 ^d	1.948 ^d	4.485 ^c	0.078 ^d	0.147 ^d	2.489 ^c	0.359 ^d	2.622 ^d	0.288 ^d	0.408 ^d													
Bed height growth (cm/year)	485	2.5 [#]	60	105	negl	2 [#]	60	5 [#]	60	negl	negl													
Iron accumulated in RSF (kg Fe/(m ² bed area, day))	6.938	0.036	0.858	1.502	negl	0.029	0.858	0.072	0.858	negl	negl													
Calculated contribution heterogeneous oxidation (%)	59	10 [#]	44	33	negl	19 [#]	34	20 [#]	33	negl	negl													

(continued)

Table 2 | continued

Water treatment plant	Balén		Bunnik		Dalen		Grobbe-donk		Haaren Brabant Water		Groenekan		Harderbroek		Herentals		Loosdrecht		Macharen Brabant Water		Veghel Brabant Water		Vlierden Brabant Water	
	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD	Pidpa	Vitens	WMD
Water utility																								
Calculation contribution iron(II) removal by biological oxidation (%)	60	46	44	34	44	44	34	95	36	94	35	76	34	99	72									
Sum homogeneous and heterogeneous oxidation (%)	40	54	56	66	56	56	66	5	64	6	65	24	66	1	28									
Calculated contribution biological oxidation (%)																								

¹Height of supernatant water on filter bed 0.25 m, in WTPs Bunnik, Groenekan and Loosdrecht 0.3 m, in WTP Dalen 0 m, in WTP Haaren 0.4 m and in WTP Harderbroek 0.2 m.

²(initial) Filter bed height 2 m, in WTPs Balén and Herentals 1.8 m, in WTP Dalen 2.5 m.

³Full length of filter bed available, ⁴upper half of filterbed relevant, ⁵calculated from filter-flux, ⁶calculated from drinking water production.

⁷As these values for the bed height growth rate may contain a large error, the corresponding values for the contribution of heterogeneous iron(II) oxidation have been omitted.

The most relevant conclusion from this table is that under usual operational conditions biological oxidation of iron(II) is the main oxidation process, except at pH > 7.6 to 7.8 where homogeneous oxidation of iron(II) is the dominant oxidation process, and with a relevant contribution of heterogeneous oxidation at pH < ca. 7.

Distribution of oxidation processes as influenced by filter velocity

Table 2 shows the combined effect of abstracted groundwater chemistry and RSF operation on iron removal. Table 3 summarizes the results of variations in filter flux on the contribution of the various iron(II) oxidation processes at WTP Balén (Pidpa).

Table 3 shows that, regardless of the operation of the RSF, the contribution of homogeneous iron(II) oxidation is anyway negligible. However, the contribution of heterogeneous iron(II) oxidation appears to be a function of filter flux: the higher the filter flux, the greater the contribution of heterogeneous iron(II) oxidation to total iron(II) oxidation. Grohmann *et al.* (1989) mention application of much higher filter fluxes.

As the contribution of homogeneous iron(II) oxidation is negligible, the contribution of biological iron(II) oxidation must be the complement of heterogeneous iron(II) oxidation. The decreasing contribution of biological iron(II) oxidation with increasing filter velocity may be most elegantly explained by a decreasing attachment capacity of *Gallionella* spp. with increasing filter velocity and, according to Table 2, with decreasing pH.

Distribution of oxidation processes in pilot-plant trickling filters

In order to get a better understanding of the removal of iron(II) in trickling filters, pilot-plant experiments ($\emptyset = 1 \text{ m}^2$) were executed. These filters were filled with anthracite (1.4 to 2.5 mm) in WTP Lekkerkerk (Oasen) and with sand (1.7 to 2.5 mm) in WTP De Hooge Boom (Oasen). They were operated with two velocities, while the bed surface height was continuously monitored and the actual yield was regularly determined.

Table 3 | Contributions of homogeneous, heterogeneous and biological iron(II) oxidation to iron removal by aeration and RSF as function of filter flux. Results from WTP Balen (Pidpa) ($K_1 = 2.2 \cdot 10^{-15} \text{ mol.l}^{-1}.\text{sec}^{-1}$, $d_{\text{coating}}^{\text{bulk}} = 1.22 \text{ kg/l}$, and $f_{\text{Fe}} = 0.428 \text{ kg/kg}$)

WTP Balen (Pidpa)

Calculation iron(II) removal by homogeneous oxidation (%)

Oxygen concentration after filtration (mg O ₂ /l)	3	3	3
pH after filtration	6.65	6.65	6.65
Filter flux (m ³ /(m ² .h))	11.3	15.6	18.4
Residence time in supernatant water (min) ¹	1.3	1	0.8
Residence time in filterbed (min) ¹	3.8	2.8	2.3
Total residence time (min) ²	5.2	3.7	3.2
Calculated contribution homogeneous oxidation (%)	0	0	0

Calculation iron(II) removal by heterogeneous oxidation (%)

Iron concentration (mg/l)	27	27	27
Iron supply (kg Fe/(m ² bed area.day))	7.17	9.90	11.67
Bed height growth (cm/year)	215	330	485
Iron accumulated in RSF (kg Fe/(m ² bed area.day))	3.08	4.72	6.94
Calculated contribution heterogeneous oxidation (%)	43	48	59

Calculation contribution iron(II) removal by biological oxidation (%)

Sum homogeneous and heterogeneous oxidation (%)	43	48	59
Calculated contribution biological oxidation (%)	57	52	41

¹Height supernatant water on filterbed 0.25 m.

²Initial filter bed height 1.8 m.

Figure 2 shows the results of the continuous bed height measurements and of the contribution of biological iron(II) oxidation to iron(II) removal of the trickling filters at WTP Lekkerkerk (Oasen).

Remarkable in Figure 2 is the sudden change in bed height growth rate in filter FC41 (filter flux 10 m/h) mid-September 2011, and the stable growth rate before and after this change. The growth rate in filter FC42 (filter flux 25 m/h) is rather constant, however after removing the growth of the filter bed mid-February 2012, the growth rate seems to decrease slightly over time. These observations clearly show that the distribution of the various iron(II) oxidation processes is not constant, but varies over time.

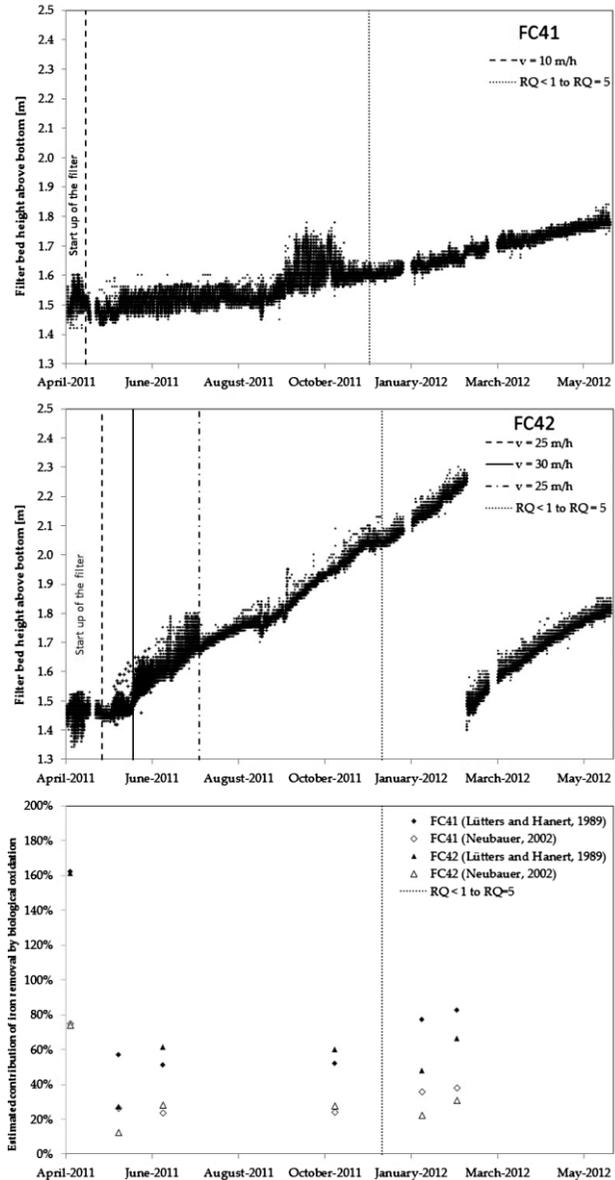


Figure 2 | Results of the continuous bed height measurements of the pilot plant trickling filters FC41 (filter flux 10 m/h) and FC42 (filter flux 25 m/h) and of the contribution of biological iron(II) oxidation to total iron(II) removal at WTP Lekkerkerk (Oasen). At the start of the experiments the filter flux was regularly increased with steps of 5 m/h, until the desired flux was reached.

Table 4 shows that the increase in the air-water ratio (RQ) from 1 to 5, mid-December 2011, resulted in a slight increase in oxygen concentration and in pH after filtration, but, according to Figure 2, this increase seems to have had no influence on the bed height growth rate.

Table 4 also shows the contribution of homogeneous iron(II) oxidation to iron(II) removal. As it is not possible

Table 4 | Contribution of homogeneous, heterogeneous and biological iron(II) oxidation to iron removal as function of air-water ratio (RQ) and filter flux in trickling filtration in pilot plant RSFs at WTPs Lekkerkerk (abstracted groundwater: pH = 7.26, EC_e = 74.7 mS/m, alkalinity = 3.89 mmol/L) and De Hooze Boom (pH = 7.09, EC_e = 78.8 mS/m, alkalinity = 6.31 mmol/L) (Oasen) ($k_1 = 2.2 \times 10^{-15} \text{ mol.l}^{-1}.\text{sec}^{-1}$, $d_{\text{coating}}^{\text{bulk}} = 1.22 \text{ kg/l}$, and $f_{\text{Fe}} = 0.428 \text{ kg/kg}$)

Water treatment plant (Oasen)	Lekkerkerk				De Hooze Boom			
Filter number	FC41		FC42		FF11		FF12	
Filter flux (m ³ /(m ² .h))	10		25		10		25	
Air-water ratio (RQ)	1	5	1	5	5	1	5	
Experimental period	May–Sept 2011	Sept 2011 June 2012	May–Sept 2011	Sept 2011 Feb 2012	Aug 2012 March 2013	May–Aug 2013	Aug 2012 March 2013	
Calculation contribution iron(II) removal by homogeneous oxidation (%)								
Oxygen concentration after filtration (mg O ₂ /l)	9.62	9.70	9.72	9.85	10.25	7.95	8.37	
pH after filtration	7.35	7.60	7.53	7.55	7.55	7.22	7.37	
Filter flux (m ³ /(m ² .h))	10	10	25	25	10	25	25	
Residence time in filterbed (min) ¹	3.6	3.6	1.4	1.4	3.6	1.4	1.4	
Calculated contribution homogeneous oxidation (%)	7	20	6	7	17	1	3	
Calculation contribution iron(II) removal by heterogeneous oxidation (%)								
Iron concentration (mg/l)	5.48	5.48	5.48	5.48	8.3	8.3	8.3	
Iron supply (kg Fe/(m ² bed area.day))	1.29	1.29	3.22	3.22	1.95	4.88	4.88	
Bed height growth (cm/year)	13	36	130	122	25	96	137	
Iron accumulated in RSF (kg Fe/(m ² bed area.day))	0.18	0.51	1.86	1.74	0.36	1.37	1.96	
Calculated contribution heterogeneous oxidation (%)	14	40	58	54	19	28	40	
Calculation contribution iron(II) removal by biological oxidation (%)								
Sum homogeneous and heterogeneous oxidation (%)	21	60	64	61	36	29	43	
Calculated contribution biological oxidation (%)	79	40	36	39	64	71	57	
Measured contribution biological oxidation (%)								
Lütters & Hanert (1989)	51-57	52-82	26-61	48-66				
Neubauer <i>et al.</i> (2002)	24-26	24-38	12-28	22-31				

¹Height supernatant water on filterbed 0 cm, and initial filterbed height 1.5 m.

here to measure pH and oxygen concentration before filtration, the values after filtration have been used. Because these waters are well buffered, substitution of these values results in a slight under-estimation of the contribution of homogeneous iron(II) oxidation to total iron(II) removal. The contribution of heterogeneous iron(II) oxidation has been calculated with the help of Equations (9) and (10), substituting the bed-height-growth rate as estimated from Figure 2.

After a start-up period of circa 6 weeks, see Figure 2, bed height growth started in both pilot plants and remained

about constant over time for FC42 (filter flux 25 m/h). The measured bed height growth rate compares with a minimum contribution of heterogeneous iron(II) oxidation of 54 to 58%, see Table 4. Conditions in FC42 are very stable. This is confirmed by the contribution of biological iron(II) oxidation: depending on the yield factor applied, the last five measurements remain constant at either circa 25 or circa 60%. As the sum of homogeneous and heterogeneous iron(II) oxidation is estimated at 60%, the contribution of biological iron(II) oxidation amounts to circa 40%, which is within

these limits. During the start-up period, the contribution of heterogeneous iron(II) oxidation is negligible, while the contribution of biological oxidation amounts to 74 or 162%. This last value is of course not possible, but it confirms the initial dominant contribution of biological iron(II) oxidation. The contribution of homogeneous iron(II) oxidation may initially also have been greater as the filtration rate was stepwise increased, resulting in a comparably decreasing retention time.

In FC41 (filter flux 10 m/h) bed height growth increased in September 2011 suddenly from 13 to 36 cm/year. These bed height growth rates compare with a minimum contribution of heterogeneous iron(II) oxidation of 14% and 40%, respectively, see Table 4. Initially iron(II) oxidation was mainly biological, see Figure 2, thereafter decreased sharply and then seemed to increase slowly: from 25 to 55% in May–June 2011 to 30 to 70% in October 2011–February 2012, see Table 4. This is only possible if the contribution of homogeneous iron(II) oxidation decreases over time, which is in contradiction with Table 4. Whatever, all these observations indicate a continuous competition between homogeneous, heterogeneous and biological iron(II) oxidation.

Table 4 also shows the results of the experiments in WTP De Hooge Boom. These results are presented here

only for information, as they confirm the results of Lekkerkerk.

Distribution of oxidation processes, all results

Figure 3 shows the contributions of the various iron(II) oxidation processes as a function of pH in iron(II) removal by aeration and RSF of all the WTPs mentioned in this study, where the contribution of homogeneous iron(II) oxidation has been calculated and of heterogeneous iron(II) oxidation estimated from filter bed height growth. The contribution of biological iron(II) oxidation has been estimated as the complement or determined by *Gallionella* spp. cell count by qPCR.

This figure shows that biological iron(II) oxidation is the main iron removal process in the pH range from pH circa 6.5 to about 7.7. At higher pH homogeneous iron(II) oxidation becomes the dominant iron(II) removal process and there is a sharp transition between both processes. The position of the inflexion point as a function of pH varies with the value of the reaction constant, temperature, chemical composition of the abstracted groundwater, etc.

Based on the field data of Figure 3 the contribution of heterogeneous iron(II) oxidation increases with decreasing pH, and may even become dominant at low pH. This

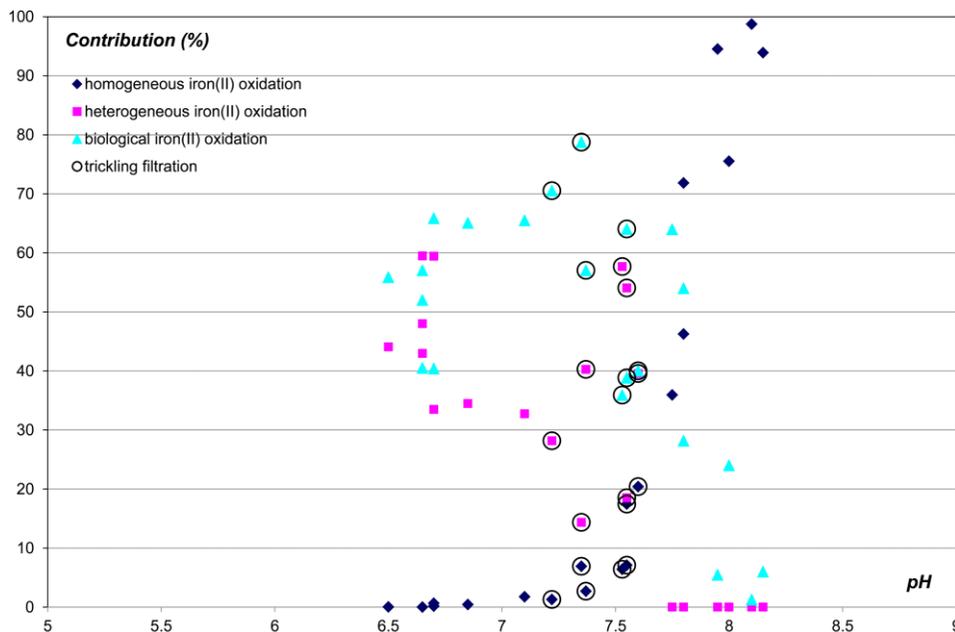


Figure 3 | Contribution of the various iron(II) oxidation processes as a function of pH (in aerated water) in iron(II) removal by aeration and RSF. The results from trickling (or dry) filtration have been indicated separately.

figure also shows that in trickling filtration conditions are favorable for heterogeneous iron(II) oxidation. The complement is mainly oxidized by biological iron(II) oxidation. The expansion of the range of occurrence of heterogeneous iron(II) oxidation at the cost of biological iron(II) oxidation may be explained by the unfavorable conditions for attachment of FeOB due to the passage of a mixture of water and air.

In our study, the lower pH values in Figure 3 equal 6.5 to 6.7. Dempsey *et al.* (2002) executed experiments with oxidation of iron(II) at even lower pH values (5 to 6.4) in Acid Mine Drainage. Here heterogeneous iron(II) oxidation accounted for 60 to 99% of total iron(II) precipitation. However, the temperature in their experiments was higher (11.7 to 19.2 °C) than that of our groundwaters (10–12 °C).

The distribution of the oxidation processes, as presented in Figure 3, may vary due to variations in construction of the RSF and in its operation. In supernatant water on the filter bed only homogeneous iron(II) oxidation may occur due to lack of attachment area for *Gallionella* spp. and of adsorption sites for dissolved iron(II). In this process HFO flocs are produced, which accumulate on top of the filter bed. On top of the filter bed there is also attachment area for *Gallionella* spp. and there will be competition between homogeneous and biological iron(II) oxidation. Inside the filter bed there are adsorption sites for iron(II), and as long as iron(II) oxidation is not complete, there will be competition between homogeneous, heterogeneous and biological iron(II) oxidation, until iron(II) oxidation is complete.

This also has consequences for back-washing: in homogeneous iron(II) oxidation the filter bed must maintain its floc retaining properties, in heterogeneous iron(II) oxidation its iron(II) adsorption properties and in biological iron(II) oxidation its *Gallionella* spp. attachment properties.

Application of various filter velocities in WTP Balen (Pidpa) and in the trickling filter pilot-plants (Oasen) showed that the contribution of heterogeneous iron(II) oxidation increased with increasing filter velocity. As the pH of the treated water was 6 to 7, the contribution of homogeneous iron(II) oxidation was either absent or minor. Apparently, by decreasing pH and by increasing filter velocity conditions for *Gallionella* spp. become adverse, which might be ascribed to problematic attachment of *Gallionella* spp. to filter bed material under these conditions.

Hässelbarth & Lüdemann (1971) applied aeration and RSF with sub-stoichiometric oxygen concentrations and called their method 'biological iron removal'. This phenomenon may only be explained by the presence of a large adsorption capacity. The presence of this large adsorption capacity for iron(II) is confirmed by the absence of breakthrough of dissolved iron(II) during periods of oxygen supply failure (e.g. Reijnen & Akkermans 2008; Schoonenberg Kegel 2013).

RSF with high filtration rates, limited oxygen supply, absence of adverse effects due to discontinuous operation and even due to prolonged shutdowns, very quick start-up times, and adverse effects due to the presence of H₂S and Zn are characteristic for adsorption processes and consequently for heterogeneous iron(II) removal. In the past, Mouchet (1992) called this method biological iron(II) removal, but, as shown before, this is only partly correct, and this has resulted in much confusion (e.g. Søgaard *et al.* 2000; Sharma *et al.* 2005), as many have considered this procedure as solely biological. Our results demonstrate that in Mouchet's method iron(II) is removed by heterogeneous as well as biological oxidation and that this distribution is influenced by many variables. Therefore it is advised to call this method heterogeneous-biological iron(II) removal. As this iron(II) removal method has many advantages, amongst others with regard to sludge production, it would be wise to substantiate this treatment method further with the help of *Gallionella* spp. counts (de Vet *et al.* 2012).

The three iron(II) oxidation processes distinguished in RSF have consequences for the type of iron sludge produced, the operation of RSF in particular for back-washing, the filter material, etc.

At high pH and in the presence of supernatant water iron sludge will be produced mainly by homogeneous iron(II) oxidation, consisting of very small, low-density flocs, which may necessitate extra treatment for settling. At lower pH biological iron(II) oxidation will produce firm, high-density sludge, and at even lower pH heterogeneous iron(II) oxidation will produce no sludge, but growth of filter grains. However, depending on the method of back-washing (whether or not turbulent, with or without air, etc.) iron sludge produced by biological iron(II) oxidation may contain variable admixtures of HFO-growths released by rubbing the HFO-coated grains against each other.

Table 5 | Relation between iron(II) oxidation process and characteristics of the sludge produced

Iron(II) oxidation process	Sludge characteristics
Homogeneous	Small, low density flocs sometimes after treatment necessary
Heterogeneous	No sludge, growth of filter grains
Biological	Firm, high density sludge

In Table 5 the various iron(II) oxidation processes are summarized, together with the characteristics of the iron sludge produced. In the field the sludge produced will vary according to the contributions of the various iron(II) oxidation processes.

The distribution of the various iron(II) oxidation processes is not constant over time. In a new filter, depending on pH there will be more or less homogeneous iron(II) oxidation and biological iron(II) oxidation. After some time heterogeneous iron(II) oxidation starts to contribute significantly. Recently, Bruins *et al.* (2015) demonstrated a similar phenomenon for the oxidation of manganese(II): initially biological oxidation, changing into heterogeneous oxidation.

CONCLUSIONS

In iron(II) removal by aeration in RSF three processes may be distinguished: homogeneous, heterogeneous and biological iron(II) oxidation. The contribution of homogeneous iron(II) oxidation may be calculated, and of heterogeneous iron(II) oxidation estimated from filter bed height growth rate. The contribution of biological iron(II) oxidation is the complement of both processes. Presently the contribution of biological oxidation can also be estimated by drawing up an iron and a *Gallionella* spp. mass balance, and comparison with standard values for the maximum biomass yield.

It appears that in drinking water production over the pH range circa 6.5 to about 7.7 biological iron(II) oxidation is the main process, while at higher pH homogeneous iron(II) oxidation is the dominant process. At lower pH (6.5–7) heterogeneous iron(II) oxidation is relevant. This distribution is sensitive to RSF operation, such as height of supernatant water, filter velocity, oxygen concentration

and whether or not there is application of trickling filtration, and does not need to be constant over time.

These three iron(II) oxidation processes produce three different types of HFO sludge, i.e. very small, low density flocs, sometimes needing after treatment for settling by homogeneous iron(II) oxidation, no sludge, but growth of filter grains by heterogeneous iron(II) oxidation, and firm, high density sludge by biological iron(II) oxidation. These characteristics are important for the use of these residuals.

A good understanding of the oxidation of iron(II) by oxygen under circum-neutral conditions is not only relevant for the treatment of groundwater to drinking water, but actually everywhere where this process is relevant, for instance clogging of groundwater abstraction wells by accumulations of HFO.

ACKNOWLEDGEMENTS

The data of WTP Dalen were supplied by Marcel Boorsma (WLN). Discussions with Hay Koppers and Tonnie Hemme (Residuals Management Cooperation, Reststoffenuie), Peter de Moel (TUD) and Benjamin van den Akker and Luc Palmen (KWR) were highly appreciated.

REFERENCES

- Appelo, C. A. J. & Postma, D. 2005 *Geochemistry, Groundwater and Pollution*. 2nd edn. Balkema, Rotterdam.
- Böhler, E. 1999 Optimization of iron and manganese removal in filtration units. In: *Actual Subjects in Drinking Water Treatment and Distribution*. Publications of the Technology Center Water, Karlsruhe, DVGW-Technology Center Water (TZW) 8, pp. 23–60 (in German).
- Bruins, J. H., Petrussevski, B., Slokar, Y. M., Huysman, K., Joris, K., Kruijthof, J. C. & Kennedy, M. D. 2015 *Biological and physico-chemical formation of Birnessite during the ripening of manganese removal filters*. *Water Res.* **69**, 154–161. Doi: 10.1016/j.watres.2014.11.019
- Davison, W. & Seed, G. 1983 *The kinetics of the oxidation of ferrous iron in synthetic and natural waters*. *Geochim. Cosmochim. Acta* **47**, 67–79.
- Dempsey, B. A., Dietz, J., Jeon, B. H., Roscoe, H. C. & Ames, R. 2002 Heterogeneous oxidation of ferrous iron for treatment of mine drainage. In: *Paper presented at the 2002 National Meeting of the American Society of Mining*, Lexington, KY, June 9–13, 2002.

- de Moel, P. J., Verberk, J. Q. J. C. & van Dijk, J. C. 2006 *Drinking Water: Principles and Practices*. World Scientific Publ., New Jersey.
- de Vet, W. W. J. M. 2011 Biological Drinking Water Treatment of Anaerobic Groundwater in Trickling Filters. PhD Thesis. Technical University Delft, The Netherlands.
- de Vet, W. W. J. M., Dinkla, I. J. T., Rietveld, L. C. & van Loosdrecht, M. C. M. 2011 Biological iron oxidation by *Gallionella* spp. in drinking water production under fully aerated conditions. *Water Res.* **45**, 5389–5398. Doi:10.1016/j.watres.2011.07.028.
- de Vet, W. W. J. M., van Loosdrecht, M. C. M. & Rietveld, L. C. 2012 Phosphorus limitation in nitrifying groundwater filters. *Water Res.* **46**, 1061–1069. Doi:10.1016/j.watres.2011.11.075.
- de Vet, W. W. J. M., Knibbe, W. J., Rietveld, L. C. & van Loosdrecht, M. C. M. 2013 Biological active groundwater filters: exploiting natural diversity. *Water Sci. Technol.: Water Supply* **13** (1), 29–35. Doi:10.2166/ws.2010.076.
- DVGW (Deutsche Vereinigung des Gas- und Wasserfaches; German Technical, Scientific Association for Gas and Water) 2005 DVGW-Regelwerk Enteisenung und Entmanganung; Teil 1: Grundsätze und Verfahren. Arbeitsblatt W 223–1. Bonn (in German).
- Emerson, D. & Weiss, J. V. 2004 Bacterial iron oxidation in circum-neutral freshwater habitats: Findings from the field and the laboratory. *Geomicrobiol. J.* **21** (6), 405–414.
- Grohmann, A., Gollasch, R. & Schumacher, G. 1989 Biological removal of iron and manganese of a methane containing ground water in Speyer (Biologische Enteisenung und Entmanganung eines methanhaltigen Grundwassers in Speyer). *GWF Wasser/Abwasser* **130** (9), 441–446 (in German).
- Hanert, H. H. 2006 *The Genus Gallionella*. *Prokaryotes* **7**, 900–995. Doi:10.1007/0-387-30747-8_46.
- Hässelbarth, U. & Lüdemann, V. 1971 The biological removal of iron and manganese (Die biologische Enteisenung und Entmanganung). *Vom Wasser* **38**, 233–253 (in German).
- Hiemstra, T. & van Riemsdijk, W. H. 2007 Adsorption and surface oxidation of Fe(II) on metal (hydr)oxides. *Geochim. Cosmochim. Acta* **71**, 5913–5933.
- Lütters, S. & Hanert, H. H. 1989 The ultrastructure of chemolithoautotrophic *Gallionella ferruginea* and *Thiobacillus ferrooxidans* as revealed by chemical fixation and freeze-etching. *Arch. Microbiol.* **151**, 245–251.
- Mouchet, P. 1992 From conventional to biological removal of iron and manganese in France. *J. Am. Water Works Assoc.* **84** (4), 158–167.
- Neubauer, S. C., Emerson, D. & Magonigal, J. P. 2002 Life at the energetic edge: kinetics of circumneutral iron oxidation by lithotrophic iron-oxidizing bacteria isolated from the wetland-plant rhizosphere. *Appl. Environ. Microbiology.* **68** (8), 3988–3995. Doi:10.1128/AEM.68.8.3988-3995.2002.
- Pacini, V. A., Ingallinella, A. M. & Sanguinetti, G. 2005 Removal of iron and manganese using biological roughing up flow filtration technology. *Water Res.* **39**, 4463–4475. Doi:10.016/j.watres.2005.08.027.
- Qin, S., Ma, F., Huang, P. & Yang, J. 2009 Fe(II) and Mn(II) removal from drilled well water: a case study from a biological treatment unit in Harbin. *Desalination* **245**, 183–193.
- Reijnen, G. & Akkermans, W. 2008 Biological-adsorptive iron removal on well field Susteren (Biologisch-adsorptieve ontijzering op pompstation Susteren). *H₂O* **41** (21), 36–39 (in Dutch).
- Schoonenberg Kegel, F. 2013 Optimization of Iron Removal in Rapid Sand Filters, Increasing Heterogenic Iron Removal by Reducing the Supernatant Level. Additional Master Thesis. Delft University of Technology, The Netherlands.
- Sharma, S. K., Petrusevski, B. & Schippers, J. C. 2005 Biological iron removal from groundwater, a review. *J. Water Supply Res. Technol. Aqua* **54** (4), 239–247.
- Søgaard, E. G., Medenwaldt, R. & Abraham-Peskir, J. V. 2000 Conditions and rates of biotic and abiotic iron precipitation in selected Danish fresh-water plants and microscopic analysis of precipitate morphology. *Water Res.* **34**, 2675–2682.
- Štembal, T., Markić, M., Ribičić, N., Briški, F. & Sipos, L. 2005 Removal of ammonia, iron and manganese from groundwaters of northern Croatia, pilot plant studies. *Process Biochem.* **40**, 327–335.
- Stumm, W. & Morgan, J. J. 1996 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd edn. Wiley Interscience, New York.
- Sung, W. & Morgan, J. J. 1980 Kinetics and products of ferrous iron oxygenation in aqueous systems. *Environ. Sci. Technol.* **14**, 561–568.
- Tamura, H., Kawamura, S. & Hagayama, M. 1980 Acceleration of the oxidation of Fe²⁺ ions by Fe(III)-oxyhydroxides. *Corrosion Sci.* **20**, 963–971.
- Tekerlekopoulou, A. G., Pavlou, S. & Vayenas, D. V. 2013 Removal of ammonium, iron and manganese from potable water. *J. Chem. Technol. Biotechnol.* **88** (5), 751–773. Doi:10.1002/jctb.4031.
- van Beek, C. G. E. M. 1985 Experiences with underground water treatment in the Netherlands. *Water Supply* **3** (Berlin B), 1–11.
- van Beek, C. G. E. M., Hiemstra, T., Hofs, B., Nederlof, M. M., van Paassen, J. A. M. & Reijnen, G. K. 2012 Homogeneous, heterogeneous and biological oxidation of iron(II) in rapid sand filtration. *J. Water Supply: Res. Technol. Aqua* **61** (1), 1–13. Doi:10.2166/aqua.2012.033.

First received 23 April 2015; accepted in revised form 14 November 2015. Available online 19 December 2015