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


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 ≈ 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 (=floculent) 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:

\[
\text{Oxidation: } \text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \quad (1a)
\]
Hydrolysis: $\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \downarrow + 3\text{H}^+$  

Sum: $\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \downarrow + 2\text{H}^+$  

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 tank and/or in the supernatant water on top of 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-OH$^0$: surface hydroxyl group), followed by oxidation of the adsorbed iron(II). The final step is hydrolysis of the adsorbed ferric iron:

Iron(II) adsorption: $S - \text{OH}^0 + \text{Fe}^{2+} 
\rightarrow S - \text{OFe(II)}^+ + \text{H}^+$  

Oxidation: $S - \text{OFe(II)}^+ + \frac{1}{4}\text{O}_2 + \text{H}^+$  
\rightarrow S - \text{OFe(III)}^{2+} + \frac{1}{2}\text{H}_2\text{O}$ 

Hydrolysis: $S - \text{OFe(III)}^{2+} + 2\text{H}_2\text{O} 
\rightarrow S - \text{OFe(III)(OH)}_2^0 + 2\text{H}^+$ 

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 advantageous applied in subsoil iron removal (SIR) (van Beek 1983).

Biological iron(II) oxidation may be represented as:

\[
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\text{H}_2\text{O} 
\rightarrow \text{Fe(OH)}_3 \downarrow + 2\text{H}^+ + \text{FeOB} - \text{biomass}
\]

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):

\[
\frac{d}{dt}[\text{Fe}^{2+}] = -k_1 \frac{[\text{Fe}^{2+}][\text{O}_2]}{[\text{H}^+]^2}
\]
where \( k_1 \) represents the rate constant for homogeneous oxidation (mol.l\(^{-1}\).sec\(^{-1}\)). This relation is generally accepted and applied (e.g. de Vet et al., 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:

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

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 \(\tau\) (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 (Stembal 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 (1985) 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: \(k_1 = 2.2 \times 10^{-15}\) mol.l\(^{-1}\).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 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](https://iwaponline.com/aqua/article-pdf/65/3/195/398671/jws0650195.pdf)
The rate equation for heterogeneous oxidation may, in analogy to Sung & Morgan (1980) and Tamura et al. (1980), be represented as:

$$\frac{d[Fe^{2+}]}{dt} = -k_2 \frac{[S-OH]^0[Fe^{2+}][O_2]}{[H^+]}$$  \hspace{1cm} (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:

$$\frac{[Fe^{2+}]_0 - [Fe^{2+}]}{[Fe^{2+}]_0} = 1 - \exp \left( -k_2 \frac{[S-OH]^0[O_2]}{[H^+]} \right)$$  \hspace{1cm} (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 m² of filter bed per day equals:

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

with $m_{Fe,supplied}$ mass of iron supplied (kg Fe.m⁻².day⁻¹), $V$ total volume water treated each day (m³/day), $A$ total surface area of the filter bed (m²), 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:

$$m_{Fe,supplied} = \frac{qc_c_\ell h}{1,000}$$  \hspace{1cm} (9)

with $q$ filter-flux (m³.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:

$$m_{Fe,removed} = \frac{10}{365}r_{bed} d_{bulk}^c f_{Fe}$$  \hspace{1cm} (10)

with $r_{bed}$ bed height growth rate (cm/year), $d_{bulk}^c$ 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 Grobben-donk 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: Reststoffen- nie). 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

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Very intensive aeration, resulting in high pH and high oxygen concentration On top of the filter, supernatant water is present</td>
</tr>
<tr>
<td>II</td>
<td>Intensive aeration, resulting in medium pH and medium oxygen concentration On top of the filter, there is supernatant water</td>
</tr>
<tr>
<td>III</td>
<td>Moderate aeration, slight increase of pH and low oxygen concentration Some supernatant water. Compared to other types, usually higher filter velocity</td>
</tr>
<tr>
<td>IV</td>
<td>Very intensive aeration, resulting in high pH and high oxygen concentration Filtration of mixture of air and water (dry or trickling infiltration)</td>
</tr>
</tbody>
</table>
Table 2 | Estimated contributions of homogeneous, heterogeneous and biological iron(II) oxidation to iron removal in aeration and RSF ($k_1 = 2.2 \times 10^{-10}$ mol L$^{-1}$ sec$^{-1}$, $d_{\text{Fe}^{2+}} = 1.22$ kg/l, and $\xi_a = 0.428$ kg/kg)

<table>
<thead>
<tr>
<th>Water treatment plant</th>
<th>Balen</th>
<th>Bunnik</th>
<th>Dalen</th>
<th>Grobben-donk</th>
<th>Haar-laken</th>
<th>Harder-broek</th>
<th>Herentals</th>
<th>Loos-drecht</th>
<th>Macharen</th>
<th>Brabant Water</th>
<th>Veghel</th>
<th>Brabant Water</th>
<th>Vlierden</th>
<th>Brabant Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water utility</td>
<td>Pidpa</td>
<td>Viten</td>
<td>WMD</td>
<td>Pidpa</td>
<td>Viten</td>
<td>Viten</td>
<td>Pidpa</td>
<td>Viten</td>
<td>Pidpa</td>
<td>Brabant Water</td>
<td>Brabant</td>
<td>Water</td>
<td>Brabant</td>
<td>Water</td>
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<tr>
<td>Chemical composition abstracted groundwater</td>
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<tr>
<td>pH</td>
<td>6.60</td>
<td>7.39</td>
<td>6.30</td>
<td>6.60</td>
<td>7.82</td>
<td>7.46</td>
<td>7.65</td>
<td>6.75</td>
<td>7.47</td>
<td>7.05</td>
<td>7.32</td>
<td>7.10</td>
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</tr>
<tr>
<td>Electrical conductivity, EC (mS/m)</td>
<td>31.0</td>
<td>44.0</td>
<td>44.7</td>
<td>47.3</td>
<td>26.9</td>
<td>39.9</td>
<td>16.7</td>
<td>34.4</td>
<td>26.6</td>
<td>59.5</td>
<td>65.6</td>
<td>45.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkalinity (mmol$_c$/l)</td>
<td>2.92</td>
<td>4.43</td>
<td>1.07</td>
<td>3.94</td>
<td>2.80</td>
<td>2.57</td>
<td>1.72</td>
<td>4.00</td>
<td>1.90</td>
<td>4.16</td>
<td>5.80</td>
<td>5.20</td>
<td></td>
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</tr>
<tr>
<td>Iron concentration (mg/l)</td>
<td>27</td>
<td>3.25</td>
<td>12</td>
<td>34.7</td>
<td>0.46</td>
<td>3.79</td>
<td>1.41</td>
<td>19.7</td>
<td>5.34</td>
<td>12</td>
<td>2.5</td>
<td>4.3</td>
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<tr>
<td><strong>Aeration and RSF class</strong></td>
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<tr>
<td><strong>Calculation contribution iron(II) removal by homogeneous oxidation (%)</strong></td>
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</tr>
<tr>
<td>Oxygen concentration after aeration (mg O$_2$/l)</td>
<td>5</td>
<td>9</td>
<td>2</td>
<td>5.5</td>
<td>9</td>
<td>6.5</td>
<td>8.5</td>
<td>3</td>
<td>6.5</td>
<td>6</td>
<td>9</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH after aeration</td>
<td>6.7</td>
<td>7.8</td>
<td>6.5</td>
<td>6.7</td>
<td>7.95</td>
<td>7.75</td>
<td>8.15</td>
<td>6.85</td>
<td>8</td>
<td>7.1</td>
<td>8.1</td>
<td>7.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter flux (m$^3$/m$^2$.h))</td>
<td>18.4</td>
<td>10</td>
<td>11.8</td>
<td>5.5</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>8.1</td>
<td>8</td>
<td>14</td>
<td>8.8</td>
<td>7</td>
<td></td>
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</tr>
<tr>
<td>Residence time in aeration tower (min)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>3</td>
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<tr>
<td>Residence time in supernatant water (min)$^1$</td>
<td>0.8</td>
<td>1.8</td>
<td>0.0</td>
<td>2.7</td>
<td>3.4</td>
<td>2.3</td>
<td>1.3</td>
<td>1.9</td>
<td>2.3</td>
<td>1.1</td>
<td>1.7</td>
<td>2.1</td>
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<tr>
<td>Residence time in filter bed (min)$^2$</td>
<td>2.3</td>
<td>2.4</td>
<td>5.1</td>
<td>8.7</td>
<td>3.4</td>
<td>3.0</td>
<td>2.7</td>
<td>5.3</td>
<td>3.0</td>
<td>3.4</td>
<td>2.7</td>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total residence time (min)</td>
<td>3.2$^a$</td>
<td>4.2$^b$</td>
<td>5.1$^a$</td>
<td>11.5$^a$</td>
<td>9.9$^b$</td>
<td>5.3$^b$</td>
<td>4.0$^b$</td>
<td>7.2$^a$</td>
<td>5.3$^b$</td>
<td>4.5$^a$</td>
<td>7.4$^b$</td>
<td>8.6$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated contribution homogeneous oxidation (%)</td>
<td>0</td>
<td>46</td>
<td>0</td>
<td>1</td>
<td>95</td>
<td>36</td>
<td>94</td>
<td>0</td>
<td>76</td>
<td>2</td>
<td>99</td>
<td>72</td>
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<tr>
<td><strong>Calculation contribution iron(II) removal by heterogeneous oxidation (%)</strong></td>
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</tr>
<tr>
<td>Iron supply (kg Fe/(m$^2$ bed area. day))</td>
<td>11.675</td>
<td>0.355</td>
<td>1.948</td>
<td>4.485</td>
<td>0.078</td>
<td>0.386</td>
<td>0.147</td>
<td>2.489</td>
<td>0.359</td>
<td>2.622</td>
<td>0.288</td>
<td>0.408</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bed height growth (cm/year)</td>
<td>485</td>
<td>2.5$^a$</td>
<td>50</td>
<td>105</td>
<td>negl</td>
<td>2.5$^a$</td>
<td>2$^a$</td>
<td>60</td>
<td>5$^a$</td>
<td>60</td>
<td>negl</td>
<td>negl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron accumulated in RSF (kg Fe/(m$^2$ bed area.day))</td>
<td>6.938</td>
<td>0.056</td>
<td>0.858</td>
<td>1.502</td>
<td>negl</td>
<td>0.056</td>
<td>0.29</td>
<td>0.858</td>
<td>0.072</td>
<td>0.858</td>
<td>negl</td>
<td>negl</td>
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<tr>
<td>Calculated contribution heterogeneous oxidation (%)</td>
<td>59</td>
<td>10$^a$</td>
<td>44</td>
<td>33</td>
<td>negl</td>
<td>9$^a$</td>
<td>19$^a$</td>
<td>34</td>
<td>20$^a$</td>
<td>33</td>
<td>negl</td>
<td>negl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
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 Balen (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 (Ø = 1 m²) 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.
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.

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...
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

### 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 = 74.7 mS/m, alkalinity = 3.89 mmol/L) and De Hooge Boom (pH = 7.09, EC = 78.8 mS/m, alkalinity = 6.31 mmol/L) (Oasen) $k_1 = 2.2 \times 10^{-15}$ mol L $^{-1}$ sec $^{-1}$, $d_{Fe^{2+}} = 1.22$ kg/l, and $f_{Fe} = 0.428$ kg/kg

<table>
<thead>
<tr>
<th>Water treatment plant (Oasen)</th>
<th>Lekkerkerk</th>
<th>De Hooge Boom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter number</td>
<td>FC41</td>
<td>FF11</td>
</tr>
<tr>
<td>Filter flux (m$^3$/m$^2$.h))</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Air-water ratio (RQ)</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Experimental period</td>
<td>May–Sept 2011</td>
<td>May–Sept 2011</td>
</tr>
<tr>
<td>Oxygen concentration after filtration (mg O$_2$/L)</td>
<td>9.62</td>
<td>9.70</td>
</tr>
<tr>
<td>pH after filtration</td>
<td>7.35</td>
<td>7.60</td>
</tr>
<tr>
<td>Filter flux (m$^3$/m$^2$.h))</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Residence time in filterbed (min)$^1$</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Calculated contribution homogeneous oxidation (%)</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>Calculated contribution iron(II) removal by homogeneous oxidation (%)</td>
<td>5.48</td>
<td>5.48</td>
</tr>
<tr>
<td>Iron concentration (mg/l)</td>
<td>5.48</td>
<td>5.48</td>
</tr>
<tr>
<td>Iron supply (kg Fe/(m$^2$ bed area.day))</td>
<td>1.29</td>
<td>1.29</td>
</tr>
<tr>
<td>Bed height growth (cm/year)</td>
<td>13</td>
<td>36</td>
</tr>
<tr>
<td>Iron accumulated in RSF (kg Fe/(m$^2$ bed area.day))</td>
<td>0.18</td>
<td>0.51</td>
</tr>
<tr>
<td>Calculated contribution heterogeneous oxidation (%)</td>
<td>14</td>
<td>40</td>
</tr>
<tr>
<td>Calculated contribution iron(II) removal by heterogeneous oxidation (%)</td>
<td>21</td>
<td>60</td>
</tr>
<tr>
<td>Sum homogeneous and heterogeneous oxidation (%)</td>
<td>21</td>
<td>60</td>
</tr>
<tr>
<td>Calculated contribution biological oxidation (%)</td>
<td>79</td>
<td>40</td>
</tr>
<tr>
<td>Measured contribution biological oxidation (%)</td>
<td>79</td>
<td>40</td>
</tr>
<tr>
<td>Lütters &amp; Hanert (1989)</td>
<td>51-57</td>
<td>52-82</td>
</tr>
<tr>
<td>Neubauer et al. (2002)</td>
<td>24-26</td>
<td>24-38</td>
</tr>
</tbody>
</table>

$^1$Height supernatant water on filterbed 0 cm, and initial filterbed height 1.5 m.
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 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 (Pida) 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 backwashing, 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 backwashing (whether or not turbulent, with or without air, etc.) iron sludge produced by biological iron(II) oxidation may contain variable admixtures of HFO-growth released by rubbing the HFO-coated grains against each other.
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

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