

Homogeneous, heterogeneous and biological oxidation of iron(II) in rapid sand filtration

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ABSTRACT

Homogeneous, heterogeneous and biological oxidation may precipitate iron(II) as iron(III) hydroxides. In this paper we evaluate the conditions under which each of these processes is dominant in rapid sand filtration (RSF). It is demonstrated that in the presence of iron(III) hydroxide precipitates homogeneous oxidation is negligible compared with heterogeneous oxidation. As soon as iron oxidizing bacteria (IOB) are present, biological oxidation may contribute substantially, in particular under conditions of slight acidity and low oxygen concentration. As the oxidation step is preceded by an adsorption/uptake step, the competition between heterogeneous and biological oxidation is not determined by the oxidation rate, but by the adsorption or uptake rate. Extracellular polymeric substance (EPS), excreted by all kinds of bacteria, may serve as an initial adsorbent for dissolved iron(II) and iron(III) hydroxides. Because adsorption and oxidation of iron (II) either on biofilms (or EPS) or on mineral surfaces, are chemical processes, 'EPS iron oxidation' is not considered as a biological process. The so-called 'biological iron oxidation' actually refers to a treatment method characterized by high filtration rates and limited oxygen supply, where iron(II) is removed mainly by heterogeneous oxidation. The contribution of oxidation of iron(II) by IOB in this method is variable and may even be absent.

Key words | drinking water, groundwater, hydrous ferric oxides, iron(II) oxidation, iron removal, rapid sand filtration

INTRODUCTION

Removal of iron is usually one of the first steps in the treatment of groundwater to drinking water and is generally achieved by rapid sand filtration (RSF), where trial and error play an important role (Sommerfeld 1999). Our goal is to arrive at a relationship between groundwater quality and preferred dominant iron removal process and subsequently preferred process conditions (Groth & Czékalla 2004; DVGW 2005).

This presentation starts with a short description of the relations between the relevant solid phases and the solubility of iron(II) and iron(III). In the oxidation and precipitation of iron(II) into hydrous ferric oxides (HFO), three processes may be distinguished (de Ridder

et al. 2008): homogeneous (= flocculent) oxidation; heterogeneous (= adsorptive, autocatalytic, or contact-) oxidation; and biological oxidation. Favorable conditions for each of these processes will be indicated. The concept of biological iron removal and/or biological iron oxidation, as mentioned in literature, is rather confusing, as it applies to a biological process as well as to a removal method. This concept will be re-evaluated in terms of heterogeneous and biological oxidation. Finally, some recommendations will be presented for iron removal from groundwater in drinking water treatment.

Oxidation and precipitation of iron is not only relevant in the treatment of groundwater to drinking water, but also in

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some industrial uses, such as feed water for boilers. In addition, it is applied in agricultural practices, such as irrigation in glass houses, and is relevant for understanding processes in, for instance, screen slot (or chemical) well clogging (Houben & Treskatis 2007; Stuyfzand 2007; van Beek *et al.* 2009). Therefore, a good understanding of iron removal can be of great economic value.

The focus of this contribution is on iron(II) oxidation in drinking water treatment. As the pH of groundwater abstracted for public drinking water supply usually varies between 5.5 and 8, only processes occurring in this pH interval will be evaluated.

IRON HYDROXIDES AND SOLUBILITY OF IRON

Iron(III) hydroxide precipitates

Iron(III) hydroxide precipitates occur in a series of minerals, showing differences in solubility and surface area, and in surface properties such as charge density and pH_{ZPC} (Stumm & Morgan 1981) that may affect adsorption and surface oxidation of iron(II) (Hiemstra & van Riemsdijk 2007). Figure 1 presents the solubility product and reactive surface area of a series of important iron(III) (hydr)oxides and various pathways of formation and transformation.

Fast oxidation of dissolved iron(II) may produce an iron hydroxide with a high reactive surface area that may adsorb or contain iron(II). Depending on the iron(II) and ligand concentration, various more stable compounds may form. HFO is an example of an iron(III) precipitate that rapidly converts into goethite under anoxic conditions in the presence of dissolved iron(II) (Hansel *et al.* 2005; Park & Dempsey 2005; Pedersen *et al.* 2005). Adsorbed iron(II) strongly enhances the rate of iron exchange between solid and solution (Handler *et al.* 2009) enabling fast mineral transformation.

Fresh iron(III) hydroxide precipitates in clogging wells may consist of HFO, and at ageing goethite may form. Sometimes, lepidocrocite occurs as a minor constituent, while the presence of hematite has never been reported (Houben & Treskatis 2007). Iron(III) hydroxides, precipitated during iron removal from groundwater in drinking water treatment, consist of HFO (Carlson & Schwertmann 1987), and in sub-soil iron removal (SIR), predominantly of goethite with some HFO (Mettler *et al.* 2001).

Solubility

The solubility of iron(II) and iron(III) depends on many variables. For instance, in the pH range 4.5–11, the solubility of iron(III) in equilibrium with HFO is $< 0.01 \mu\text{mol/L}$ ($= 0.00056 \text{ mg/L}$) (Stumm & Morgan 1996).

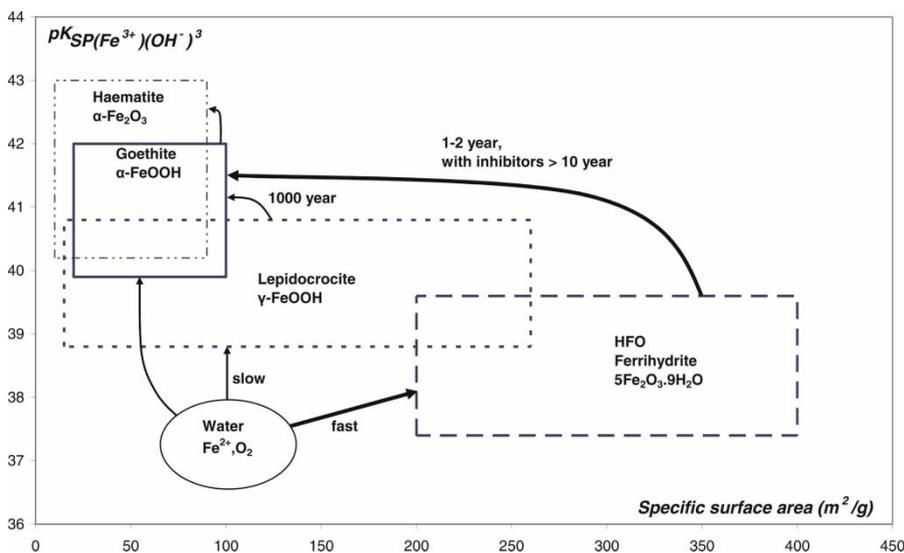


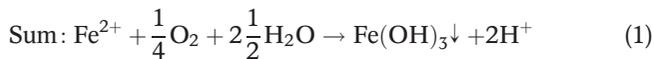
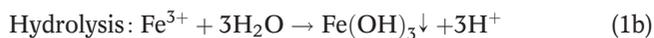
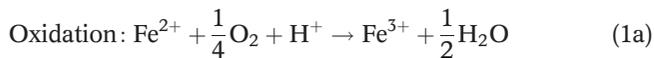
Figure 1 | Relations between various iron(III) hydroxides (modified after Stuyfzand (2007), based on data from Houben & Treskatis (2007) and Appelo & Postma (2006). Arrows without numbers denote unknown rates.

In the presence of oxygen, the concentration of iron(II) in equilibrium with HFO is negligible. For instance, if the oxygen concentration equals 1 $\mu\text{mol/L}$ (= 0.032 mg/L), the iron(II) concentration will be <0.01 $\mu\text{mol/L}$ if $\text{pH} > 2$. In the absence of oxygen, the solubility of iron(II) can be governed by $\text{Fe}(\text{OH})_2(\text{s})$ if $\text{pH} > 8.85$, or FeCO_3 (siderite) if $\text{pH} < 8.85$ (Stumm & Morgan 1996), and can be very high: >1 mol/L if $\text{pH} < 6$.

OXIDATION AND PRECIPITATION OF IRON(II)

Homogeneous oxidation

In homogeneous oxidation, iron(III) hydroxides are precipitated directly from dissolved iron(II) and oxygen by a combination of oxidation and hydrolysis:



Owing to the presence of iron(II) ion pairs besides iron(II) ions, homogeneous oxidation is somewhat more complicated than represented here (Lerk 1965; Morgan & Lahav 2007), but this is not relevant for the present discussion.

The rate equation for homogeneous oxidation may be represented as (Tamura *et al.* 1980; Sung & Morgan 1980):

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

This relation is valid for the pH interval 5 to 8 (Stumm & Morgan 1996). After integration of rate Equation (2), at constant oxygen concentration and pH, the half-life of this reaction reads as (Applin & Zhao 1989; Appelo & Postma 2006):

$$t_{1/2} = \frac{\ln 2}{k_1} \frac{[\text{H}^+]^2}{[\text{O}_2]} \quad (3)$$

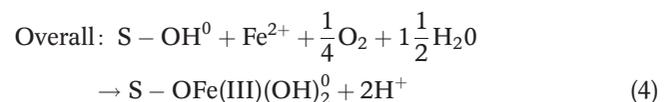
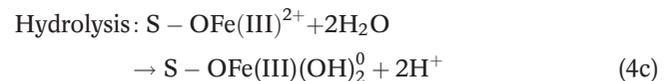
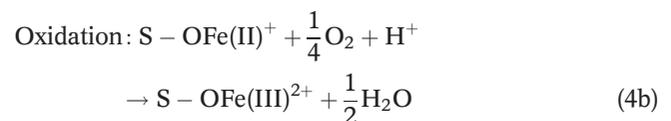
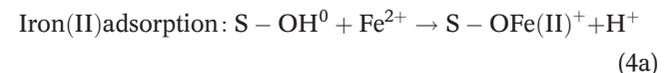
The value for the rate constant k_1 at 25 °C equals $1.08 \times 10^{-13} \text{ mol L}^{-1} \text{ s}^{-1}$ (Stumm & Morgan 1996). This value is very much dependent on the temperature. At 10 °C, which is the average temperature of groundwater in

The Netherlands, k_1 is exactly a factor 10 lower, $1.08 \times 10^{-14} \text{ mol L}^{-1} \text{ s}^{-1}$ (Stuyfzand 2007), which corresponds with a 10 times longer half-life. Apart from temperature, the reaction rate also depends on the presence of interfering cations and anions (Stumm & Lee 1961) and organic matter and the magnitude of the buffer capacity (Jobin & Ghosh 1972).

Figure 2 presents the half-life of 1 min for iron(II) as a function of oxygen concentration and pH (dotted line). According to Equation (3) a one-unit change in pH results in a 100-fold change in reaction rate, where the rate is inversely proportional to the oxygen concentration.

Heterogeneous oxidation

In heterogeneous iron oxidation, oxidation and precipitation are preceded by adsorption of iron(II) at existing surfaces. Iron(II) surface complexes are formed and these may transfer an electron to the mineral bulk (Hiemstra & van Riemsdijk 2007), leading to an adsorbed iron(III) surface complex that is unstable and will hydrolyze. This process can be described with variable charge models (Hiemstra & van Riemsdijk 1996, 2007). Modeling shows that in the pH range of interest about one proton per adsorbed Fe^{2+} is released. In a simplified picture, one may use S-OH^0 sites to define thermodynamically the overall reaction. However, note that the actual mechanism is different (Hiemstra *et al.* 1996). With this choice of S-OH^0 , the overall reaction may be formulated as:



The overall reaction shows that removal of each Fe^{2+} will lead to the release of two protons, just as in the

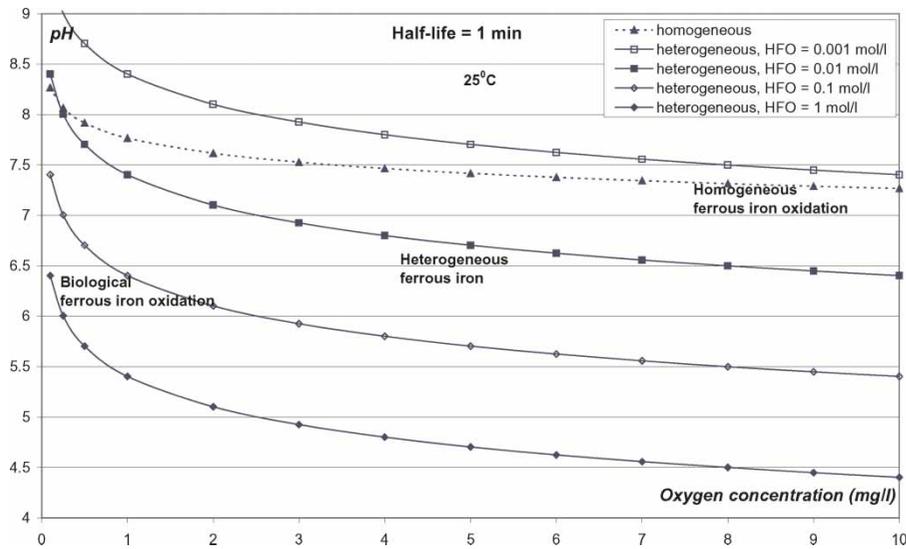


Figure 2 | Half-life of 1 minute for homogeneous oxidation of iron(II) as a function of oxygen concentration and pH at 25 °C (dotted line), and for heterogeneous oxidation for four concentrations of HFO (solid lines). The lines were calculated using the rate constants for systems with only iron(II). Conditions where homogeneous, heterogeneous or biological iron oxidation might be dominant are indicated as well.

homogeneous oxidation reaction, and that repetitive adsorption of iron(II) at the lattice will lead to crystal growth. Considering the reactions of Equation (4), the adsorption as well as the oxidation step may determine the rate. Usually, ion adsorption is fast, as is the oxidation of adsorbed metals (Wehrli 1990), where the adsorption rate also depends on pH and anion type (Jeon *et al.* 2003) and on the presence of natural organic matter (Gu *et al.* 1994).

Heterogeneous oxidation may proceed along two pathways: simultaneous adsorption and oxidation in the continuous presence of oxygen, as in the classical iron removal process; or adsorption and oxidation separated in time in the discontinuous presence of oxygen, as in SIR. Adsorption of iron(II) in SIR is confirmed by the presence of different iron(II) isotopic ratios in abstracted groundwater (Teutsch *et al.* 2005; Mikutta *et al.* 2009).

Simultaneous adsorption and oxidation

The rate equation for heterogeneous oxidation may be represented as (Sung & Morgan 1980; Tamura *et al.* 1980):

$$\frac{d}{dt}[\text{Fe}^{2+}]_{\text{hetero}} = -k_2 \frac{[\text{S} - \text{OH}^0][\text{Fe}^{2+}][\text{O}_2]}{[\text{H}^+]} \quad (5)$$

In this relation $[\text{S} - \text{OH}^0]$ represents the concentration of iron(III) hydroxide, in mol/L. In the experiments of Tamura *et al.* (1976), pH ranged between 6.2 and 6.6 while iron(III) hydroxide concentrations were up to 30 mg/L. In the experiments of Sung & Morgan (1980), pH was 7.2 and iron(III) hydroxide concentrations were up to 3 mg/L. The value for k_2 depends on the structure and the magnitude of the surface area of the iron(III) hydroxide, and ranges by a factor of 10 between the most and the least stable phase (Tamura *et al.* 1980): k_2 (HFO) $\gg k_2$ (goethite, lepidocrocite); where the value for HFO equals $1.46 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C. Mettler *et al.* (2001) and Mettler (2002) found a similar rate sequence: HFO \gg goethite \gg lepidocrocite. Tüfekci & Sarikaya (1996) reported lower values for k_2 at higher iron (III) hydroxide concentrations, which is expected if surface area is a ruling factor.

In the same way as for homogeneous oxidation, the half-life for heterogeneous oxidation may be obtained as:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k_2} \frac{[\text{H}^+]}{[\text{S} - \text{OH}^0][\text{O}_2]} \approx \frac{\ln 2}{k_2} \frac{[\text{H}^+]}{[\text{S}^*][\text{O}_2]} \quad (6)$$

In this relation the empty site concentration $[\text{S} - \text{OH}^0]$ can be replaced by the adsorption capacity $[\text{S}^*]$ as long as the amount of adsorbed iron(II) is small with respect

to this capacity: $[S^*] = [S-OH^0] + [S-OFe(II)^+] \approx [S-OH^0]$. Figure 2 shows the half-life of 1 minute for iron(II) as a function of oxygen concentration and pH for various concentrations of HFO. Equation (6) shows that a one-unit change in pH results in a 10-fold change in reaction rate, and that the rate is inversely proportional to the oxygen and the HFO concentration.

Adsorption and oxidation separated in time

Jeon *et al.* (2003) distinguish between adsorption and fixation of iron(II) by iron(III) hydroxide surfaces. This distinction is ascribed (Dixit & Hering 2006) to the conversion of initial iron(III) hydroxide into mixed iron(II)/iron(III) oxide or to the transfer of electrons of adsorbed iron(II) to the bulk iron(III) hydroxides (Wehrli *et al.* 1989; Hiemstra & van Riemsdijk 2007). Possibly this phenomenon also explains the very preferential adsorption of iron(II) by iron(III) hydroxides, as observed in SIR (van Beek 1983, 1980, 1985).

Thermodynamically, the primary iron(II) adsorption reaction can be considered as iron(II) adsorption with non-stoichiometric release of one H^+ per Fe^{2+} (see Equation 4a), where the exchange constant may be defined as:

$$K_{Fe/H} = \frac{[S - OFe(II)^+][H^+]}{[S - OH^0][Fe^{2+}]} \quad (7)$$

in which the sites are expressed in mol HFO/L. The iron(II)-proton exchange constant on iron(III) hydroxide surfaces equals (Tamura *et al.* 1976): $K_{Fe/H} = 1.41 \times 10^{-5}$. This value is identical to the value reported by Choi *et al.* (2001) for iron(II)-proton exchange on lepidocrocite surfaces, and comparable to the value reported by Wolthoorn (2003).

Substitution of Equation (7) in the fraction of iron(II) dissolved (Fe^{2+}/Fe_T) equals:

$$\begin{aligned} \frac{[Fe^{2+}]}{[Fe]_T} &= \frac{[Fe^{2+}]}{[Fe^{2+}] + [S - OFe(II)^+]} \\ &= \frac{1}{1 + (K_{Fe/H}[S - OH^0])/[H^+]} \approx \frac{1}{1 + (K_{Fe/H}[S^*])/[H^+]} \end{aligned} \quad (8)$$

Figure 3 shows the fraction of iron(II) dissolved as function of pH for several HFO concentrations at equilibrium. If

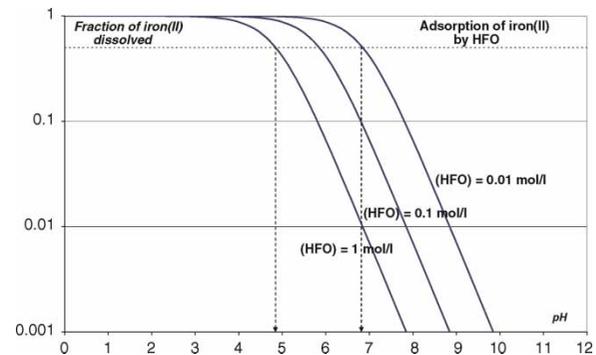


Figure 3 | Fraction of iron(II) dissolved as function of pH for several HFO concentrations. The horizontal dotted line represents the 50% adsorption/solution.

iron(II) is removed in the subsoil or in a reactor, the concentration of HFO may be high. At a specific surface area of $600 \text{ m}^2/\text{g}$ (Hiemstra & van Riemsdijk 2009), 0.1 mol HFO/L represents a surface area of about $1,500 \text{ m}^2/\text{L}$. For comparison, values of about $600\text{--}6,000 \text{ m}^2/\text{L}$ are typical for natural soils (Hiemstra *et al.* 2010). The large surface area is able to bind a very large part of the iron(II) as illustrated in Figure 3, showing that for HFO concentrations $>1 \text{ mol/L}$, less than 1% iron(II) is dissolved at pH values >6.5 to 7. This value corresponds well with experiences with SIR.

Biological oxidation

The precipitation of iron(III) hydroxides from dissolved iron(II) and oxygen produces only little energy. Therefore iron oxidizing bacteria (IOB) need to convert large quantities of iron(II) (Ghiorse 1984; Viswanathan & Boettcher 1991; Chapelle 1992). This is only possible where both oxygen and iron(II) are present. For that reason, IOB are typical representatives for oxygen-iron(II) interfaces (Emerson & Weiss 2004), characterized by variable iron(II) but low oxygen concentrations and slightly acid to neutral ($5.5 < \text{pH} < 7.0$) conditions.

From the IOB, only *Gallionella ferruginea* is able to take up dissolved iron(II) and to oxidize and precipitate internally. If IOB excrete their reaction product (i.e. HFO) into solution, this excreted HFO would start to adsorb dissolved iron(II), and in this way become a competitor with the excreting IOB. In order to prevent this competition, the reaction products should remain unavailable for adsorption. This was confirmed very recently by

Chan *et al.* (2009, 2010), who demonstrated that IOB excrete their reaction products (lepidocrocite) into their stalks.

Other IOB, such as *Leptothrix ochracea*, are able to adsorb great amounts of dissolved iron on their cell membranes and sheaths. Assuming electron (or ATP) transfer over the cell membrane, the energy gained by oxidation and hydrolysis of iron(II) will be, at least partly, of advantage to these IOB (Ghiorse 1984; Hallbeck & Pedersen 1991; Konhauser 1997; Emerson 2000; Hanert 2002; Kappler & Straub 2005).

Bacteria are able to excrete large amounts of EPS (extracellular polymeric substance) (Ehrlich *et al.* 1991; Costerton *et al.* 1995; Flemming & Wingender 2010). EPS spreads into biofilms, which may behave as an adhesive for bacteria and iron hydroxide flocs and which may have a high affinity for iron(II) (Frankel & Bazylinski 2003).

Iron hydroxide flocs caught and iron(II) adsorbed by these biofilms may serve as nuclei for heterogeneous iron (II) oxidation. Further adsorption and oxidation are not different from heterogeneous oxidation on mineral surfaces. Consequently, independent of the adhesive material, all combined adsorption and oxidation processes are called heterogeneous oxidation.

Following this reasoning, IOB will not excrete large amounts of EPS spreading into biofilms, because IOB and their excreted EPS would then compete for the same iron(II), which does not seem evolutionarily sound. This is corroborated by the presence of, in particular, *Gallionella* in iron(II)–oxygen interfaces, where conditions for biofilm formation are poor.

The backwash water of rapid sand filters in drinking water treatment often contains IOB (in particular the presence of easily recognizable *Gallionella* spp. is reported) indicating biological contribution to iron removal (Czekalla *et al.* 1985).

Synthesis

Figure 2 summarizes the occurrence of all three iron(II) oxidation and precipitation processes, and shows the conditions where each of these processes becomes dominant. From this figure, it may be derived that under conditions of high oxygen concentration, high pH and low

HFO concentration, homogeneous oxidation will be the dominant process.

Homogeneous and heterogeneous iron(II) oxidation are equal to each other if both rates are equal:

$$k_2 \frac{[S^*][Fe^{2+}][O_2]}{[H^+]} = k_1 \frac{[Fe^{2+}][O_2]}{[H^+]^2} \Rightarrow \frac{k_1}{k_2} \frac{1}{[H^+][S^*]} = 1 \quad (9)$$

If the last quotient equals 1, the rates of homogeneous and heterogeneous oxidation are equal to each other, if >1 homogeneous oxidation prevails over heterogeneous oxidation, and if <1 the opposite. This equation also shows that, compared with homogeneous oxidation, conditions become more favorable for heterogeneous oxidation at lower pH values and higher HFO concentrations.

In heterogeneous and biological iron(II) oxidation the actual oxidation step is preceded by adsorption or uptake. Consequently, the competition between heterogeneous and biological iron(II) oxidation is not so much a competition in oxidation rate, but a competition in chemical and biological adsorption or uptake rate (Cullimore & McCann 1978; Ehrlich *et al.* 1991; Böhler 1999): if iron(II) removal from solution by chemical adsorption is faster than removal by biological adsorption or uptake, heterogeneous oxidation has an advantage with respect to biological oxidation and vice versa. Because, if IOB are not successful in the uptake or adsorption of iron(II), the energy produced by oxidation and precipitation cannot be to their advantage. Equation (6) shows that the higher the oxygen and the HFO concentration and the higher the pH, the faster the rate of heterogeneous oxidation. This leaves lower oxygen and HFO concentrations and lower pH values as the favorable conditions for biological oxidation.

In the field iron(II) becomes exposed to atmospheric oxygen and consequently starts to precipitate in environments such as groundwater seeps, stratified lakes and around roots in wetlands. These environments are characterized by slightly acidic (pH 5.5 to 7) conditions and limited oxygen supply. After adding azide, biological oxidation is suppressed and the contribution to total oxidation may be calculated. In field studies, the contribution of biological oxidation to total oxidation varied between: 83% (Diez *et al.* 2007), 28–75% (Rentz *et al.*

2007), 62% (James & Ferris 2004), 18–53% (Neubauer *et al.* 2002), and in laboratory studies between 5 and 87% (Druschel *et al.* 2008) and 1–62% (Neubauer *et al.* 2002). In all these experiments, the observed oxidation rate exceeded the corresponding calculated sum of the heterogeneous and homogeneous oxidation rates. The contribution of biological oxidation seems to increase with decreasing oxygen concentration, but seems not very sensitive to pH.

In acid Alpine lake water samples, Barry *et al.* (1994) found the pseudo first-order rate constant ($k = -\{d[\text{Fe}^{2+}]/dt\}/[\text{Fe}^{2+}]$) of lake water samples containing 1 g/L sediment was about 10 times larger after gamma irradiation, about 100 times larger after autoclaving and about 10^4 times larger compared with deionized water. This observation clearly indicates the contribution of heterogeneous and biological oxidation compared with homogeneous oxidation.

Remarkably, in studies on iron removal in acid mine drainage (AMD) under slightly acidic conditions (pH 5 to 7), the contribution of biological iron(II) oxidation and/or the presence of IOB has never been mentioned (Dempsey *et al.* 2002; Park & Dempsey 2005).

IRON REMOVAL IN RSF

In the Netherlands, groundwater is abstracted from phreatic and from (semi-)confined aquifers. Groundwater abstracted from phreatic aquifers often contains iron and oxygen, and the wells (well fields) abstracting these waters are characterized by the occurrence of screen slot (or chemical) clogging (van Beek *et al.* 2009). In filters fed by such groundwater, IOB will always be present, as continuously delivered by the abstracted groundwater. In the field lines, iron(II) will precipitate by homogeneous oxidation and, as soon as the field lines are covered by biofilms, iron hydroxide precipitates also by heterogeneous and biological oxidation. Groundwater abstracted from (semi-)confined aquifers is very reduced and consequently contains no oxygen, and the well and field lines will remain completely clean.

In rapid sand filters there is an abundance of iron (hydr) oxide surfaces; consequently the contribution in these filters of homogeneous oxidation to iron removal will be

negligible. Teunissen *et al.* (2007) estimate the contribution of homogeneous oxidation at *c.* 3%. In filters fed by oxygen-free groundwater, no IOB will be present (Bruins *et al.* 1998), unless these filters have been inoculated, and conditions are favorable. Waters characterized by the absence of oxygen and by a somewhat alkaline pH are excellently suited for iron(II) removal by heterogeneous oxidation, as confirmed by Sharma *et al.* (2001).

Long residence times before filtration of aerated water will favor homogeneous iron(II) oxidation and precipitation. In case of low iron concentrations, all precipitated iron (hydr)oxide will accumulate on top of the filter, leaving the filter itself available for nitrification and manganese removal (van de Wetering 2010, personal communication). In case of high iron(II) concentrations this approach would result in frequent backwashing. Under these conditions the contribution of homogeneous oxidation should be reduced by minimizing the residence time between aeration and filtration. Short residence times are obtained by minimizing the volume of the supernatant water above the filters and increasing the filtration rate.

By accurately measuring the total concentration of iron in the backwash water, integrating these concentrations over the backwash volume, and comparing these amounts with the total amount of iron removed during the preceding backwash interval, Huysman (2010, personal communication) was able to make a minimum estimate of the fraction of iron removed by heterogeneous oxidation. For Water Treatment Plant (WTP) Grobbendonk, he arrived at 67% removal by heterogeneous oxidation and 33% by biological oxidation, and for WTP Balen at 45% removal by heterogeneous oxidation and 55% by biological oxidation. Both well fields show very high iron(II) concentrations (36 and 26 mg/L) and experience serious well clogging problems.

Owing to continuous deposition of iron(III) hydroxides by heterogeneous oxidation, the size of the iron(III) hydroxide grains will increase. This increase in size results in an increase of the height of the filter bed and in a decrease in specific surface area, necessitating, at regular intervals, the replacement of enlarged grains by smaller ones. This increase in bed height over time is indeed found in practice (Huysman 2010, personal communication) and may be used to estimate the (minimum) contribution of heterogeneous iron(II) oxidation to total oxidation. This is indeed a

minimum contribution, as part of the heterogeneous oxidized iron(II) may be scoured off during backwashing.

Iron hydroxide precipitates are excellent adsorbers and may be applied for the removal of arsenic in drinking water treatment (Wilkie & Hering 1996) and of metals (Jenne 1968), phosphates (McLaughlin *et al.* 1981) and hydrogen sulfide (Poulton *et al.* 2002) in wastewater treatment. It may even be worthwhile to optimize precipitation of iron (hydr)oxides in drinking water treatment given their valuable applications.

The results of this evaluation demonstrate that the contributions of the various processes to iron removal vary considerably, depending on groundwater quality characteristics and treatment method. Actually, different classes of groundwater quality should be treated differently. In case of groundwater with high pH and low iron concentration, complete homogeneous iron oxidation may be the preferred method.

In case of high iron concentrations, the dominant process in iron(II) removal in filter beds consists of heterogeneous oxidation (tentatively estimated at 95 to 98% of the total iron(II) oxidation), with a negligible contribution of homogeneous oxidation (tentatively estimated at 2 to 5%) (Teunissen *et al.* 2007). If biological oxidation occurs, this process will add a variable, and oxygen-concentration and pH-dependent, contribution (tentatively estimated at up to 50%) at the expense of heterogeneous oxidation.

Heterogeneous iron oxidation asks for optimal conditions for iron(II) adsorption. Homogeneous and biological iron(II) oxidation must be restrained as much as possible, as they increase filter resistance, making backwashing necessary. In heterogeneous iron(II) oxidation, the iron(III) hydroxide grains will grow continuously by precipitation of fresh material. In order to prevent cementing of these grains, and in order to achieve complete oxidation of adsorbed iron(II), periodic upflow flushing of the filter is necessary. An alternative may be continuous flushing in an upflow pellet reactor filled with floating iron(III) hydroxide pellets, where oxidation may be continuous or discontinuous. Experiences with discontinuous oxidation are available from SIR (van Beek 1983; Sharma 2000; de Vet *et al.* 2009). An advantage of an upflow reactor is a more intimate contact between liquid and surface; a disadvantage might be rubbing of the pellets against each other by

which the fresh, most reactive, surfaces are removed continuously. Optimization of iron(II) removal by heterogeneous oxidation is quite possible on plants equipped with double filtration (de Ridder *et al.* 2008).

Koreman & Heuvingh (1998a, b) have performed semi-field experiments with an 'upflow pellet reactor'. Initially, these experiments were successful, but after some time the removal efficiency decreased by unknown reason. Dietz & Dempsey (2002) and Diz & Novak (1998) successfully applied similar reactors for the removal of iron(II) in AMD.

BIOLOGICAL IRON REMOVAL IN LITERATURE

In literature biological iron oxidation is often mentioned as the main process of iron(II) removal, in particular referring to Mouchet (1992), Czekalla (1988, 2008) and Hässelbarth & Lüdemann (1971). Mouchet (1992) remarked that several conventional iron removal plants operated satisfactorily even though this was not expected from the chemical composition of the abstracted groundwater. Because microscopic examination of sludge samples revealed the abundant presence of IOB, he ascribed this favorable removal to biological activity. Moreover, there were no problems with silica interference and filter run times were longer than in conventional plants. Mouchet (1992) mentioned still other advantages of biological oxidation: formation of a more compact iron sludge, high retention capacity, high filtration rates and insensitivity to discontinuous operation. Moreover, prolonged shutdowns did not negatively affect treatment results (Czekalla & Kotulla 1990), nor did variations in water composition (Groth & Czekalla 2004). In applying this method, the oxygen concentration should not exceed the concentration necessary for oxidation of iron(II). Moreover, toxic constituents such as H₂S, heavy metals and hydrocarbons should be absent. Later, Czekalla (1997) successfully applied biological iron removal with higher oxygen concentrations (4 to 11 mg/L), which was only possible as long as the residence time between aeration and filtration was short in order to prevent premature (homogeneous) iron(II) oxidation.

The above phenomena were attributed to biological iron(II) removal, but they are considered here as characteristics of heterogeneous oxidation.

Based upon the density of the iron sludge and the characteristics of the abstracted groundwater, such as redox potential, pH and oxygen concentration, [Søgaard *et al.* \(2000, 2001\)](#) classified their ground WTPs as either biological or chemical. They classified the iron removal process in WTP Forum (pH = 5.5) as chemical, and in the plants Astrup and Grindsted (pH = 7.2 to 7.3) as biological. Considering pH one would expect just the opposite classification.

Considering the results of the preceding evaluation concerning iron(II) oxidation and iron(III) hydroxide precipitation, 'biological iron removal' is evidently not identical to biological iron oxidation. This conclusion is confirmed by results of [Tremblay *et al.* \(1998\)](#). After backwashing a biological iron removal filter, they could not detect any IOB in the sludge. Nevertheless, despite the absence of IOB, they still called the process biological iron removal.

Besides oxygen, iron(II) may also be removed from groundwater with the help of disinfectants such as chlorine ([Wong 1984](#); [Sommerfeld 1999](#)) and chlorine dioxide ([Knocke *et al.* 1991](#)), indicating the minor contribution, or even redundancy, of biological processes.

Evidently, what in process technology papers is called 'biological iron oxidation' or 'biological iron removal', actually refers to a water treatment method, characterized by high filter velocities and limited oxygen supply. Here it is suggested to restrict the notion of biological iron(II) oxidation to the process of oxidation of iron(II) by IOB, excluding oxidation on EPS surfaces. In order to avoid confusion ([Sharma *et al.* 2005](#)), it is advisable to call this method biological-heterogeneous (or biological-adsorptive or biological-auto-catalytic) iron(II) removal. This advice has already been applied in recent papers ([Reijnen & Akkermans 2008](#)).

Also, 'EPS iron oxidation' is not considered as a biological process. EPS, excreted by all kinds of bacteria, may spread into biofilms and serve as an initial adsorbent for dissolved iron(II) and iron(III) hydroxides. These adsorbed species cause further adsorption and oxidation of iron(II), which are chemical processes. Consequently, 'EPS iron oxidation' is considered comparable to heterogeneous iron(II) oxidation; the only difference between them is the type of adhesive material. Evidently, EPS excretion and biofilm formation are biological processes.

Some observations provide additional evidence that iron is principally removed by adsorption and not by (homogeneous) oxidation. Oxidation processes proceed along a standard sequence ([Stumm & Morgan 1996](#); [Appelo & Postma 2006](#)), i.e. $\text{CH}_4 > \text{H}_2\text{S} > \text{Fe}^{2+} > \text{NH}_4^+ > \text{Mn}^{2+}$. Consequently, one would expect that CH_4 and H_2S are oxidized before iron(II). However, [Grohmann *et al.* \(1989\)](#) and [Böhler \(1999\)](#) mention that methane does not disturb biological iron removal. They attribute this phenomenon to the quantity of oxygen, which is less than equivalent for complete iron(II) oxidation: $(\text{O}_2) < 0.14(\text{Fe}^{2+})$, in mg/L. This observation may be more conveniently explained by a difference in processes: iron(II) is removed by adsorption and CH_4 by oxidation. [De Vet *et al.* \(2002\)](#) confirmed the absence of interference of methane with iron in iron removal in RSF.

The distinction between the method of biological-adsorptive iron(II) removal and the process of biological iron(II) oxidation leads for some observations to alternative views. According to [Czekalla \(1988\)](#) and [Mouchet \(1992\)](#), chemical iron(II) removal changes into biological removal by restricted aeration, because lower oxygen concentrations result in more favorable conditions for *Gallionella*. However, the contribution of heterogeneous and of biological iron(II) oxidation to iron(II) removal is governed by the adsorption rate, which is independent of the oxygen concentration. The favorable effect of lowering the oxygen concentration (longer runtimes) consists of minimizing homogeneous oxidation (and in this way indirectly favoring heterogeneous and biological oxidation).

Regularly backwashing the filters with aerated water has a favorable effect on biological-adsorptive iron(II) removal ([Bourgine *et al.* 1994](#)). In biological-adsorptive iron removal, the oxygen supply is critically adjusted to the iron(II) concentration, which may lead to incomplete oxidation of adsorbed iron(II) in (a part of) the filter. Backwashing with aerated water then results in a thorough oxidation of the adsorbed iron(II). Moreover, backwashing is also necessary in order to separate the growing iron(III) hydroxide grains from each other.

By backwashing, some IOB biomass will be removed and, by consequence, immediately after this washing the contribution of biological oxidation to iron removal will be smaller. Over time the IOB biomass will increase, and

concurrently the contribution of biological oxidation until the next backwashing, after which the cycle starts over again. Thus, backwashing results in a cyclic variable contribution of biological oxidation to iron(II) removal.

CONCLUSIONS

Three processes are able to remove iron in RSF: homogeneous (also called flocculent), heterogeneous (also called adsorptive, autocatalytic or contact) and biological oxidation. Homogeneous and heterogeneous oxidation are defined unambiguously, contrary to biological oxidation. Here, biological oxidation is defined as oxidation directly mediated by IOB, where the energy released becomes available for these bacteria. Consequently, the contribution of biofilms as an (initial) adsorbent for iron(II) or iron(III) hydroxide precipitates, the so-called 'EPS iron oxidation', is not considered as biological oxidation.

Iron removal in RSF is a combination of homogeneous, heterogeneous and biological iron oxidation. The distribution between these processes is governed on the one side by water chemistry and the presence of iron(III) hydroxide precipitates and of IOB including EPS, and on the other side by the treatment method applied. Low iron concentrations may be removed completely with the help of homogeneous oxidation in the supernatant water. High iron concentrations may be removed by up to 5% by homogeneous, 50 to 95% by heterogeneous and 25 to 50% by biological oxidation, as tentative estimates, in the filter itself. If present, the contribution of biological oxidation is not constant over time: after backwashing the contribution by IOB will be lowered, and will increase over time at the expense of heterogeneous iron oxidation until the next backwashing.

The 'biological iron removal system' or 'biological iron removal process' do not imply a complete biological iron oxidation process. Actually these notions refer to a treatment or technological method, characterized by high filtration rates together with limited oxygen supply (presently with higher oxygen concentrations). The contribution of biological processes in this method is variable and may even be absent, as shown by the application of disinfectants as oxidants.

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